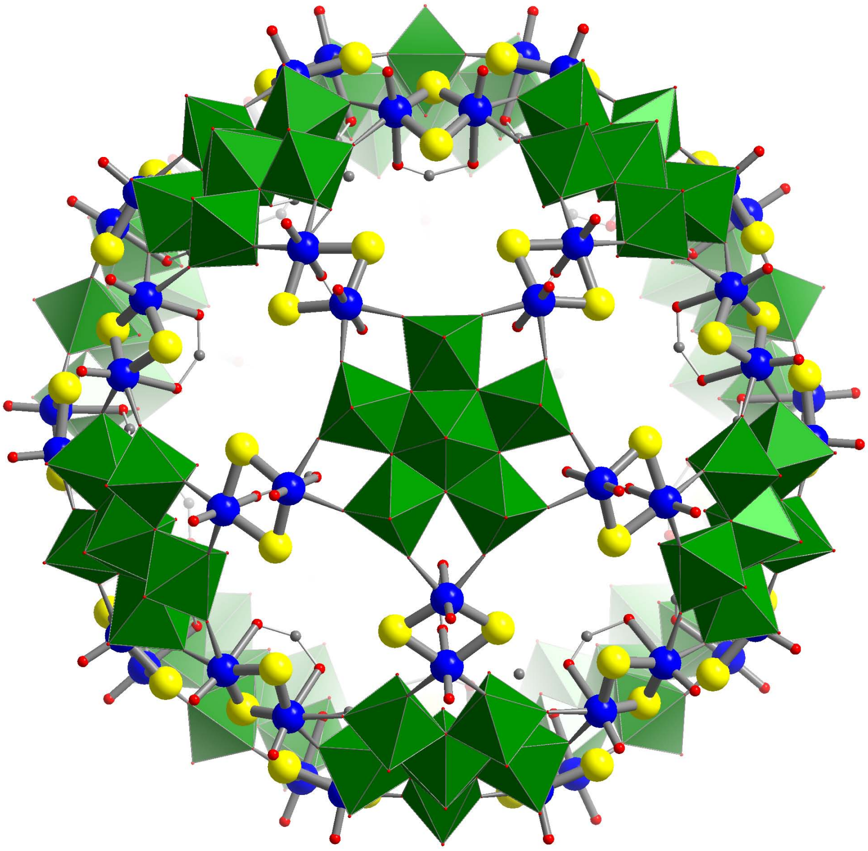
Grundlegende Beiträge zur Chemie von Kepleraten des Typs $\{(\mathrm{M})\mathrm{M}_5\}_{12}\{\mathrm{Mo}_2\}_{30}$ (M = Mo, W)



KUMULATIVE DISSERTATION

zur Erlangung des akademischen Grades des
Doktors der Naturwissenschaften
der Fakultät für Chemie der Universität Bielefeld

von
Christian Schäffer
aus Bielefeld

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Die Abbildung auf dem Titelblatt zeigt das in dieser Arbeit beschriebene $\{(W)W_5\}_{12}\{Mo_2O_2S_2\}_{30}$-Keplerat in kombinierter Polyeder-/Kugel-Stabdarstellung in Blickrichtung einer C_5-Achse. 12 pentagonale $\{(W)W_5\}$-Einheiten (grün) sind mit 30 $\{Mo_2O_2S_2\}^{2+}$-Einheiten verknüpft (Mo: blau, O: rot, S: gelb).

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Inhaltsverzeichnis

Einleitung

Die vorliegende kumulierte Dissertationsschrift besteht aus drei Teilen. In der Einleitung wird neben einer kurzen Einführung in das Gebiet der Polyoxometallate die Zielsetzung und Motivation des Forschungsvorhabens erläutert. Der zweite Teil enthält die aus den Ergebnissen dieser Arbeit hervorgegangenen Veröffentlichungen, zuvor wird der jeweilige persönliche Beitrag des Autors angegeben. Die Arbeit schließt mit einer Zusammenfassung.

Polyoxometallate

Tetraoxoanionen der frühen Übergangsmetalle M = V, Nb, Ta, Mo, W, die in einer alkalisch-wässrigen Lösung mononuklear vorliegen, bilden bei Ansäuerung anionische polynukleare Metall-Sauerstoff-Cluster, sogenannte Polyoxometallate, deren kleinste Baueinheit $\{MO_x\}$-Polyeder sind (x = 4, 5, 6, 7 für V^{V}; x = 6, selten x = 4, 7 für Mo^{VI}; x = 6 für W^{VI}, Nb^{V}, Ta^{V}). Diese sind über Ecken, Kanten und selten über Flächen miteinander verknüpft.[1] Die meisten der heute bekannten Polyoxometallate sind aus den Elementen Molybdän und Wolfram aufgebaut. Dies liegt in der günstigen Kombination von Ionenradius und -ladung sowie der Verfügbarkeit freier d-Orbitale für die Ausbildung von Metall-Sauerstoff-π-Bindungen begründet.[2] Der strukturelle Aufbau von Polyoxometallaten folgt zwei grundlegenden Prinzipien:[2,3]

- Jedes Metallatom befindet sich in einem $\{MO_x\}$-Koordinationspolyeder. Das Metallatom befindet sich jedoch nicht im Zentrum, sondern ist auf Grund von Metall-Sauerstoff-π-Bindungen in Richtung der Polyederspitzen, die die Oberfläche der Struktur bilden, verschoben.[3]
- Es werden in der Regel keine Strukturen von $\{MO_6\}$-Oktaedern beobachtet, die drei oder mehr freie Spitzen aufweisen. Dieses sogenannte LIPSCOMB-Prinzip[4] wird auf den starken *trans*-Effekt der terminalen M=O-Bindung zurückgeführt.[5]

Auf Grund ihrer chemischen Zusammensetzung wird in der Literatur häufig zwischen zwei Typen von Polyoxometallaten unterschieden: Isopoly- und Heteropoly-Anionen.[6,7] Die allgemeine Summenformel für Isopoly-Anionen lautet $[M_mO_y]^{n-}$, wobei M das Metallatom des Gerüstes bezeichnet.[6] Ein bedeutender Strukturtyp für

Isopoly-Anionen, der von Mo^{VI}, W^{VI}, Nb^{V} und Ta^{V} gebildet wird, ist die LINDQVIST-Struktur $[M_6O_{19}]^{n-}$, die aus sechs kantenverknüpften $\{MO_6\}$-Oktaedern aufgebaut ist. Die allgemeine Summenformel für Heteropoly-Anionen ist $[X_xM_mO_y]^{n-}$, mit $x \leq m$, X bezeichnet das Heteroatom.[6] Heteropoly-Anionen entstehen, wenn man z.B. wässrige Molybdat- oder Wolframat-Lösungen ansäuert, die zugleich noch Anionen oder Kationen weiterer Elemente wie z.B. B^{III}, Si^{IV}, P^{V} enthalten. Das am längsten bekannte Heteropoly-Anion ist das Phosphomolybdat $[PMo_{12}O_{40}]^{3-}$, das von BERZELIUS 1826 in Form des Ammoniumsalzes als gelber Niederschlag bei der Hinzugabe von Ammoniummolybdat im Überschuss zu Phosporsäure erhalten wurde.[8] Die Strukturaufklärung des Anions ist KEGGIN 1934 gelungen.[9] Nach ihm wurde dieser wichtige Strukturtyp mit der allgemeinen Summenformel $[XM_{12}O_{40}]^{n-}$ (M = W, Mo) und für den es zahlreiche Beispiele gibt,[10] benannt. Im Zentrum des KEGGIN-Anions befindet sich ein tetraedrisch koordiniertes Heteroatom, das in einem Käfig aus 12 $\{MO_6\}$-Oktaedern eingeschlossen ist. Ein weiterer wichtiger gemeinsamer Strukturtyp für Heteropoly-Anionen, in der das Heteroatom ebenfalls tetraedrisch koordiniert ist, ist die DAWSON-Struktur (allgemeine Formel: $[X_2M_{18}O_{62}]^{n-}$, M = W, Mo).[10] Die Heteropolyoxowolframate dieser beiden Strukturtypen eignen sich auf Grund ihrer Stabilität für die Erzeugung von Anionen mit Defekten, die dann unter Verwendung von Elektrophilen gezielt zu größeren Aggregaten verknüpft werden können. Dies ist eine häufig angewandte Strategie zur Synthese sehr großer Polyoxowolframate.[11,12]

Da die Einteilung in Iso- und Heteropolyanionen historisch gewachsen, jedoch für viele Verbindungen nicht unproblematisch ist, wird von M. POPE und A. MÜLLER die übergreifende Bezeichnung „Metall-Sauerstoff-Cluster“ vorgeschlagen.[3] Diese Bezeichnung wird in der vorliegenden Arbeit neben der Bezeichnung „Polyoxometallat“ verwendet.

Polyoxometallate haben in den letzten Jahrzehnten vielfältige Anwendungen in Analytik, Katalyse, Elektrochemie, Magnetochemie, Materialwissenschaft, Medizin und Nanochemie gefunden.[12,13]

Die Reaktionsmechanismen, die zur Bildung von Polyoxometallaten auf Basis von Selbstorganisationsprozessen führen, sind sehr kompliziert und nur für strukturell einfache Isopolyoxometallate umfassend untersucht.[14,15] Dass die Reaktion von einfachen Monomeren zu z.T. hochkomplexen Strukturen freiwillig verläuft, ist auf die hohe freie Enthalpie der Polykondensationsprozesse zurückzuführen.

Die größten heute bekannten reinvalenten, d.h. unter nicht-reduzierenden Bedingungen erhaltenen (Iso-)polyoxometallate sind $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$[16] und $[H_{12}W_{36}O_{120}]^{12-}$.[17] Wesentliche größere Aggregate wurden nur über die Verknüpfung einzelner Fragmente wie Defekt-Heteropolyoxowolframate aber auch Heptamolybdat-Einheiten insbesondere durch Lanthanoid-Kationen erhalten. Beispiele hierfür sind die Wolframat-Cluster $[As^{III}{}_{12}Ce^{III}{}_{16}W_{148}O_{524}(H_2O)_{36}]^{76-}$[18] und $[Ln_{16}As_{16}W_{164}O_{576}(OH)_8(H_2O)_{42}]^{80-}$ (Ln = Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III})[19] sowie der Molybdat-Cluster $[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ (Ln = La^{III}, Ce^{III}, Pr^{III}, Sm^{III}, Gd^{III}).[20]

Nanoskalige sphärische Polyoxomolybdate

Der entscheidende Durchbruch, der zur Synthese nanoskaliger Polyoxomolybdate führte, gelang durch intensive Untersuchungen wässriger angesäuerter Molybdat-Lösungen unter reduzierenden Bedingungen. Die geschickte Wahl der Reaktionsparameter (Molybdat-/Heteroelementkonzentration, pH-Wert, Grad der Reduktion, Anwesenheit geeigneter Liganden, Ionenstärke der Reaktionslösung, Temperatur, Reaktionszeit) ermöglicht die *in situ* Generierung vielseitiger Baueinheiten, die in einem schrittweisen Selbstorganisationsprozess zu großen Clustern mit einzigartigen Architekturen und Funktionen wachsen. So konnten u.a. der $\{Mo_{57}M_6\}$-Cluster (M = Fe^{III}, V^{IV}),[21] die molekularen Räder $\{Mo_{154}\}$,[22] $\{Mo_{176}\}$[23] und $\{Mo_{248}\}$,[24] die molekulare Kapsel $\{Mo_{132}\}$[25] und der bislang größte diskrete anorganische Cluster $\{Mo_{368}\}$,[26] dessen Form an eine Zitrone erinnert, erhalten werden.*

Der Aufbau dieser komplexen Strukturen aus einer (virtuellen) dynamischen Bibliothek verschiedener Baueinheiten wird durch die Kombination einiger Eigenschaften von (Polyoxo-)molybdaten ermöglicht:[26]

- die einfache Erweiterung der Mo-Koordinationssphäre sowie der einfache Austausch von H_2O-Liganden an Mo-Zentren
- die moderate Stärke der Mo–O–Mo-Bindung (die einen „Split-and Link“ Prozess erlaubt)

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*Eine detaillierte Übersicht der bislang in der Arbeitsgruppe von A. MÜLLER dargestellten nanoskaligen Metall-Sauerstoff-Cluster – einschließlich einiger der in der vorliegenden Arbeit erhaltenen neuen Verbindungen – sind inzwischen in einem Review publiziert worden (siehe Referenz [27]).

- die einfache, von den Redoxbedingungen abhängige, Veränderung der Elektronendichte sowohl in den Mo–O-Bindungen als auch an den Sauerstoffatomen (bedeutend für die Protonierung)
- die geringe Tendenz des Molybdäns, Metall-Metall-Bindungen zu bilden
- die Existenz terminaler Mo=O-Gruppen mit wenig reaktiven Sauerstoffatomen, die das Wachstum zu unbegrenzten oxidischen Strukturen verhindern.

Zum Verständnis des Themas dieser Arbeit soll im Folgenden näher auf die Molybdänoxid-Kapseln mit dem allgemeinen geometrischen Aufbauprinzip $(\text{Pentagon})_{12}(\text{Linker})_{30}$ eingegangen werden. Allen bislang bekannten sphärischen Metall-Sauerstoff-Cluster gemein sind die 12 pentagonalen $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}{}_5\text{O}_{21}(\text{H}_2\text{O})_6\}^{6-}$ ($\equiv\{(\text{Mo})\text{Mo}_5\}$)-Einheiten, die auf den Ecken eines Ikosaeders platziert und durch 30 dinukleare $\{\text{Mo}_2{}^{\text{V}}\text{O}_4(\text{L})\}^{(2-n)+}$-Linker (z.B. mit L^{n-} = CH_3COO^- [25]) oder 30 mononukleare Linker (Fe^{3+},[28] VO^{2+},[29] Cr^{3+}[30] oder $[\text{Mo}^{\text{V}}\text{O}(\text{H}_2\text{O})]^{3+}$[31]) miteinander verbunden sind (siehe Abb. 1). Je nach dem, ob die Pentagone mit mono- oder dinuklearen Linkern verknüpft sind, lassen sich zwei Kapsel-Typen unterscheiden: Die größere $\{(\text{Mo})\text{Mo}_5\}_{12}\{\text{Mo}_2\text{O}_4(\text{L})\}_{30} \equiv \{\text{Mo}_{132}\}$-Kapsel und die kleinere $\{(\text{Mo})\text{Mo}_5\}_{12}\text{M}_{30} \equiv \{\text{Mo}_{72}\text{M}_{30}\}$-Kapsel (M = Fe^{III}, V^{IV}, Cr^{III}, Mo^{V}). Die pentagonalen $\{(\text{Mo})\text{Mo}_5\}$-

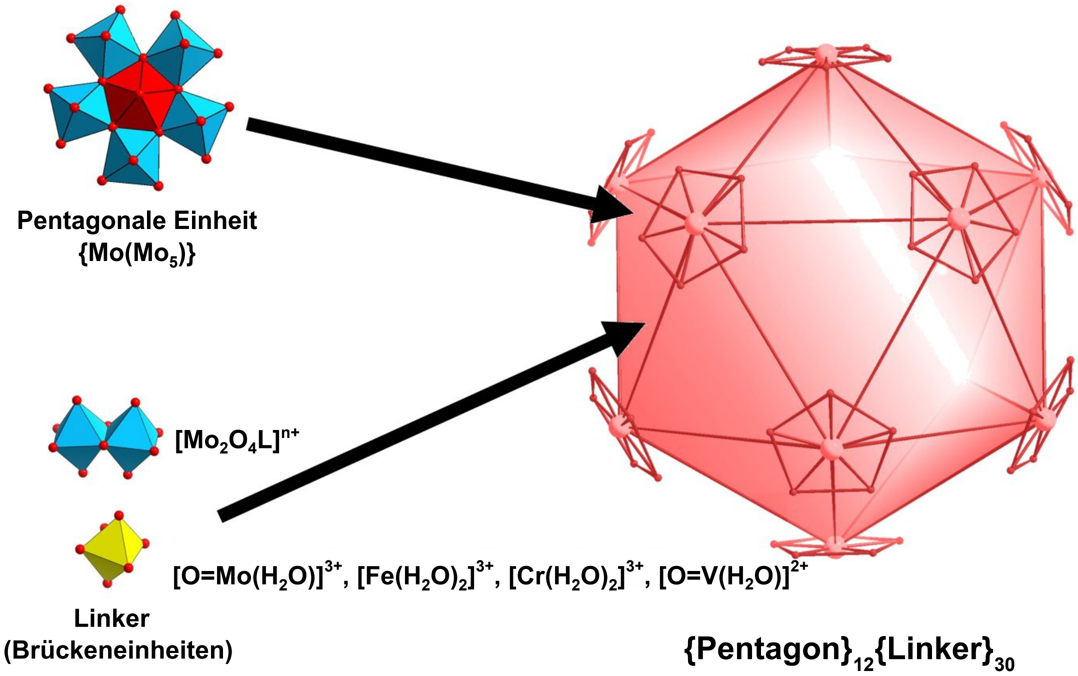

Abb. 1: Allgemeines Konstruktionsprinzip der $\{\text{Mo}_{132}\}$ und $\{\text{Mo}_{72}\text{M}_{30}\}$-Keplerate.

Einheiten bestehen aus einer zentralen pentagonalen $\{MoO_7\}$-Bipyramide, die mit fünf $\{MoO_6\}$-Oktaedern kantenverknüpft ist. Die dinukleare Brückeneinheit weist eine Mo^V-Mo^V-Metallbindung auf und besteht aus zwei kantenverknüpften Oktaedern, wobei jedes Mo^V-Zentrum an zwei Sauerstoffatome zweier benachbarter $\{MoO_6\}$-Oktaeder einer pentagonalen $\{(Mo)Mo_5\}$-Einheit gebunden ist. Die Metallzentren der mononuklearen Brückeneinheiten sind an jeweils zwei Sauerstoffatome zweier gegenüberliegender $\{MoO_6\}$-Einheiten, die zu zwei pentagonalen Einheiten gehören, gebunden. Das Konstruktionsprinzip der Kapseln führt zur Bildung von 20 $\{Mo_9O_9\}$-Poren ($\{Mo_{132}\}$-Kapsel) bzw. 20 $\{Mo_3M_3O_6\}$-Poren ($\{Mo_{72}M_{30}\}$-Kapsel) mit 20 Porenkanälen, die durch an die Brückeneinheiten koordinierenden, ins Kapselinnere gerichteten Liganden entstehen.

Interessanterweise spannen sowohl di- als auch mononukleare Linker verzerrte Archimedische Körper mit annähernder Ikosaeder-Symmetrie auf: Während die dinuklearen Linker im $\{Mo_{132}\}$-Cluster die 90 Kanten eines verzerrten (nicht-regulären) Ikosaederstumpfes mit 20 Hexagonen und 12 Pentagonen definieren, bilden die Zentren der mononuklearen Linker $\{Mo_{72}M_{30}\}$-Cluster ein Ikosidodekahedron, bestehend aus 12 Pentagonen und 30 Dreiecken.[32] Auf Grund der Ähnlichkeit ihrer geometrischen Eigenschaften zu J. KEPPLERs frühen, auf Platonischen Körpern basierenden Planetenmodell wurde von A. MÜLLER für diese sphärischen Metall-Sauerstoff-Cluster die Bezeichnung „Keplerat“ vorgeschlagen.[25] Die Atome eines Keplerats sind in einer oder mehr sphärischen Schalen um einen zentralen Punkt (der nicht notwendigerweise durch ein Atom besetzt sein muss) angeordnet, wobei jedes Set von äquivalenten Atomen einen Platonischen oder (verallgemeinert) einen Archimedischen Körper formt.[32]

Die Synthese des prototypischen $\{(Mo)Mo_5\}_{12}\{Mo_2O_4(CH_3COO)\}_{30} \equiv \{Mo_{132}\text{-Ac}\}$-Keplerats, das $[Mo^{VI}{}_{72}Mo^{V}{}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$-Anion, gelang A. MÜLLER und seinen Mitarbeitern im Jahre 1998. Die Darstellung erfolgte in einer „Eintopf“-Reaktion durch die teilweise Reduktion einer wässrigen Lösung von Ammoniumheptamolybdat mittels Hydraziniumsulfat in Gegenwart von Ammoniumacetat und anschließender Senkung des pH-Wertes mit Essigsäure auf pH = 4.[25] In darauffolgenden Studien gelang das „Sizing“ der sphärischen Cluster durch die Darstellung der bereits oben beschriebenen $\{Mo_{72}M_{30}\}$-Keplerate auf direktem Wege durch Zugabe von $Fe(aq)^{3+}$,[28] $VO(aq)^{2+}$[29] oder $Cr(aq)^{3+}$[30] zu einem geeigneten Reaktionssystem auf Molybdatbasis oder durch die Reaktion von z.B. Fe^{3+} mit dem $\{Mo_{132}\text{-Ac}\}$-Cluster unter Austausch der dinuklearen gegen mononukleare Linker.[33] Diese Verbindungen sind vor allem auf Grund ihrer magnetischen Eigenschaften von großem Interesse.[34] Das

$\{(\mathrm{Mo}^{\mathrm{VI}})\mathrm{Mo}^{\mathrm{VI}}{}_5\}_{12}\mathrm{Mo}^{\mathrm{V}}{}_{30} \equiv \{\mathrm{Mo}_{102}\}$-Keplerat wurde aus dem $\{\mathrm{Mo}_{132}\text{-Ac}\}$-Keplerat durch milde Oxidation hergestellt.[31]

Im Falle des $\{\mathrm{Mo}_{132}\}$-Clusters besteht die Möglichkeit, die anionischen Liganden, die an die Mo^{V}-Zentren des dinuklearen Linkers koordinieren, zu variieren. Dies kann während der Synthese durch die Verwendung einer anderen Carbonsäure (z.B. Butan-[35] und Propionsäure[36]) oder durch Austausch der nur schwach gebundenen Liganden in bereits bestehenden Kapseln (z.B. gegen Formiat,[37] Sulfat,[38,39] Phosphat,[40] Hypophosphit,[41] Carbonat[42]) erfolgen, wobei das Kapselgerüst intakt bleibt. Der Austausch der Liganden ist auch teilweise möglich, z.B. können Sulfat-/Hyphophosphit-Liganden nebeneinander in einer Kapsel vorliegen.[40] Der Ligandentausch erlaubt in einfacher Weise die präzise Veränderung der inneren Funktionalitäten, des hydrophilen/hydrophoben Charakters des Kapselinneren und der Gesamtladung der $\{\mathrm{Mo}_{132}\}$-Kapsel. Diese weitreichende Modifikationsmöglichkeit und die 20 flexiblen $\{\mathrm{Mo}_9\mathrm{O}_9\}$-Poren, jede einzelne vergleichbar mit einem [27]Krone-9 Polyether (siehe Abb. 2),[43] machen die $\{\mathrm{Mo}_{132}\}$-Kapsel zu einem polytopen Rezeptor für zahlreiche Substrate, deren Aufnahme/Koordination sich unter definierten Bedingungen untersuchen lässt.† Wichtig anzumerken ist in diesem Zusammenhang, dass die $\{\mathrm{Mo}_{132}\}$-Kapseln sehr gut wasserlöslich sind und eine hohe Stabilität in wässrigen Systemen besitzen.

Bei $\{\mathrm{Mo}_{132}\}$-Kapseln mit Sulfatliganden mit einer hohen negativen Ladung und einem hydrophilen Innenraum konnte der Transport verschiedener Metallkationen durch die Poren ins Kapselinnere beobachtet werden, wobei die Kapseln als eine Art „Nano-Ionenchromatograph“ agieren: Kleine Kationen wie Li^+, Na^+, Ca^{2+}, Ce^{3+} und Pr^{3+} werden nach Porendurchtritt aufgetrennt und an wohldefinierten Positionen oberhalb, unterhalb und innerhalb der Porenkanäle fixiert.[40,45] Bemerkenswert ist außerdem das für Li^+-Ionen NMR-spektroskopisch untersuchte temperaturabhängige Aufnahme-/Abgabe-Gleichgewicht.[46] Die $\{\mathrm{Mo}_9\mathrm{O}_9\}$-Poren können mit organischen Kationen (wie Guanidinium-,[47] Uronium-,[40] oder Formamidiniumkationen[45]) oder hydratisierten Metallkationen (z.B. $[\mathrm{Ni(H_2O)_6}]^{2+}$,[40] $[\mathrm{Al(H_2O)_6}]^{3+}$,[48] $[\mathrm{Pr(H_2O)}_n]^{3+}$[39]) über die Ausbildung von Wasserstoffbrückenbindungen interagieren, wobei all diese Kationen als eine Art „Korken“ fungieren und die Kapselporen verschließen. Das Verschließen der Poren verhindert die Aufnahme von Kationen und führt in hydrophilen Kavitäten zur hochstrukturierten Anordnung eingekapselter Wassermoleküle. Es wurden hochsymmetrische Wasseraggregate aus bis zu 100 Molekülen mit Schalenstruktur entdeckt.[37]

[†] Eine zusammenfassende Darstellung aller faszinierenden Eigenschaften und Funktionen dieses sphärischen Clusters kann Referenz [44] entnommen werden.

$\{\mathrm{Mo}_{132}\}$-Kapseln können durch die Wahl geeigneter Liganden auch mit hydrophoben Innenräumen konstruiert werden, die das Studium hydrophober Effekte (d.h. die molekulare Erkennung und Clusterbildung von hydrophoben Materialen in Wasser) erlauben. So konnte z.B. kürzlich gezeigt werden, dass eine Kapsel mit 30 hydrophoben Proponiatliganden auf Grund von inneren hydrophoben Wechselwirkungen in der Lage ist, *n*-Hexanol-Moleküle im Kapselinneren aufzunehmen.[36]

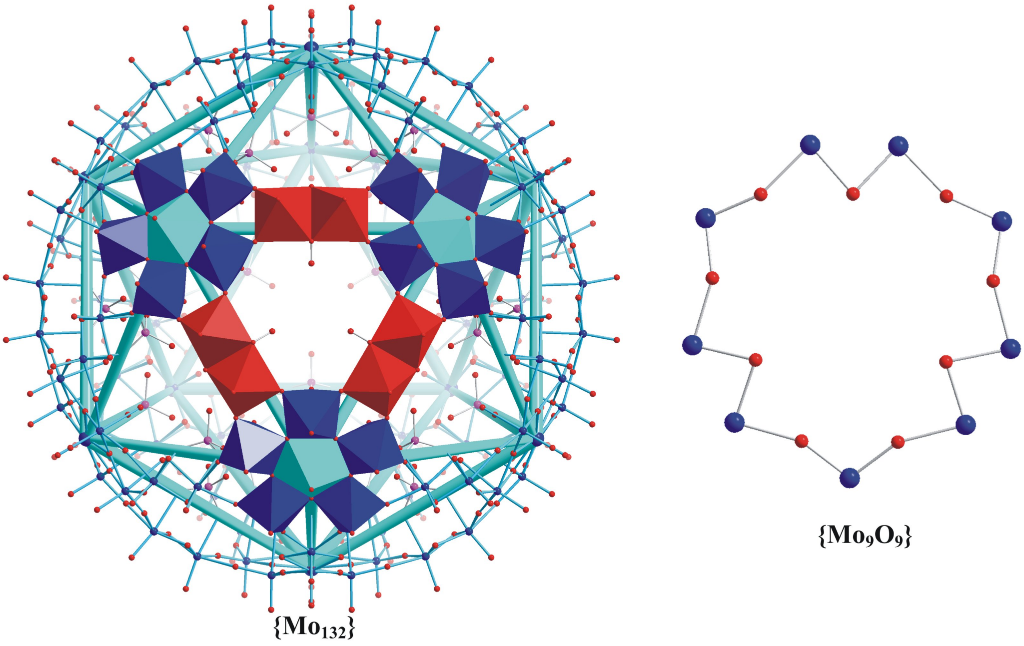

Abb. 2: *Links:* Das $\{\mathrm{Mo}_{132}\}$-Keplerat in kombinierter Polyeder-/Kugel-Stab-Darstellung zur Hervorhebung einer der 20 $\{\mathrm{Mo}_9\mathrm{O}_9\}$-Poren, deren Kontur durch drei pentagonale $\{(\mathrm{Mo})\mathrm{Mo}_5\}$- (hell- und dunkelblau) und drei $\{\mathrm{Mo}_2{}^{\mathrm{V}}\}$-Einheiten (rot) definiert wird. *Rechts:* Einzeldarstellung einer $\{\mathrm{Mo}_9\mathrm{O}_9\}$-Pore, die die Ähnlichkeit zu einem [27]Krone-9 Polyether zeigt (rot: Sauerstoffatome, blau: Molybdänatome). Entnommen aus Referenz [27] – Abdruck mit freundlicher Genehmigung der Royal Society of Chemistry (RSC). Copyright © The Royal Society of Chemistry 2012.

Motivation und Zielsetzung

Die Bildung des $\{Mo_{132}\}$-Keplerats verläuft in einem im Detail noch nicht verstandenen komplizierten Mehrstufenprozess. Bekannt ist, dass das richtige Verhältnis von $[Mo^{V}]$ zu $[Mo^{VI}]$, der pH-Wert und die Pufferkapazität entscheidende Faktoren für seine Bildung sind.[25,49] Darüber hinaus wird angenommen, dass die $\{Mo_2{}^{V}O_4\}^{2+}$-Einheit, die sich in der oben beschriebenen „Eintopf“-Synthese bei Zugabe eines Reduktionsmittels bildet, eine Schlüsselrolle während des Selbstorganisationsprozesses bei der Formierung der pentagonalen $\{(Mo)Mo_5\}$-Einheit spielt.[50] Diese Einheit konnte bislang nicht als eigenständige Spezies isoliert werden, sie ist aber vermutlich kinetisch stabil und als Baueinheit transferierbar.‡ Als treibende Kraft der Reaktion wird die hohe Bildungstendenz sphärischer Cluster vermutet.[52]

Im Rahmen dieser Arbeit ist es zunächst von Interesse, zu untersuchen, ob nach Zugabe vorsynthetisierter $\{Mo_2{}^{V}O_4\}^{2+}$-Einheiten zu einer wässrigen Lösung von Ammoniumheptamolybdat, die in Anwesenheit von Ammoniumacetat mit Essigsäure auf pH = 4 eingestellt wird (gleiche Reaktionsbedingungen wie in der „Eintopf“-Synthese), die Bildung des $\{Mo_{132}\}$-Clusters zu beobachten ist. Dies wäre nur dann möglich, wenn sich die pentagonalen $\{(Mo)Mo_5\}$-Einheiten unmittelbar nach Zugabe der Brückenbaueinheiten aus den in Lösung vorliegenden Polyoxomolybdat-Spezies§ formieren. Zur Beobachtung des Reaktionsverlaufes eignet sich die Raman-Spektroskopie, da das $\{Mo_{132}\}$-Keplerat auf Grund der hohen, fast ikosahedralen Symmetrie seines Gerüstes ein typisches Raman-Spektrum mit einer geringen Zahl an zu beobachtenden Banden aufweist.[46,53]

Pentagonale Baueinheiten werden zwingend zur Synthese sphärischer Metall-Sauerstoff-Cluster benötigt, ihre Existenz ist bislang aber nur in Polyoxomolybdaten belegt. Eine naheliegende Frage ist daher, ob $\{Mo^{V}{}_2\}$-Einheiten in der Lage sind, die spontane Bildung anderer $\{(M)M_5\}$-Einheiten und somit auch die Bildung sphärischer Cluster des Typs $\{M_{72}M_{60}\}$ zu steuern. Auf Grund der chemischen Ähnlichkeit kommt hier das Element Wolfram in Betracht. Zwar wird davon ausgegangen, dass die im Vergleich zum Molybdän stärker ausgeprägte Tendenz zur Bildung von M–M-Bindungen die struk-

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‡Darauf deuten die Austauschmöglichkeit der dinuklearen $\{Mo_2{}^{V}O_4\}^{2+}$-Brücken gegen die mononuklearen $[Fe(H_2O)_2]^{3+}$ und $[Mo^{V}O(H_2O)]^{3+}$-Brücken als auch die Verwendung des $\{Mo_{132}\}$-Clusters als Edukt zur Darstellung des orthorhombischen Metalloxids Mo-V-Sb mit pentagonalen $\{(Mo)Mo_5\}$-Einheiten hin.[51]

§Bei pH = 4 liegen vermutlich ausschließlich Hepta- ($[H_xMo_7O_{24}]^{x-6}$, $0 \leq x \leq 2$) und Oktamolybdate ($[Mo_8O_{26}]^{4-}$) vor.[15]

turelle Vielseitigkeit des Wolframs einschränkt,[26] die prinzipielle Ersetzbarkeit von Molybdän- durch Wolframzentren in den pentagonalen Einheiten konnte aber bereits in früheren Studien gezeigt werden.[54] In der vorliegenden Arbeit sollen diese Studien fortgeführt und untersucht werden, ob die Zugabe vorsynthetisierter $\{Mo_2{}^{V}O_2X_2\}^{2+}$-Baueinheiten (X = O, S) zu einem geeigneten Polyoxowolframat-Reaktionssystem zur Bildung von Kepleraten mit $\{(W)(W_5)\}$-Pentagonen führt. Hierbei soll zudem der Versuch unternommen werden, das Heteroelement Schwefel erstmalig in das Kapselgerüst eines Keplerats einzuführen, um sowohl die Oberflächen als auch die bislang bekannten „oxidischen" Poren zu modifizieren.

Publikationen

In diesem Abschnitt werden die Publikationen, die die Forschungsergebnisse enthalten, aufgeführt und der jeweilige Beitrag des Autors angegeben. Die Volltexte der in Fachzeitschriften veröffentlichten Originalartikel folgen im Anschluss. Zugehörige Supporting Information ist nicht enthalten, diese können auf den Verlagsseiten kostenlos abgerufen werden.

Spontaneous self-assembly of a giant spherical metal-oxide Keplerate: addition of one building block induces immediate formation of the complementary one from a constitutional dynamic library
C. Schäffer, A. M. Todea, P. Gouzerh, A. Müller, *Chem. Commun.* **2012**, *48*, 350–352. DOI: 10.1039/C1CC15907K – Abdruck der Originalveröffentlichung mit freundlicher Genehmigung der Royal Society of Chemistry (RSC). Copyright © The Royal Society of Chemistry 2012.

Eigener Beitrag zur Veröffentlichung: Alternativer Weg zur Synthese des $\{Mo_{132}\}$-Keplerats, basierend auf der Verwendung der vorsynthetisierten $\{Mo_2{}^{V}O_4\}^{2+}$-Einheit.

Unprecedented and Differently Applicable Pentagonal Units in a Dynamic Library: A Keplerate of the Type $\{(W)W_5\}_{12}\{Mo_2\}_{30}$
C. Schäffer, A. Merca, H. Bögge, A. M. Todea, M. Kistler, T. Liu, R. Thouvenot, P. Gouzerh, A. Müller, *Angew. Chem.* **2009**, *121*, 155–159. DOI: 10.1002/ange.200804496; *Angew. Chem. Int. Ed.* **2009**, *48*, 149–153. DOI: 10.1002/anie.200804496 – Abdruck der Originalveröffentlichung mit freundlicher Genehmigung des Verlages John Wiley & Sons, Inc. Copyright © 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Eigener Beitrag zur Veröffentlichung: Entwicklung der stufenweisen Synthesestrategie und Charakterisierung (Raman-, IR- und UV/Vis-Spektroskopie) des neuen $\{(W)W_5\}_{12}\{Mo_2O_4\}_{30}$-Keplerats.

Softening of Pore and Interior Properties of a Metal-Oxide-Based Capsule: Substituting 60 Oxide by 60 Sulfide Ligands

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Eigener Beitrag zur Veröffentlichung: Entwicklung der stufenweisen Synthesestrategie und Charakterisierung (Raman-, IR- und UV/Vis-Spektroskopie) des neuen $\{(W)W_5\}_{12}\{Mo_2O_2S_2\}_{30}$-Keplerats.

A further step towards tuning the properties of metal-chalcogenide nanocapsules by replacing skeletal oxide by sulphide ligands

C. Schäffer, A. M. Todea, H. Bögge, S. Floquet, E. Cadot, V. S. Korenev, V. P. Fedin, P. Gouzerh, A. Müller, *Dalton Trans.* **2013**, *42*, 330–333. DOI: 10.1039/c2dt32247a – Abdruck der Originalveröffentlichung mit freundlicher Genehmigung der Royal Society of Chemistry (RSC). Copyright © The Royal Society of Chemistry 2013.

Eigener Beitrag zur Veröffentlichung: Entwicklung der stufenweise Synthesestrategie und Charakterisierung (Raman-, IR- und UV/Vis-Spektroskopie) des neuen $\{(W)W_5\}_{12}\{Mo_2O_3S\}_{30}$-Keplerats.

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Spontaneous self-assembly of a giant spherical metal-oxide Keplerate: addition of one building block induces "immediate" formation of the complementary one from a constitutional dynamic library†

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The addition of dinuclear $\{Mo_2\}$ units to a dynamic library containing molybdates results in the spontaneous self-assembly of a giant spherical metal-oxide species of the type $\{(Mo)Mo_5\}_{12}\{Mo_2\}_{30}$ while the required pentagonal $\{(Mo)Mo_5\}$ building blocks are "immediately" formed.

Self-assembly, which in its broadest sense is defined as 'the evolution towards spatial confinement through spontaneous connection of a few/many components, resulting in the formation of discrete/extended entities at either the molecular, covalent or the supramolecular, non-covalent level',[1] plays a key role in many areas of chemistry, biochemistry and nanoscience in general and is an essential tool for engineering of multifunctional nanostructured materials.[1,2] Self-assembly requires molecular building blocks capable of establishing multiple connections. While metallo-supramolecular assemblies are often obtained by symmetry-driven self-assembly of preformed building blocks,[3,4] virtual combinatorial libraries allow also target-driven self-assembly by expression of the appropriate/necessary constituent among all possible components.[5,6] Here we refer to a related unprecedented phenomenon as expressed in the present title.

Aqueous solutions of molybdates are unique in the sense that they allow to generate a huge variety of combinatorial building blocks from which a large number of clusters and solid-state structures can be obtained (see *e.g.* ref. 7) and this especially under reducing conditions.[7*d*,*e*] This flexibility arises from a combination of favourable kinetic, thermodynamic and structural factors (low kinetic stability, easy exchange of H_2O ligands at Mo sites, comparable thermodynamic stability of many species, not too strong and not too weak Mo–O–Mo bonds, easy change of the coordination number of Mo; see for instance ref. 7*d*)—these factors taken together allow easily split and link processes. Among the related polyoxomolybdates, giant spherical water soluble porous molybdenum-oxide-based nanocapsules of the type $\{(Mo^{VI})Mo^{VI}_5\}_{12}(\text{linker})_{30}$, belonging to the family of Keplerates,[8] are attracting considerable interest due to their unique properties and their relevance to various disciplines.[9–11] Those with dinuclear linkers are built up of 12 pentagonal units of the type $\{(Mo^{VI})Mo^{VI}_5\}$ that are positioned at the vertices of an icosahedron and connected by 30 linking groups, *e.g.* of the type $\{Mo^V_2O_4(L)\}^{(2-n)+}$ where L^{n-} is a bridging bidentate ligand (RCO_2^-, SO_4^{2-}…) (see Fig. 1 as an example). The topological similarity between Keplerates and certain spherical viruses—comprising 12 pentagonal capsomers placed at the 12 corners of an icosahedron—is worth noting.[12,13]

The classical synthesis of the prototypal acetate-stabilized $\{(Mo^{VI})Mo^{VI}_5\}_{12}\{Mo^V_2\}_{30}$-type Keplerate is based on the reduction of an acidified aqueous solution of ammonium molybdate containing a rather high concentration of acetate. The resulting compound, $(NH_4)_{42}[Mo^{VI}_{72}Mo^V_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ *ca.* $(300\ H_2O + 10\ CH_3COONH_4) \equiv (NH_4)_{42}$ **1a** *ca.* $(300\ H_2O + 10\ CH_3CO_2NH_4)$ (**1**), which was

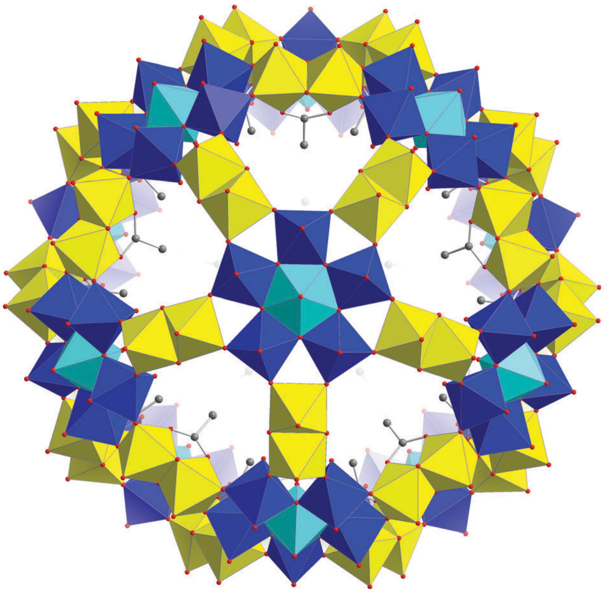

Fig. 1 Combined polyhedral/ball-and-stick representation of **1a** with a view along a fivefold symmetry axis highlighting a central pentagonal $\{(Mo^{VI})Mo^{VI}_5\}$-type unit and five related $\{Mo^V_2O_4\}$ linkers stabilized by the acetate ligands ($\{(Mo^{VI})Mo^{VI}_5\}$ groups blue and $\{Mo^V_2\}$ ones yellow, O small red spheres, C black spheres).

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† In memory of Prof. Dr. P. Aymonino.

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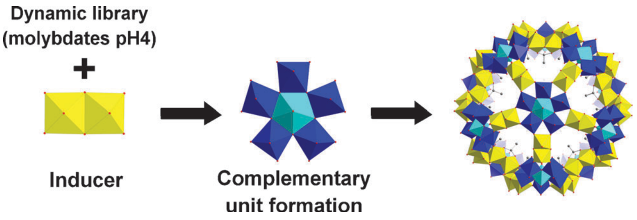
the basis for numerous studies, is isolated in 52% yield.[13,14] Under these conditions the formation of **1a** (Fig. 1) is obviously a complicated multi-step process since none of the constituents of **1a** is present at the start of the reaction. It was soon assumed that the $[Mo^{V}]/[Mo^{VI}]$ ratio and the pH are crucial for the formation of **1a**[13] and that the $\{Mo^{V}_2O_4\}^{2+}$ groups may play a key role in different scenarios for the formation and subsequent linking of various building blocks under different boundary conditions.[15] In a similar way it has been recently found that $\{Mo^{V}_2O_2S_2\}^{2+}$ groups allow to trap a new isomer of the $[Mo_8O_{26}]^{4-}$ ion from an acidified aqueous solution of molybdate.[16]

Now we were interested to investigate whether the addition of the preformed $\{Mo^{V}_2O_4\}^{2+}$ unit/building block to an aqueous solution of molybdate (practically identical to the published method leading to **1**[13,14]) would result in the spontaneous formation of **1a** based on the fast formation of the mentioned pentagonal building blocks (Scheme 1). Indeed **1a** begins to form immediately after the addition of the building block of **1a**, *i.e.* $\{Mo_2O_4\}^{2+}$ (present in $(NH_4)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$) to an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ acidified to pH 4 with acetic acid.‡

The Raman spectrum (Fig. 2) of the reaction mixture—measured after *ca.* 5 min—shows correspondingly the known characteristic bands of **1a**.§ Because of the high, even approximately icosahedral symmetry of the skeleton, only a few bands are observed (see below): the medium intensity bands above 900 cm^{-1} are assigned as usual to $\nu(Mo{=}O)$-type vibrations, and the very intense band at *ca.* 870 cm^{-1}—typical for the high symmetry and observed for all Keplerates of the present type—to the totally symmetric A_g-type breathing vibration of the μ_3-O atoms.

The spectrum can be considered as a unique textbook example for giant species with icosahedral symmetry because of the quite small number of observed lines. This results due to the fact that only the g-modes (and only those belonging to A_g and H_g) are Raman active and that the point group has fivefold degeneracy.[17a,b] The most intense lines have to be assigned to vibrations having the largest change of the electronic polarizability (tensor); this is the case for A_g-type modes and especially for stretching-type ones.[17a,b] Based on the bond polarizability model,[17a,b] the present most intense line can be understood in context with the large number of 180 μ_3-O bonds involved in the above mentioned vibration. (The assignment is based on the fact that $\nu(Mo{=}O)$-type vibrations are expected to occur above 900 cm^{-1}.) The intensity of bands of totally symmetric vibrations has been correlated with bond polarizabilities[17b] and even bond orders.[17c]

The spontaneous self-assembly of **1a** upon addition of the $\{Mo^{V}_2O_4\}^{2+}$ building block thus means that the latter acts as a potent effector/stimulant for the expression of the other building block, the $\{(Mo^{VI})Mo^{VI}_5\}$ unit, while the driving force of the reaction is the high formation tendency of spherical clusters.[18] The fascinating result in other words: the $\{Mo^{V}_2O_4\}^{2+}$ units direct the formation of the necessary $\{(Mo^{VI})Mo^{VI}_5\}$ units/building blocks in a complex mixture based on constitutional dynamic chemistry and their subsequent linking. $\{(Mo^{VI})Mo^{VI}_5\}$ pentagonal units are found in $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ which forms in strongly acidified aqueous solutions of molybdate,[19] but are not expected to be present in aqueous solutions of molybdates at pH 4.¶



Scheme 1

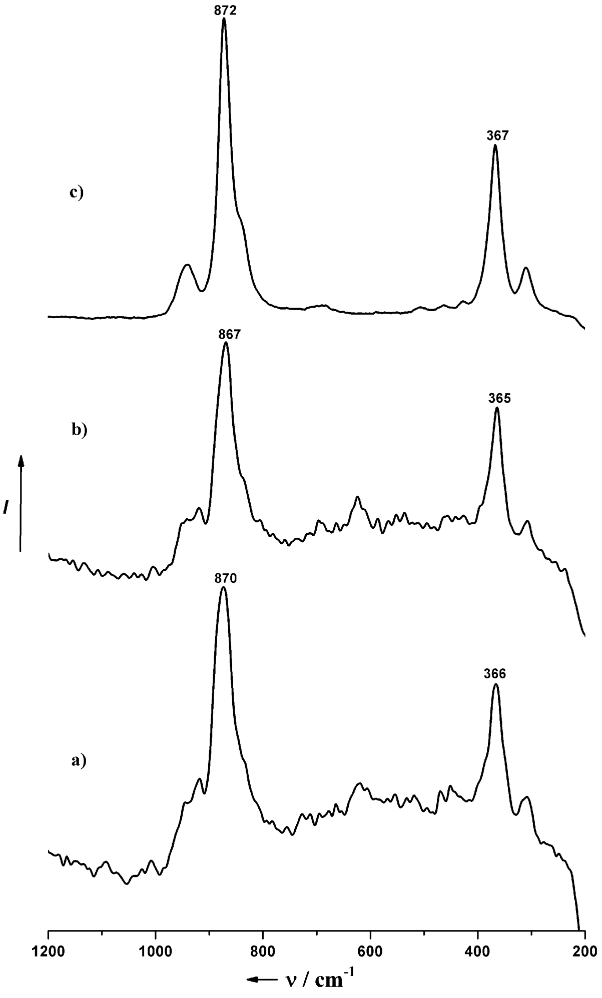


Fig. 2 Time dependence investigation of the formation of **1a**, using Raman spectroscopy (λ_{exc} = 785 nm): the Raman spectra of the reaction mixture are measured after 5 minutes (a), 30 minutes (b); for comparison the aqueous solution Raman spectrum of the crystals (homogeneous precipitate) separated from this reaction mixture is given which practically agrees with that of an authentic sample of crystals of **1**[7a] (c).

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Notes and references

‡ After to a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1 g, 0.81 mmol) in 50 mL of water, 30 mL of 50% acetic acid was added and the pH adjusted to

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4 with 25% aqueous ammonia (*ca.* 4 mL), the powdered oxalato complex $(NH_4)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$[20] (1.5 g, 2.7 mmol) was added. The Raman spectrum of the solution was measured after 5 min and again after 30 min. (In a parallel experiment the reaction process was followed by UV-Vis spectroscopy by removing 1 mL aliquots of the reaction mixture at different times and diluting to 10 mL with water.) Precipitation started slowly and shortly after *ca.* 30 min. The solid was collected after 4 h, washed with ethanol and air-dried (yield: 0.35 g, 16% based on $\{Mo^V_2\}$), and identified as compound **1** by comparison with an authentic sample based on X-ray crystallography and analyses.[13,14] More of the compound deposited as expected from the reaction mixture upon standing.

§ Raman spectroscopic studies indicate that **1a** is present since the very early stages of the reaction. However, due to the high intensity of the bands characteristic for **1a**, the method does not allow an unambiguous identification of the other species present with low intensity Raman lines in the reaction mixture, *i.e.* in the dynamic library. The extent of formation of **1a** was investigated from complementary UV-Vis spectroscopic measurements, on the basis that only **1a** and the dinuclear Mo(V) complex absorb at *ca.* 450 nm which is considered to be correct; the result: *ca.* 15% (based on $\{Mo^V_2\}$ units) after 15 min.

¶ There has been some controversy on the polycondensation processes that occur upon acidification of aqueous molybdate solutions.[21] Nevertheless there is now wide agreement, based on Raman and ^{95}Mo NMR spectroscopic studies, that $[H_xMo_7O_{24}]^{x-6}$ (x = 0–2) and $[Mo_8O_{26}]^{4-}$ are present at pH 4 (value of our present investigation) in aqueous solutions of molybdates acidified by hydrochloric or nitric acid.[22,23] The nature of the Mo(VI) species present in ammonium acetate/acetic acid has been investigated by electrochemical techniques in order to get information about the present type of reaction pathway but no definite conclusion was obtained.[24] This will be subject of our further investigation.

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VIP Polyoxometalates

Unprecedented and Differently Applicable Pentagonal Units in a Dynamic Library: A Keplerate of the Type $\{(W)W_5\}_{12}\{Mo_2\}_{30}$**

Christian Schäffer, Alice Merca, Hartmut Bögge, Ana Maria Todea, Melissa L. Kistler, Tianbo Liu, René Thouvenot, Pierre Gouzerh, and Achim Müller**

Dedicated to Professor Peter Day on the occasion of his 70th birthday

In the field of polyoxometalate chemistry, porous spherical molybdenum oxide-based clusters of the type $\{(Mo^{VI})Mo^{VI}{}_5\}_{12}(linker)_{30}$,[1] called Keplerates,[2a,b] are notable not only from an aesthetic point of view[2c] but also because they show properties of interest for different areas of science. Some of these clusters can act as artificial cells exhibiting gated pores while interacting specifically with their environments; others are of interest for several aspects of materials science.[3–5] In detail, of interest are a) solution properties in connection with a new type of assembly process leading to vesicles, including magnetic ones,[6a,b] b) the option to employ the characteristic interactions with amphiphiles for the generation of monolayers and Langmuir–Blodgett films[6c] as well as highly ordered honeycomb nanostructures at air–water interfaces,[6d] c) the integration into sol–gel-derived silica to obtain unprecedented hybrids,[6e] and d) the discovery of novel magnetic properties,[6f] which are of interest for the understanding of Kagomé lattices' spin states.[6g,h]

While Keplerates of the mentioned type with binuclear linkers $\{Mo^V{}_2O_4\}^{2+}$ have been synthesized by partly reducing an aqueous molybdate solution in the presence of appropriate bidentate bridging ligands[1b,7] (leading in the case of acetate to $\{Mo^V{}_2O_4(OOCCH_3)\}^+$ linkers), Keplerates of the type $\{(Mo)Mo_5\}_{12}M_{30}$ ($\equiv \{Mo_{72}M_{30}\}$) can be obtained directly by the addition of mononuclear linkers M such as Fe^{3+}, Cr^{3+}, and VO^{2+} to a dynamic library of the pentagonal units $\{(Mo)Mo_5O_{21}(H_2O)_6\}^{6-}$,[8] or by reaction of, for example, Fe^{3+} with $\{(Mo)Mo_5\}_{12}\{Mo_2\}_{30}$ ($\equiv \{Mo_{132}\}$), thereby exchanging binuclear for mononuclear linkers.[9] As the pentagonal $\{(Mo)Mo_5\}$-type units appear in this context as transferable ligands (parallels have been made between infinite coordination polymers and discrete metallosupramolecular arrays), the mentioned clusters can be called coordination polymers with spherical periodicity.[8c,10] This analogy points to a route for the planned syntheses of other corresponding molecular spheres based on a careful selection of appropriate ligands and metal ions with specific coordination behavior. Herein we report the synthesis of a $\{(W)W_5\}_{12}\{Mo_2\}_{30}$ ($\equiv \{W_{72}Mo_{60}\}$)-type species with 30 $\{Mo^V{}_2O_4(acetate)\}^+$ linkers with metal–metal bonds and 12 unprecedented pentagonal $\{(W)W_5O_{21}(H_2O)_6\}^{6-}$ ($\equiv \{(W)W_5\}$) ligands, which are necessary for the formation of the spherical cluster and are generated in a dynamic library of tungstates (see below). Whereas the $\{(Mo)Mo_5\}$-type building blocks were known to occur in $[Mo_{36}O_{112}(H_2O)_8]^{8-}$ present at low pH values in H_2O,[11] no corresponding pentagonal unit has been observed to date among the thousands of polyoxotungstates. On the basis of the present work, there is the option for the extension of the molybdate-based Keplerate chemistry to the tungstates, which is possible owing to the use of the transferable pentagonal $\{(W)W_5\}$-type units now available; this allows, for example, the synthesis of $\{(W)W_5\}_{12}M_{30}$ clusters, which are of importance for materials science aspects, with the above-mentioned magnetic M^{3+} linkers.[12a] Transferable, pentagonal building blocks are extremely rare in chemistry but are, generally speaking, relevant for the construction of curved giant species, such as the often highlighted hedgehog $\{Mo_{368}\}$ cluster.[4,5] On the other hand, pentagons in a general sense play a unique role starting from modern solid-state chemistry and dating backwards via many topics to the ideas of the ancient Greek mathematicians.[13] In any case, the present discovery allows us to follow new interesting routes in chemistry and materials science, especially because the surface properties of tungsten oxide based systems are different from those of the molybdates. Whereas the high formation tendency of the spherical shell of the type $(pentagon)_{12}(linker)_{30}$ based on pentagonal units has been discussed earlier in terms of a general chemical principle,[12b] it is also evident that the formation of the present pentagonal units can be considered in the framework of a "constitutional dynamic chemistry" formulated by Lehn, that is, with respect to systems responding to external stimuli (see below).

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Compound **1** was obtained by "recrystallization" of the red-brown microcrystalline ammonium salt of **1a** (obtained by treating an acidified aqueous solution of sodium tungstate containing a rather high concentration of acetate with $(NH_4)_2[Mo^V{}_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ in aqueous solution after adding dimethylammonium chloride. **1**, which crystallizes in the space group $R\bar{3}$, was characterized by elemental analysis, thermogravimetry (to determine the crystal water content), redox titrations (to determine the number of Mo^V centers), spectroscopic methods (IR, Raman, UV/Vis, and ^1H and ^{13}C NMR) and single-crystal X-ray structure analysis[14] including bond valence sum (BVS) calculations.

$$[(CH_3)_2NH_2]_{48}[\{(W^{VI})W^{VI}{}_5O_{21}(H_2O)_5(CH_3COO)_{0.5}\}_{12}\{Mo^V{}_2O_4\text{-}(CH_3COO)\}_{30}]\cdot \text{ca.}\ \{270\,H_2O + 7\,CH_3COO^- + 7\,(CH_3)_2NH_2{}^+\} \equiv [(CH_3)_2NH_2]_{48}\cdot \mathbf{1a}\cdot \text{ca.}\ \{270\,H_2O + 7\,CH_3COO^- + 7\,(CH_3)_2NH_2{}^+\} \quad \mathbf{1}$$

The anionic capsule **1a** is built up of 12 pentagonal units of the type $\{(W^{VI})W^{VI}{}_5\}$ that are positioned at the vertices of an icosahedron and connected by 30 $\{Mo^V{}_2O_4(CH_3COO)\}^+$ linking groups (Figure 1). Correspondingly, the seven-coordinated W centers of the 12 pentagonal units span an icosahedron and the 30 linkers a distorted truncated icosahedron. The single-crystal X-ray structure analysis additionally shows the presence of six disordered acetate ligands positioned under the pentagonal units; each of them connects a central W atom to a peripheral W atom.

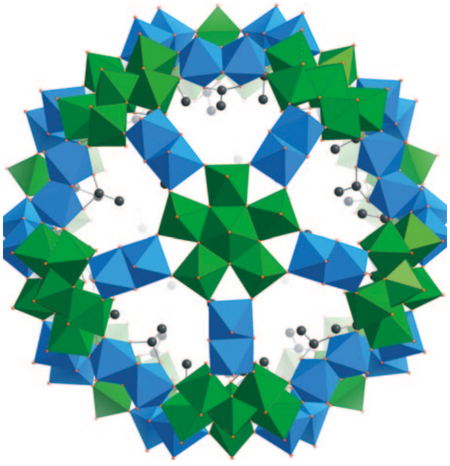

Figure 1. Structure of **1a** with perspective view along a fivefold symmetry axis highlighting a pentagonal $\{(W^{VI})W^{VI}{}_5\}$-type unit (in the center) and the five related $\{Mo^V{}_2O_4\}^{2+}$ ($=\{Mo^V{}_2\}$) linkers stabilized by the acetate ligands (not visible) attached to it. ($\{(W^{VI})W^{VI}{}_5\}$ groups green, $\{Mo^V{}_2\}$ bridges blue and both in polyhedral representation, C atoms black spheres).

The construction of $\{Mo_{132}\}$- and $\{W_{72}Mo_{60}\}$-type Keplerates requires the presence of pentagonal units $\{(M)M_5\}$ (M = Mo or W) along with suitable linkers. While it was known that $\{(Mo^{VI})Mo^{VI}{}_5\}$-type fragments (or building blocks) are abundant in acidified molybdate solutions, that is, occur in the $[Mo_{36}O_{112}(H_2O)_8]^{8-}$ anion,[11] a related situation does not apply for tungstate chemistry. None of the polyoxotungstates reported to date,[15] including the largest ones,[16] contains the corresponding important pentagonal $\{(W)W_5\}$ units.[17] Aqueous tungstate solutions at pH values of about 4 contain ψ-, β-, and α-metatungstates, which are built up of WO_6 octahedra (metastable β- and thermodynamically stable α-$[H_2W_{12}O_{40}]^{6-}$ species have Keggin-type structures).[15] The linkers, which are important for the syntheses of the two Keplerates mentioned above, can either be produced in situ from molybdate solutions under reducing conditions (which led to the deliberate synthesis of $\{Mo_{132}\}$-type clusters)[1] or added in the form of $[Mo^V{}_2O_4(C_2O_4)_2]^{2-}$, as in the case of the synthesis of **1** and of the corresponding $\{Mo_{132}\}$ compound.[18] The formation of **1a** under the present conditions demonstrates that the reaction is symmetry-driven and free-energy-favored.

The Raman spectra of **1** in H_2O have been recorded for various concentrations, starting from a nearly saturated solution (i.e. ca. 1 g mL^{-1}); no significant change was observed upon dilution. This finding indicates that self-assembly into supramolecular structures does not occur in aqueous solutions under these conditions (see below). The solution spectrum of **1** is practically identical to that of solid **1** (Figure 2), which supports the stability of **1a** in solution. (The same holds for the $\{Mo_{132}\}$-type species with different ligands.[1,19]) Though the spectrum is, as expected, similar to that of its $\{Mo_{132}\}$ counterpart, [1,7c] significant (but expected) differences arising from a change in the M=O bond polarizability are observed: the line at 976 cm^{-1}, which is assigned to the $\nu(W{=}O_{term})$ A_g-type vibration (assuming I_h symmetry), is much more intense than the corresponding line of the $\nu(Mo{=}O_{term})$ vibration of $\{Mo_{132}\}$, in agreement with the higher bond polarizability of the terminal W=O bond (effect not caused by the different excitation lines). $\nu(W{=}O_{term})$ at 976 cm^{-1} also occurs at higher wavenumbers than the corresponding vibrations of $\{Mo_{132}\}$ (the weak band at ca. 957 cm^{-1} of **1a** could be assigned to the $\nu_s(Mo{=}O_{term})$ vibration of the linkers) in accordance with the higher W=O bond strength in **1a**. This leads to a lower electron density on the corresponding O atoms, which changes the nanosurface properties (see below).

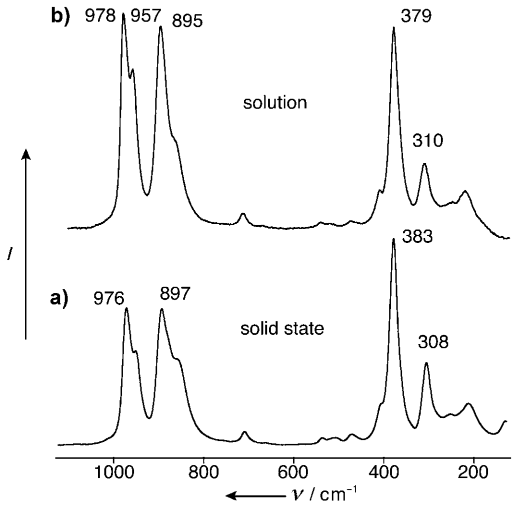

Figure 2. Raman spectra ($\lambda_{exc} = 765$ nm) of **1** a) in the solid state and b) in aqueous solution as evidence of the stability of **1a** in solution; see text for a discussion of the related metal oxide surface characteristics.

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Further evidence for the stability of {$W_{72}Mo_{60}$} clusters in solution is provided by NMR spectroscopy studies. The ^{1}H NMR spectrum of **1** in D_2O (Figure 3 a) shows two sharp singlets at $\delta = 2.84$ and 1.97 ppm, which are assigned to the methyl groups of the dimethylammonium cation and to free acetate, respectively. The broad feature centered near 1 ppm is attributed to coordinated acetate. The latter signal clearly exhibits several components spanning approximately 1 ppm, which indicates non-equivalent ligands; this finding is consistent with the results of the single-crystal structure analysis for **1**. The ^{13}C NMR spectrum of **1** in D_2O (Figure 3 b) shows partially overlapping broad resonances for the methyl (maxima at ca. $\delta = 23.6$ and 24.8 ppm) and carboxylate groups (maxima at ca. $\delta = 178.9$, 179.8, and 180.6 ppm) of coordinated acetate ligands, while the resonances of free acetate are hardly detectable at $\delta = 22.1$ and 177.4 ppm. No significant change, in particular no increase in the intensity of free acetate signals, is observed upon raising the temperature to 353 K. (Our attempts to obtain a clean ^{183}W NMR spectrum of **1** in solution were unsuccessful. Broad features were observed, likely arising from the expected fast relaxation of the ^{183}W nuclei in such large species.) Most spectroscopic measurements were performed on deaerated solutions, which, however, did not appear to be especially sensitive to oxidation. Raman and ^{1}H and ^{13}C NMR spectroscopy therefore demonstrate the stability of **1a** in aqueous solutions, a feature shared with its {Mo_{132}} counterpart.[19]

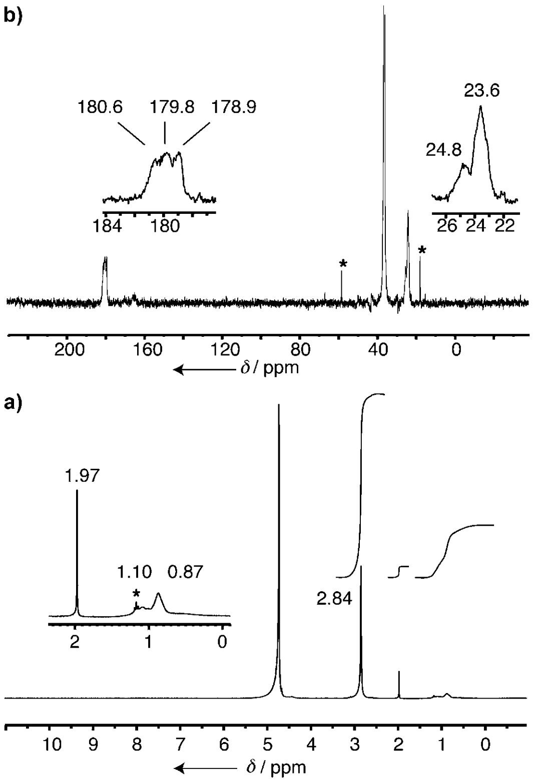

Figure 3. NMR spectra of **1** in D_2O solutions: a) 300.13 MHz ^{1}H spectrum ($c = 0.5$ mmol L^{-1}) with relative integration of $(CH_3)_2NH_2^+$ and of free and coordinated acetate resonances, in agreement with the stoichiometry of **1**; b) 125.7 MHz ^{13}C spectrum ($c = 20$ mmol L^{-1}). The signals of residual ethanol are marked by *.

Detailed knowledge of the properties of the structurally well-defined nanosurfaces of the present type of metal oxide based system is of interest for several aspects of materials science. In this context, we have studied solution properties of the new cluster **1a** and compared them to those of the molybdenum analogue {Mo_{132}}.[6a] Both cluster anions are soluble in polar solvents owing to their high negative charges and the hydrophilic nature of their surfaces. The {$W_{72}Mo_{60}$} clusters, which exist in aqueous solution as discrete, hydrophilic macroanions carrying a few more charges than the {Mo_{132}} ones (these contain fewer integrated acetate ligands[1]), show self-assembly when acetone is introduced into the solution to decrease the solvent polarity. In solvents containing 30–75 vol % acetone, the macroions **1a** form spherical, single-layer, hollow, vesicle-like blackberry-type structures, as confirmed by static and dynamic laser light scattering studies. The size of the assemblies increases with increasing acetone content, while a linear relationship between the hydrodynamic radius R_h of the assemblies and ε^{-1} is observed (Figure 4; ε is the solvent dielectric constant). This relationship is consistent with our previous results obtained for {Mo_{132}} macroions in water/acetone mixed solvents.[6a,20] The supramolecular structure formation occurs when the macroions carry some (but not too many) negative charges, which leads to attraction influenced by the cations positioned between the anions.[6a,20] But when the macroions are too highly charged, the strong electrostatic repulsion prevents them from moving close to each other. Nor does assembly occur if the clusters are (almost) uncharged, owing to the lack of the above-mentioned charge-based effect, for example, in pure acetone solution. Importantly, the {$W_{72}Mo_{60}$} blackberry-type structures have a smaller average size than the {Mo_{132}} ions under the same conditions, owing to the higher charge density on {$W_{72}Mo_{60}$} clusters (for an explanation, see reference [6b]). The influence on the surface charge caused by the larger number of integrated acetate ligands of **1a** overcompensates the influence of the smaller bond

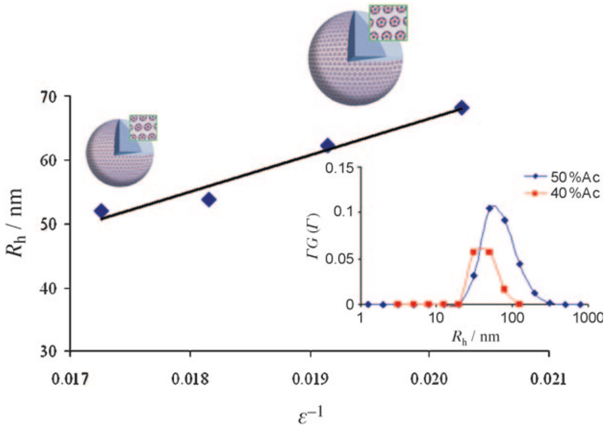

Figure 4. The {$W_{72}Mo_{60}$} macroions self-assemble in water/acetone solutions into blackberry-type structures, the size of which increases with increasing acetone content, that is, decreasing dielectric constant. Inset: CONTIN analysis[23] of the dynamic light scattering results for {$W_{72}Mo_{60}$}/water/acetone solutions containing 40 and 50 vol % acetone.

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polarity of the W=O bonds corresponding to a smaller electron density on the O atoms (see above).

It is an important result that the high formation tendency of the spherical cluster **1a** influences the composition of the units present in the dynamic library. Pentagonal units of the type {(W)W$_5$} were not observed in any known polyoxotungstate but are necessary for the formation of **1a** and corresponding spherical and, generally speaking, giant curved species. In the present scenario, we can refer to constitutional dynamic chemistry, as described by Lehn, "whereby a chemical entity, be it as well molecular as supramolecular, undergoes continuous change in its constitution through dissociation into various components and reconstitution into the same entity or into different ones".[21] Another impressive directly related example is provided by the formation of the {Mo$_{72}$Fe$_{30}$}-type Keplerate containing an encapsulated Keggin ion (a new type of supramolecular species with a cluster noncovalently bound inside a cluster). The necessary pentagonal units are formed by an unprecedented reaction of $[PMo_{12}O_{40}]^{3-}$ with Fe^{3+} ions and finally generate the spherical shell through linking with the Fe^{3+} ions. This result was originally discussed with reference to "supramolecular Darwinism,"[13] as the terms "adaptation" and "protection" as well as "symbiosis" hold, and was later referred to and highlighted by Lehn in the statement, "The supramolecular organization drives the selection of the components giving the 'fittest constituent'".[21]

Experimental Section

1: $Na_2WO_4 \cdot 2H_2O$ (8.0 g, 24.25 mmol) and $NaCH_3COO \cdot 3H_2O$ (36.0 g, 264.6 mmol) were dissolved in degassed water (100 mL) while the pH value of the reaction mixture was adjusted to approximately 4 with degassed 100 % acetic acid (60 mL). After the finely powdered oxalato complex $(NH_4)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$[22] (9.0 g, 16.13 mmol) was added quickly, the solution was heated under an argon atmosphere for 90 min at 120 °C (oil bath temperature) under vigorous stirring (color change to dark brown). The solution was cooled to room temperature, and the red-brown microcrystalline powder was filtered off, washed thoroughly with ethanol, and dried with diethyl ether (yield: 1.8 g, 15 % based on W). Then $(CH_3)_2NH_2Cl$ (200 mg, 2.45 mmol) was added to a solution of the obtained microcrystalline product (200 mg, 0.0056 mmol) in water (10 mL). After two to three days, the red-brown crystals were filtered off, washed with ethanol, and dried with diethyl ether. In ongoing studies, attempts are being made to improve the yield (Thesis, C. Schäffer). Elemental analysis (%) calcd: C 6.61, N 2.16, W 37.18, Mo 16.17 (values refer only to 250 H_2O corresponding to the relevant (i.e. for the analysis) loss of crystal water); found: C 6.6, N 2.4, W 37.9, Mo 17.1 (W and Mo analyses were performed by Mikroanalytisches Labor Egmont Pascher, An der Pulvermühle 3, 53424 Remagen, Germany). Cerimetric titrations: 60 ± 2 Mo^V. IR (KBr pellet; characteristic bands): $\tilde{\nu} = 1625$ (m, $\delta(H_2O)$), 1539 (m, $\nu_{as}(COO)$), 1440 (m), 1420 (m, $\delta(CH_3)$, $\delta_{as}(NH_4^+)$, $\nu_s(COO)$), 972 (m) and 960 (w-m, $\nu(W{=}O)$), 879 (m), 812 (vs), 733 (s), 658 (w), 577 (s), 519 (w), 470 cm^{-1} (w). Characteristic Raman bands: see Figure 2. ^1H NMR (D_2O): $\delta = 2.84$ (s, $(C\mathit{H}_3)_2NH_2^+$), 1.97 (s, free $C\mathit{H}_3CO_2^-$), 1.10, 0.87 ppm (coordinated $C\mathit{H}_3CO_2^-$). ^{13}C NMR (D_2O): $\delta = 180.6$, 179.8, 178.9 (coordinated $CH_3\mathit{C}O_2^-$), 35.77 ($(\mathit{C}H_3)_2NH_2^+$), 24.8, 23.6 ppm (coordinated $\mathit{C}H_3CO_2^-$). Characteristic UV/Vis bands (H_2O, absorption): $\lambda = 240$, 375 nm (vs, br).

Raman spectra were collected with a Kaiser Optical Systems HL5R Raman spectrometer equipped with a near-IR laser diode working at 785 nm. The laser power was adjusted to 15–20 mW at the sample position for all spectra. The average resolution is 3 cm^{-1}.

^1H and ^{13}C NMR spectra of **1a** were obtained from D_2O solutions at 300.13 and 125.7 MHz on Bruker AvanceII 300 and DRX 500 spectrometers, respectively. Chemical shifts were referenced to external tetramethylsilane by setting the methyl resonance of residual ethanol to 1.17 (^1H) and 17.33 ppm (^{13}C). A commercial Brookhaven Instrument laser light scattering spectrometer equipped with a solid-state laser operating at 532 nm was used for static and dynamic light scattering experiments. The data, analyzed by the CONTIN method,[23] can be used to determine the average hydrodynamic radius R_h of the particles. Detailed descriptions of the SLS and DLS technique can be found in an earlier publication.[6a]

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[13] The "magic" pentagons play an extraordinary role in culture and the history of science as well as in modern solid-state chemistry and physics, beginning with the Pythagoreans (the pentagram was the emblem of their school), via Archimedean and Keplerian type tilings, Fibonacci chains, Goethe's Faust (the pentagram) to Weyl and Penrose. They are of interest in many scientific disciplines: in discrete mathematics (one of the five regular bodies is built up of pentagons), in architecture and art history (in the sense of Fuller's domes and in the context of the golden section), in solid-state chemistry and physics (in the context of the fascinating quasicrystals and hybrids of real and quasicrystals), in virology (owing to the structure of spherical viruses), and last but not least in modern synthetic chemistry, allowing novel design strategies of curved species, that is, of molecular spheres (fullerenes and Keplerates) and wheels (molybdenum-blue-based) as well as of others, such as the {Mo$_{368}$} cluster (A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann, A. Dress, *Angew. Chem.* **2002**, *114*, 1210 – 1215; *Angew. Chem. Int. Ed.* **2002**, *41*, 1162 – 1167); remarkably, the {(M)M$_5$}-type units also play a role in catalysis, while it was proposed that they are even precursors in case of the syntheses of the corresponding vanadium molybdenum oxide based catalysts. The pentagonal units can be considered as magic, as Casper and Klug were inspired by Fuller's domes to understand the structure of spherical viruses; see section title "Viral Capsids Resemble Geodesic Domes" and a picture of the latter (Figure 32.12) in: D. Voet, J. G. Voet, *Biochemistry*, 2nd ed., Wiley, New York, **1995**, pp. 1082 – 1083; see also Ref. [1b]. Related information: a) *Quasicrystals, Networks, and Molecules of Fivefold Symmetry* (Ed.: I. Hargittai), VCH, New York, **1990**; b) A. Müller in *Facetten einer Wissenschaft: Chemie aus ungewöhnlichen Perspektiven* (Eds.: A. Müller, H.-J. Quadbeck-Seeger, E. Diemann), Wiley-VCH, Weinheim, **2004**, pp. 65 – 90; c) S. C. Glotzer, A. S. Keys, *Nature* **2008**, *454*, 420 – 421; d) A. Müller, P. Kögerler, H. Bögge, *Struct. Bonding (Berlin)* **2000**, *96*, 203 – 236; e) M. Sadakane, N. Watanabe, T. Katou, Y. Nodasaka, W. Ueda, *Angew. Chem.* **2007**, *119*, 1515 – 1518; *Angew. Chem. Int. Ed.* **2007**, *46*, 1493 – 1496; f) W. Ueda, M. Sadakane, H. Ogihara, *Catal. Today* **2008**, *132*, 2 – 8.

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[17] Interestingly, pentagonal {(M)M$_5$}-type units occur without M=O (double) bonds in solid-state structures of some lower-valence molybdenum and tungsten oxides, e.g., Mo_5O_{14} (L. Kihlborg, *Ark. Kemi* **1963**, *21*, 427 – 437) and $W_{18}O_{49}$ (A. Magnéli, *Ark. Kemi* **1949**, *1*, 223 – 230; M. Lundberg, M. Sundberg, A. Magnéli, *J. Solid State Chem.* **1982**, *44*, 32 – 40); see also: D. L. Kepert, *The Early Transition Metals*, Academic Press, London, **1972**, pp. 260 – 263 and F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, **1980**, p. 847 and Figure 22-C-2. In this case, the formation of the pentagonal units seems to be favored by the high temperatures of the solid-state reactions.

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Porous Capsules

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Softening of Pore and Interior Properties of a Metal-Oxide-Based Capsule: Substituting 60 Oxide by 60 Sulfide Ligands[**]

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In memory of Jerzy Haber

The discovery of fullerenes[1] has induced considerable interest in spherical molecular clusters, see for example Refs. [2–5]. Among fullerene-like molecules, spherical water-soluble metal-oxide-based nanocapsules of the type $\{(M^{VI})M^{VI}_5\}_{12}(\text{linker})_{30}$ (M = Mo or W), belonging to the family of Keplerates,[5,6] show quite attractive features in the context of nano- and materials science, especially in confined scenarios.[7–9] Correspondingly, they have been the focus of reviews[10,11] and highlights, including some in recent textbooks.[12] The nanocapsules contain 12 metal-oxide-based pentagonal units linked by either mononuclear (e.g. Fe^{3+}, Cr^{3+} or VO^{2+})[7b] or dinuclear ($\{Mo^V_2O_4\}^{2+}$) spacers and 20 pores/channels.[10,11] In case of the Mo_{132}-type cluster, the interiors of the capsules can be fine-tuned by changing the internal ligands coordinated to the $\{Mo^V_2O_4\}$ linkers. Most importantly, the above-mentioned Keplerates can interact specifically with their environment.[10–12] Especially the crown ether-type $\{Mo_9O_9\}$ pores can react through hydrogen bonding with organic cations (like the guanidinium, amidinium, or protonated urea type),[13] as well as with hydrated metal ions, whereby all act as plugs leading to the closing of the capsules.[14] The 20 smaller $\{M_3M'_3O_6\}$ pores of the negatively charged $M_{72}M'_{30}$-type Keplerates ($M = Mo^{VI}$, W^{VI}; $M' = V^{IV}$, Fe^{III}) have a high affinity for K^+ and $NH_4{}^+$ ions similar to 18-crown-6 receptors;[15] this corresponds to sphere surface supramolecular chemistry. The present type of Keplerates also has the potential for being used as nanoreactors.[16] Replacement of the bridging oxo ligands of the above-mentioned $\{Mo^V_2O_4\}$ linkers by softer sulfido ligands provides a new option to change the properties/reactivities of Mo_{132}- and $W_{72}Mo_{60}$-type capsules. This change of linkers has now been achieved: We report here the synthesis, crystal structure, and spectroscopic characterization of $W_{72}Mo_{60}$-type capsules with $\{Mo^V_2O_2(\mu\text{-}S)_2(L)\}$ linkers ($L = CH_3COO^-$). The important result is that the pore sizes and reactivities/flexibilities as well as the interior capsule properties—also in context of an increase in the internal shell polarizability—are changed by substituting 60 oxide atoms of the known Keplerate containing $\{Mo^V_2O_4\}$ linkers by 60 sulfide atoms; this has, for example, consequences for ligand and cation uptake/release processes[17] as well of course as for the structure of encapsulated species.

The synthesis process follows that of previously reported mixed metal Keplerates where the basic $\{(M^{VI})M^{VI}_5\}$-type units (M = Mo, W) form in solution according to the principles of "Constitutional Dynamic Chemistry" of Lehn[18] while finally 12 of the units get appropriately linked when cations, like $\{Mo_2O_4(aq)\}^{2+}$,[19] $VO(aq)^{2+}$,[15a] or $Fe(aq)^{3+}$ [15b] are added to a dynamic library of molybdates and tungstates. In the present case, an aqueous solution of the new dinuclear linker $\{Mo^V_2O_2(\mu\text{-}S)_2(aq)\}^{2+}$—prepared by hydrolysis of the oxo/thio compound usually used as a source of $\{Mo^V_2O_2(\mu\text{-}S)_2\}^{2+}$[20]—allowed to obtain the water-soluble Keplerate-type compound **1** (which allows future reactivity studies in solution) as starting material for the less soluble compound **2**[***] which was isolated by "recrystallization" of the nonrecrystallized **1** in the presence of cobalt (II) ions to get suitable crystals (for details see the Experimental Section). Whereas compound **1** could be only partially characterized because of the poor crystal quality (for the "approximate" formula see Experimental Section), this was not the case for compound **2** which is the focus of our present work. Compound **2**, which crystallizes in the space group *Immm*, was fully characterized by elemental analysis,

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[***] $Co_{12}[\{W^{VI}_6O_{21}(H_2O)_6\}_{11}\{W^{VI}_6O_{21}(H_2O)(H_2Mo^{VI}_2O_8(H_2O))\}\{Mo^V_2O_2S_2(CH_3COO)\}_{10}\{Mo^V_2O_2S_2(H_2O)_2\}_{20}]\cdot\text{ca.}\ \{11[(CH_3)_4N]^+ + 8\,Na^+ + 11\,CH_3COO^- + 4\,SO_4{}^{2-} + 350\,H_2O\} \equiv Co_{12}\cdot$**2a**$\cdot$lattice ingredients $\equiv$ **2** (formally written regarding the cation positioning).

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spectroscopic methods (IR, UV/Vis, and X-ray photoelectron spectroscopy), magnetic suceptibility measurements and single-crystal X-ray structure analysis (see Ref. [21] and the Experimental Section).

The obtained $W_{72}Mo_{60}$-type cluster **2a** belongs to the family of porous capsules having the general composition $\{(M^{VI})M^{VI}_5\}_{12}\{Mo^{V}_2O_2(\mu\text{-}X)_2\}_{30}$ (M = Mo or W; X = O or S). The 12 centers of the pentagonal $\{(W^{VI})W^{VI}_5\}$-type units are positioned at the vertices of an icosahedron and are connected by 30 $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}^{2+}$ linkers, the Mo atoms of which span a distorted truncated icosahedon (Figure 1); for general aspects of the related problem of interpenetrations of the Platonic and Archimedean solids see Refs. [3a,5,6a]. Ten CH_3COO^- are bound as bidentate bridging ligands to the Mo atoms of the 10 dinuclear linkers and 2 × 20 monodentate H_2O ligands to the Mo atoms of the other 20 (see the formula).

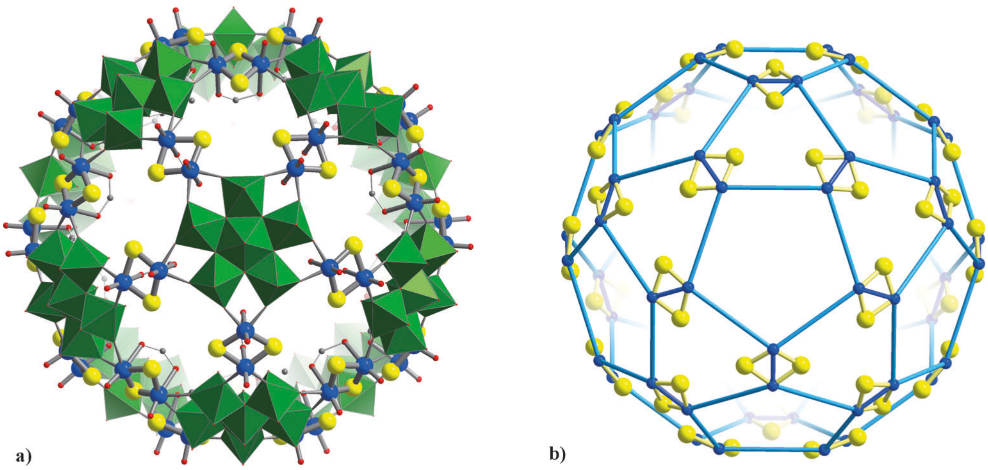

Figure 1. a) Combined polyhedral/ball-and-stick picture of **2a** with view along a five-fold symmetry axis highlighting a central pentagonal $\{(W^{VI})W^{VI}_5\}$-type unit (which can be considered as a ligand[7c]) and five related $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}$ linkers (stabilized by acetate ligands) as well as the pores which are obviously decreased in size by substituting oxide by sulfide ligands ($\{(W^{VI})W^{VI}_5\}$ groups in polyhedral representation green, Mo blue, S yellow, O red, C grey spheres). b) Structure of the $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}_{30}$ fragment, of which the Mo atoms form a distorted truncated icosahedron with 12 regular pentagons and 20 (trigonal) hexagons (60 Mo–S–Mo bridges in yellow and 30 Mo^{V}–Mo^{V} bonds in dark blue).

The average Mo–Mo distance of 2.84 Å is in close agreement with the corresponding values in dinuclear complexes containing the $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}$ core,[22] but is—as expected—larger than in the $\{M^{VI}_{72}Mo^{V}_{60}\}$-type Keplerates with the $\{Mo^{V}_2O_4\}$ linkers (2.58 Å for M = Mo[23a] and 2.57 Å for M = W[19]). The Mo–S–Mo bridges are nearly symmetrical (average Mo–S distance: 2.31 Å) and the average distance from the center of the pores, spanned by the three bridging S atoms to each of the latter atoms, is 3.00 Å (see Figure S1 in the Supporting Information); this gives, based on a van der Waals radius of S of 1.80 Å,[24] an indication of the geometric pore size, whereas the effective one depends on the experimental conditions. Anyhow the opening and receptor properties of the $\{W_3Mo_6O_6S_3\}$ pore are significantly different from those of the $\{Mo_9O_9\}$ and $\{W_3Mo_6O_9\}$ pores in the $\{Mo_{132}\}$- and $\{W^{VI}_{72}Mo^{V}_{60}\}$-type Keplerates with $\{Mo^{V}_2O_4\}$ linkers[19,23] (see also Figure S1 in the Supporting Information).

A result of general importance refers to the impressive segregation between the mostly hydrophobic internal wall—spanned/influenced by the ten internal acetate ligands—and the encapsulated "water molecule collection" which forms a rather well-defined unprecedented shell with no water molecules inside (for details including distances see Figure S2 in the Supporting Information). This type of "water" under confined conditions has unique properties[25] ("water" in hydrophobic cavities is considered to be of tremendous interdisciplinary interest[25]). One fascinating aspect is that one can tune the "water assembly" by changing the ratio of acetate and water ligands. But as this is not our major topic here it will be discussed in detail in the future (see also related comments in our recent publication[25]).

The IR spectrum of **2** shows—in addition to the very characteristic molybdenum-oxide-based band pattern of the $\{M^{VI}_{72}Mo^{V}_{60}\}$ clusters[19,23]—the bands of stretching vibrations of the acetate ligands. The band at 457 cm^{-1} is assigned to ν_{as}(Mo–S–Mo) stretching modes of the linkers (see Figure S3 in the Supporting Information for further details).

The stability of the $\{(W)W_5\}_{12}\{Mo_2O_2S_2\}_{30}$ skeleton in solution had to be proven by measuring the Raman spectrum of the soluble compound **1**—an important aspect for future studies. The very characteristic spectrum for the spherical/icosahedral system—showing correspondingly only a very few intense lines (see also Refs. [11e,19])—is shown in Figure S4 in the Supporting Information, together with correspondingly similar ones of the related $\{(W)W_5\}_{12}\{Mo_2O_4\}_{30}$-[19] and $\{(Mo)Mo_5\}_{12}\{Mo_2O_4\}_{30}$-type[23] clusters; the comparison allows to get information about the capsule property changes due to the replacement of molybdenum by tungsten atoms. This leads to different M=O bond strengths and bond polarizabilities as well as to different interactions of the metal atoms with the internal ligands (see the Supporting Information with additional literature for a detailed discussion). Preliminary NMR studies of the solution have also been performed (see the Supporting Information).

In conclusion, the family of metal-oxide-based $\{(W^{VI})W^{VI}_5\}_{12}\{Mo^{V}_2O_4\}_{30}$-type capsules has been extended to those with $\{Mo^{V}_2O_2(\mu\text{-}S)_2\}$ linkers, that is, substituting correspondingly 60 oxide by 60 sulfide atoms. The $\{W_3Mo_6O_6S_3\}$-type pores differ from their $\{M_3Mo_6O_9\}$ (M = Mo, W) counterparts with respect to their openings, their flexibilities, and their reactivities, especially in the context of cation and ligand uptake/release processes as well as strength of

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interactions of the internal ligands with the metal cations and consequentially the influence on the encapsulated species. Furthermore, the pore affinity for hydrogen-bonded guests/plugs is decreased thereby decreasing the tendency/option of pore closing. Also important, the replacement of 60 oxide by 60 sulfide ligands in the porous capsule skeleton increases the internal shell polarizability which influences reactions inside the capsules and the structure of encapsulated species. These remarks should give rise to corresponding future investigations of solutions of the soluble compound **1**, especially in the context that several materials science problems have been studied based on the metal-oxide-type Keplerates. In this context it is also intended to get structural data for **1**.

Experimental Section

Synthesis of **1** (a precursor for **2**, the focus of our article): A sample of the oxo/thio cluster of empirical composition "$K_{0.4}\{N(CH_3)_4\}_{0.1}I_{0.5}[Mo_2S_2O_2(OH)_2(H_2O)]\cdot 6.3\,H_2O$"[20a] (1.0 g, 2 mmol) was dissolved in hydrochloric acid (4 M, 10 mL) by mild heating (50 °C). The red solution was filtered and added to a solution of $Na_2WO_4\cdot 2\,H_2O$ (4.5 g, 13.64 mmol) and $NaCH_3COO\cdot 3\,H_2O$ (10.0 g, 73.49 mmol) in water (40 mL) acidified to a pH around 4 with 100 % acetic acid (18 mL). The milky orange suspension was heated quickly to 80 °C (oil bath temperature) by vigorous stirring in an argon atmosphere before some water (30 mL) was added. The reaction mixture was heated further (120 °C, oil bath temperature) under continuing vigorous stirring until a clear red solution was obtained (after 90 min). The solution was cooled to room temperature, and the red microcrystalline powder that started to precipitate during this time was filtered off, washed thoroughly with ethanol, and dried with diethyl ether (crude product, yield: 0.7 g, around 30 % based on Mo). Cubic crystals ($a = 38.0$ Å, $V = 54891$ Å^3) of compound **1** were obtained within 1–2 days by recrystallization of the crude product in water (1 g, 5 mL; yield: 0.6 g). The crystal structure could not be fully refined (poor quality of the crystals), but there is unambiguous evidence that the spherical $W_{72}Mo_{60}$-type Keplerate **1a** is quite similar to **2a** according to results from IR, Raman, UV/Vis and NMR data (note: the numbers of coordinated acetate ligands and $[(CH_3)_4N]^+$ (TMA) ions do not need to be identical). Anyhow in the absence of a detailed crystal structure analysis and on account of the low abundance of several elements, only an approximate formula for compound **1** can be given: $[(CH_3)_4N]_7Na_{25}[\{W^{VI}{}_6O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_2S_2(CH_3COO)\}_{20}\{Mo^{V}{}_2O_2S_2(H_2O)_2\}_{10}]\cdot$ca.$\{8\,Na^+ + 8\,CH_3COO^- + 300\,H_2O\}$ (formally written regarding cation positioning) $\equiv [(CH_3)_4N]_7Na_{25}\cdot$**1a**$\cdot$lattice ingredients $\equiv$ **1**. Anal. calc. (%) for: $C_{84}H_{952}Mo_{60}Na_{33}N_7O_{760}S_{60}W_{72}$: C 2.81, N 0.27, S 5.36, Na 2.11, W 36.87; found: C 3.4, N 0.2, S 5.6, Na 2.6, W 39.0. (Na and W analyses were performed by the Forschungszentrum Jülich GmbH, ZCH, 52425 Jülich, Germany.) The formula corresponds to the NMR results, especially regarding the ratio of the total number of TMA ions to the total number of acetate ions, that is, around 4. The vibrational spectra (Raman, IR), UV/Vis and preliminary ^{1}H NMR spectra of **1**, the starting material of **2**, are given in the Supporting Information.

Synthesis of **2**: Crystals of better quality of the less soluble (!) compound were obtained by adding $CoCl_2\cdot 6\,H_2O$ (0.03 g) to a solution of the crude compound **1** (0.2 g) in water (10 mL). Red crystals appeared within 2–3 days. Anal. Calc. (%) for: $C_{86}H_{1013}Co_{12}Mo_{62}Na_8N_{11}O_{786}S_{64}W_{72}$: C 2.8, N 0.42, S 5.56, Na 0.5, Co 1.92 (values refer to the small number of 300 H_2O caused by weathering, see also Ref. [26]); found: C 2.8, N 0.3, S 5.8, Na 0.4, Co 2.1. (S, Na and Co analyses were performed by the Mikroanalytisches Labor Egmont Pascher, An der Pulvermühle 3, 53424 Remagen, Germany). Characteristic UV/Vis bands: 293, 342, 384 (sh) nm. The vibrational data (Raman, IR) of **2** are given in the Supporting Information.

Crystal data for **2**: $C_{86}H_{1113}Co_{12}Mo_{62}Na_8N_{11}O_{836}S_{64}W_{72}$ (refers to 350 H_2O), $M = 37813.27$ g mol^{-1}, orthorhombic, space group *Immm*, $a = 34.5430(14)$, $b = 37.5676(14)$, $c = 42.2049(17)$ Å, $V = 54769(4)$ Å^3, $Z = 2$, $\rho = 2.293$ g cm^{-3}, $\mu = 8.608$ mm^{-1}, $F(000) = 35524$, crystal size $= 0.20 \times 0.16 \times 0.12$ mm^3. A total of 164400 reflections ($1.45 < \Theta < 27.01°$) were collected, of which 31201 reflections were unique ($R_{int} = 0.1316$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.03. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0732$ for 12508 reflections with $I > 2\sigma(I)$, $R = 0.2063$ for all reflections; max/min residual electron density 1.484 and -1.357 e Å^3. Crystals of **2** were removed from the mother liquor and immediately cooled to 173(2) K on a Bruker AXS SMART diffractometer (three circle goniometer with 1 K CCD detector, MoKα radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames ($\phi = 0$, 88 and 180°) at a detector distance of 5 cm). (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen 1997/2001; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001.) CCDC 831156 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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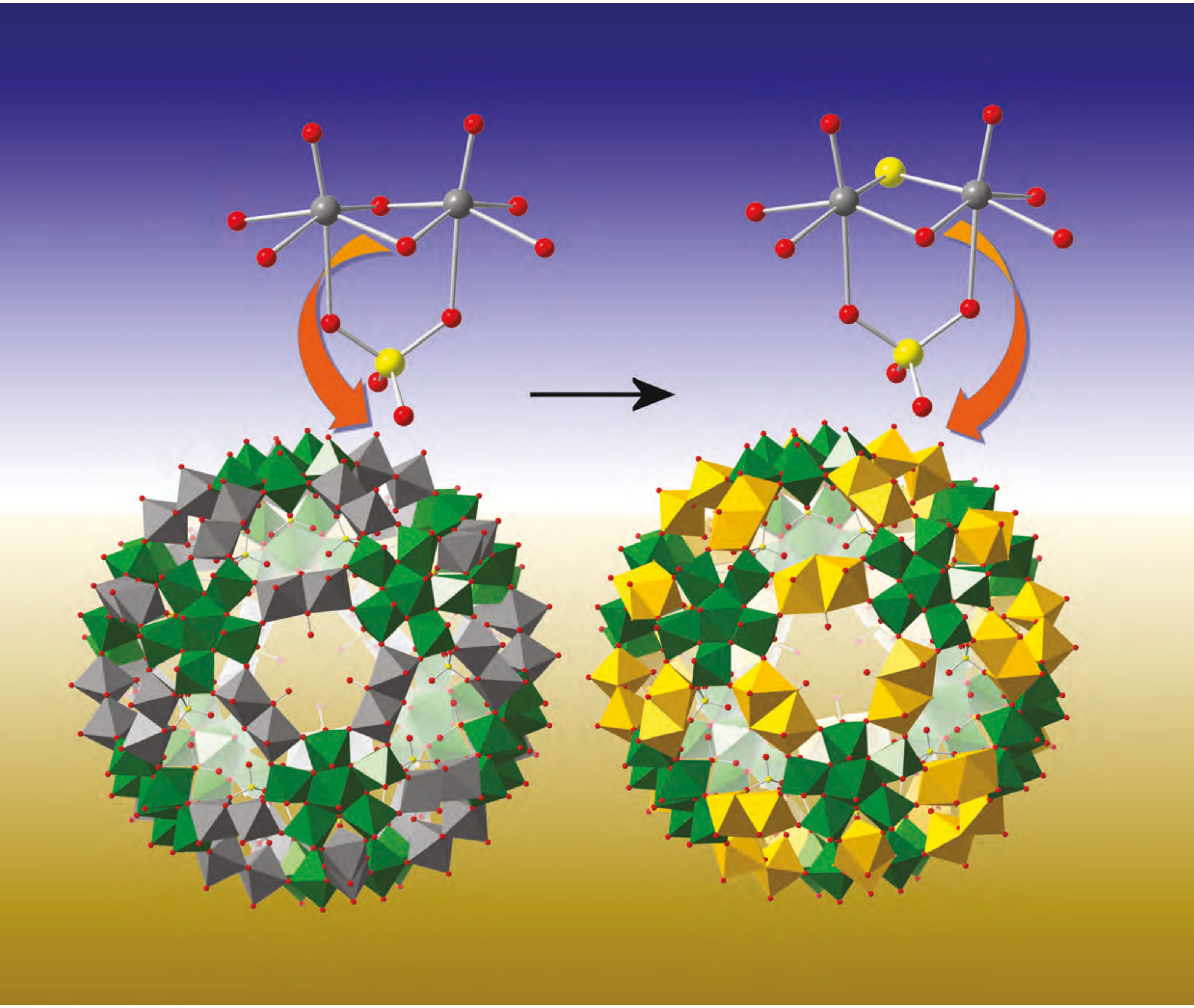

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A further step towards tuning the properties of metal-chalcogenide nanocapsules by replacing skeletal oxide by sulphide ligands†‡

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Addition of $[\mathrm{Mo_2^VO_2(\mu\text{-}O)(\mu\text{-}S)(aq)}]^{2+}$ linker-type units to a solution/dynamic library containing tungstates results *via* the formation of the complementary pentagonal $\{\mathrm{(W)W_5}\}$ units logically in the self-assembly of a mixed oxide/sulphide $\{\mathrm{W^{VI}_{72}Mo^V_{60}}\}$-type Keplerate, thereby demonstrating the ability to tune the capsule's skeletal softness (the $(\mu\text{-O})_2$ and $(\mu\text{-S})_2$ scenarios are known) and providing options to influence differently important capsule–substrate interactions.

Since their initial discovery in the late 90s[1,2] porous metal-oxide-based nanocapsules of the type $\{\mathrm{(M^{VI})M^{VI}_5}\}_{12}\{\mathrm{Mo^V_2}\}_{30}$ ($\{\mathrm{M^{VI}_{72}Mo^V_{60}}\}$) and $\{\mathrm{(M^{VI})M^{VI}_5}\}_{12}\{\mathrm{M'}\}_{30}$ (M = Mo or W; M′ = $\mathrm{VO^{2+}}$, $\mathrm{Fe^{3+}}$ or $\mathrm{Cr^{3+}}$), also called Keplerates,[3] have been attracting considerable interest due to their unique properties and relevance to various disciplines, like mathematics, molecular physics, magnetism, chemistry, materials science and biology.[4,5] Most importantly, $\{\mathrm{Mo^{VI}_{72}Mo^V_{60}}\}$-type Keplerates provide opportunities to study structures and properties of encapsulated water[6] as well as to perform reactions and catalysis under confined conditions[7] and to get new insight into the hydrophobic effect.[8] The capsule properties can be finely tuned by partial reduction of the molybdenum-oxide-based $\{\mathrm{(Mo)Mo_5}\}$ pentagonal units,[9] their replacement by the related tungsten-oxide-based units,[10] by ligand exchanges at the $\{\mathrm{Mo^V_2O_2(\mu\text{-}O)_2(L)}\}$ linkers[11] and by varying the linkers.[2,12] Following our recent report on Keplerate-type nanocapsules with $\{\mathrm{Mo^V_2O_2(\mu\text{-}S)_2(L)}\}$ linkers,[13] we report herein the syntheses and analytical as well as spectroscopic characterization of $\{\mathrm{W^{VI}_{72}Mo^V_{60}}\}$-type Keplerates with $\{\mathrm{Mo^V_2O_2(\mu\text{-}O)(\mu\text{-}S)(L)}\}$ linkers (L = $\mathrm{CH_3COO^-}$ (**1**); L = $\mathrm{SO_4^{2-}}$ (**2**)) as well as the single-crystal structure analysis of **2** thereby generating a capsule with a new skeleton providing new internal reactivities.

$\mathrm{Na_{42}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_3S(CH_3COO)\}_{30}]}\cdot$*ca.* $250\mathrm{H_2O}\cdot$*ca* $15\mathrm{CH_3COONa} \equiv \mathrm{Na_{42}}$**1a**$\cdot$*ca.* $250\mathrm{H_2O}\cdot$*ca* $15\mathrm{CH_3COONa} \equiv$ **1**

$\mathrm{Na_4(CH_3NH_3)_{68}[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_3S(SO_4)\}_{30}]}\cdot$*ca.* $230\mathrm{H_2O} \equiv \mathrm{Na_4(CH_3NH_3)_{68}}$**2a**$\cdot$*ca.* $230\mathrm{H_2O} \equiv$ **2**

Compound **1** was obtained by treating an acidified (pH ~ 4) aqueous solution of sodium tungstate and sodium acetate with an aqueous solution containing $[\mathrm{Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(aq)}]^{2+}$ building blocks.§ The method is similar to that used for the syntheses of previously reported tungsten-oxide-based Keplerates where the $\{\mathrm{(W)W_5}\}$-type units form in solution and are "trapped" in spherical nanocapsules when appropriate linkers, *e.g.* $[\mathrm{Mo_2O_2(\mu\text{-}O)_2(aq)}]^{2+}$,[10a] $[\mathrm{Mo_2O_2(\mu\text{-}S)_2(aq)}]^{2+}$,[13] $\mathrm{VO(aq)^{2+}}$ [10b] or $\mathrm{Fe(aq)^{3+}}$,[10c] are added to a dynamic library containing tungstates. As in the case of the $\{\mathrm{Mo^{VI}_{72}Mo^V_{60}}\}$-type Keplerate with $\{\mathrm{Mo_2O_4(CH_3COO)}\}^+$ linkers,[11] the acetate ligands can be easily exchanged, *e.g.* by sulphate ligands as exemplified here by the synthesis of **2**.¶

Compound **2** crystallizing in the space group $R\bar{3}$‖ contains the $\{\mathrm{W^{VI}_{72}Mo^V_{60}}\}$ cluster **2a** and belongs to the family of porous capsules of the type $\{\mathrm{M^{VI}_{72}Mo^V_{60}}\}$ (M = Mo, W). Compound **1**, the educt for **2**, could only be characterized spectroscopically and analytically. The 12 centres of the pentagonal $\{\mathrm{(W^{VI})W^{VI}_5}\}$-type units are positioned at the vertices of an icosahedron and are connected by 30 $\{\mathrm{Mo^V_2O_2(\mu\text{-}O)(\mu\text{-}S)}\}$ spacers, the Mo atoms of which span a distorted truncated icosahedron (Fig. 1, top). The 30 $\mathrm{SO_4^{2-}}$ anions – located inside the cavity – act as bidentate bridging ligands for the 30 $\{\mathrm{Mo^V_2}\}$ groups. The average Mo–Mo distance of 2.68 Å within the linkers is in agreement with the corresponding distance in dinuclear

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† Dedicated to Prof. Dr Francis Sécheresse on the occasion of his official retirement.

‡ Electronic supplementary information (ESI) available: Estimate of the pore size in **2** (Fig. S1), IR spectra of **1** and **2** (Fig. S2), aqueous solution Raman (Fig. S3) and UV-Vis absorption (Fig. S4) spectra of **2**. CCDC 884952 for **2**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32247a

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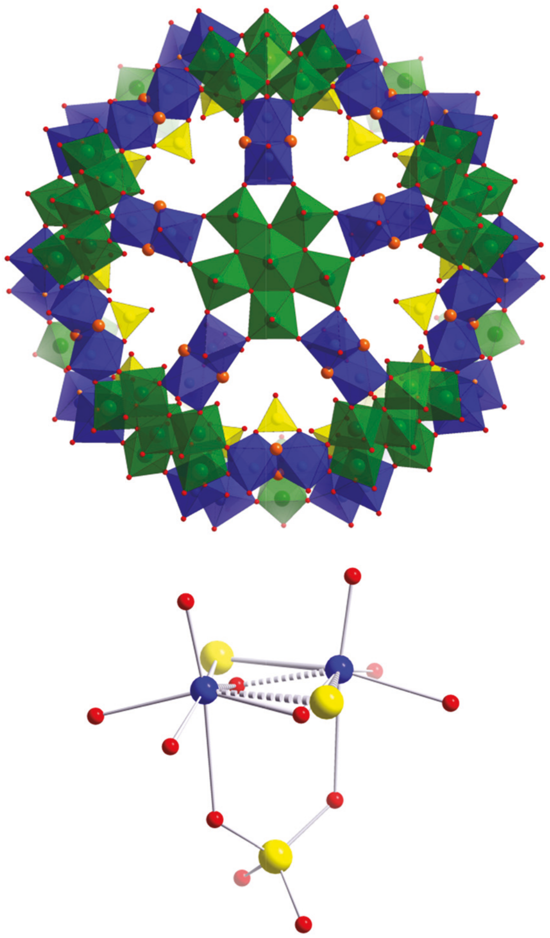

Fig. 1 Top: Polyhedral representation of **2a** with view along a fivefold symmetry axis highlighting a pentagonal $\{(W^{VI})W^{VI}_5\}$-type unit and the related five $\{Mo^V_2O_2(\mu\text{-}O)(\mu\text{-}S)\}^{2+}$ linkers stabilized by sulphate ligands, and showing the characteristic pore scenarios not considering the disorder of the bridging oxo and sulphido ligands (W green polyhedra, Mo blue octahedra, SO_4^{2-} yellow tetrahedra, O red, disordered O/S orange spheres). Bottom: Side view of one $\{Mo^V_2O_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SO_4)\}$ linker showing the S/O disorder (colour code as above, S yellow).

complexes containing the $\{Mo^V_2O_2(\mu\text{-}O)(\mu\text{-}S)\}$ core,[14] and lies as expected between the values of 2.58 and 2.84 Å in the $\{W^{VI}_{72}Mo^V_{60}\}$-type Keplerates with $\{Mo^V_2O_2(\mu\text{-}O)_2\}^{2+}$ [10*a*] and $\{Mo^V_2O_2(\mu\text{-}S)_2\}^{2+}$ [13] linkers, respectively. The Mo–O–Mo and Mo–S–Mo bridges are practically symmetrical with average Mo–O and Mo–S distances of 1.89 and 2.36 Å, respectively.

As the bridging oxide and sulphide ligands in **2a** are disordered over two positions with half occupancy (Fig. 1, bottom), this precludes a detailed description of the pores. Four different types of pores, *i.e.* $\{W_3Mo_6O_9\}$, $\{W_3Mo_6O_8S\}$, $\{W_3Mo_6O_7S_2\}$ and $\{W_3Mo_6O_6S_3\}$, are in principle possible; the opening diameters should lie in between the respective values of *ca.* 3.8 Å and 2.2 Å estimated for the two extreme (hypothetical) $\{W_3Mo_6O_9\}$ and $\{W_3Mo_6O_6S_3\}$ pores; for details see ESI (Fig. S1‡).

The IR spectra of **1** and **2** (ESI, Fig. S2‡) show the characteristic band pattern for the metal-oxide skeleton of the $\{M^{VI}_{72}Mo^V_{60}\}$-type Keplerates between 1000 and 400 cm^{-1} (see *e.g.* ref. 10*c* and 15). Additionally they show the characteristic features of the (symmetrically) bridging acetate and sulphate ligands, respectively. (See ESI‡ for details regarding the absorption bands of the linkers in **1** and **2**.)

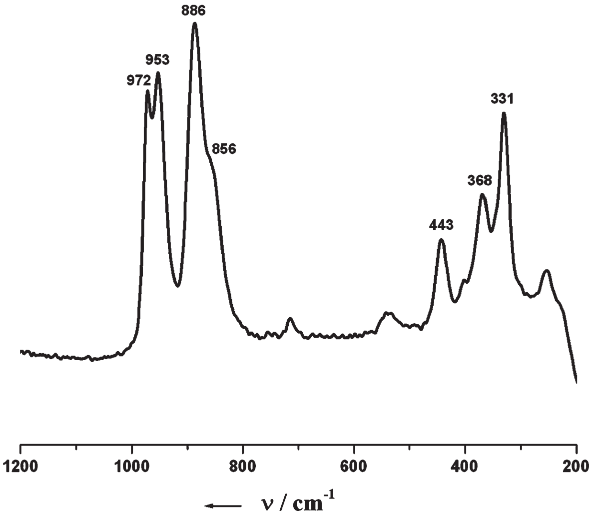

Fig. 2 Raman spectrum (λ_{exc} = 785 nm) of an aqueous solution of **1**.

The Raman spectra of aqueous solutions of **1** and **2** are typical for Keplerates of the type $\{M^{VI}_{72}Mo^V_{60}\}$ (M = Mo, W) as they display only a small number of lines due to the high (approximately icosahedral) symmetry of the metal-oxide skeleton (Fig. 2 and Fig. S3‡).[16] They are similar to those of other $\{W^{VI}_{72}Mo^V_{60}\}$-type clusters[10*a*,13] while the band pattern differs markedly from that observed for $\{Mo^{VI}_{72}Mo^V_{60}\}$-type Keplerates,[16,17] between 900 and 1000 cm^{-1}. This is due to the fact that the band associated with the $\nu(W{=}O)\text{-}A_g$-type vibration (assuming I_h symmetry) is more intense than that of the corresponding $\nu_s(Mo{=}O)$ vibration of $\{Mo_{132}\}$-type clusters in agreement with the higher W=O-bond polarisability (see ref. 10*a*). The observed characteristic intense band at *ca.* 890 cm^{-1} – observed for all Keplerates of the type $\{M^{VI}_{72}Mo^V_{60}\}$ – is assigned to the totally A_g-type breathing vibration of the μ_3-O atoms.

To summarize: the $\{(W^{VI})W^{VI}_5\}_{12}\{Mo^V_2O_2(\mu\text{-}X)_2\}_{30}$ Keplerate sequence (X = O;[10*a*] X = S[13]) has been extended to $\{Mo^V_2O_2(\mu\text{-}O)(\mu\text{-}S)\}$ linkers. Sulphur substitution for bridging oxygen atoms alters significantly the properties of the capsule regarding those of the pore (size, flexibility, host–guest interactions) as well as those of the skeleton (especially internal ligand binding affinity to the $\{Mo^V_2\}$ linkers, affecting consequently their interactions with substrates, *e.g.* encapsulated cations). Changes of the capsule skeleton allow one to change all types of interactions of the capsule with its environment and especially to control the ratio of different hydrophobic and hydrophilic internal ligands and *e.g.* correspondingly to tune the segregation between the resulting hydrophobic interior ligand wall and encapsulated water collections, thereby providing new information about the hydrophobic effect (see ref. 13, especially the ESI‡ with a new type of water clustering in a special hydrophobic environment).

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Notes and references

§ Synthesis of **1**. An aqueous solution of the aqua ion dimer $[\mathrm{Mo^{V}}_2\mathrm{O}_2(\mu\text{-O})(\mu\text{-S})(\mathrm{aq})]^{2+}$ prepared from $\mathrm{Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O}$ (3.0 g, 4.8 mmol) as described in the literature[18] (see ESI for details) was added to a solution of $\mathrm{Na_2WO_4\cdot 2H_2O}$ (4.5 g, 13.6 mmol) and $\mathrm{NaCH_3COO\cdot 3H_2O}$ (10.0 g, 73.5 mmol) in water (30 mL) which had been adjusted to pH ~ 4 with 100% acetic acid (18 mL). The milky red-brown suspension was heated quickly to 80 °C (oil bath temperature) with vigorous stirring under an argon atmosphere before an additional amount of water (30 mL) was added. The reaction mixture was heated for 90 min at 120 °C (oil bath temperature) under continuous vigorous stirring while the reaction product started to precipitate. After cooling to room temperature, the brown microcrystalline powder was filtered off, washed thoroughly with ethanol, and dried with diethyl ether (**1**; yield: 3.0 g). (Found: C, 2.9; Mo, 16.0; Na, 3.9; S, 2.8; W 37.0; Calcd for $\mathrm{C_{90}H_{779}Mo_{60}Na_{57}O_{754}S_{30}W_{72}}$: C, 3.07; Mo, 16.36; Na, 3.72; S, 2.73; W, 37.61). Crystals were obtained by adding CsCl (0.014 g) or dimethylammonium chloride (0.1 g) to a solution of **1** (0.2 g) in water (10 mL). Crystals of the $\mathrm{Cs^+}$ salt belong to the rhombohedral crystal system with cell parameters $a = 32.56$ and $c = 79.77$ Å, however their quality was not good enough for further investigation. Characteristic spectroscopic data for **1**: IR (KBr; $\nu_{\max}/\mathrm{cm^{-1}}$): 1626_{m} ($\delta(\mathrm{H_2O})$), 1537_{m} ($\nu_{\mathrm{as}}(\mathrm{COO})$), 1447_{m} ($\nu_{\mathrm{s}}(\mathrm{COO})$), $957_{\mathrm{m\text{-}s}}$ ($\nu(\mathrm{W{=}O})$), 876_{s}, 810_{vs}, $716_{\mathrm{m\text{-}s}}$, 665_{m}, $586_{\mathrm{m\text{-}s}}$, 532_{m}, 440_{m} (see Fig. S2‡); Raman ($\mathrm{H_2O}$; $\nu_{\max}/\mathrm{cm^{-1}}$): 972_{s}, 953_{s}, 886_{s}, 856_{sh}, 443_{m}, $368_{\mathrm{m\text{-}s}}$, 331_{s} (see Fig. 2).

¶ Synthesis of **2**. A solution of **1** (0.2 g) in water (10 mL) was acidified with $\mathrm{H_2SO_4}$ (0.5 M, 1.5 mL) under stirring (pH ~ 2). After addition of methylammonium chloride (0.2 g) the reaction mixture was stirred for 30 min and then kept in an open beaker. After 3 to 4 days, red-brown crystals of **2** could be isolated (Found: C, 2.1; Mo, 16.5; Na, 0.25; N, 2.4; S, 5.3; Calcd for $\mathrm{C_{68}H_{1052}Mo_{60}Na_4N_{68}O_{784}S_{60}W_{72}}$: C, 2.24; Mo, 15.82; Na, 0.25; N, 2.62; S, 5.29). Characteristic spectroscopic data: IR (KBr; $\nu_{\max}/\mathrm{cm^{-1}}$): 1629_{m} ($\delta(\mathrm{H_2O})$), 1189_{m}, 1134_{m}, 1044_{m} ($\nu_{\mathrm{as}}(\mathrm{SO_4})$), $961_{\mathrm{m\text{-}s}}$ ($\nu(\mathrm{W{=}O})$), 874_{s}, 810_{vs}, $712_{\mathrm{m\text{-}s}}$, 670_{m}, $581_{\mathrm{m\text{-}s}}$, 513_{m}, 446_{m} (see Fig. S2‡). Raman ($\mathrm{H_2O}$; $\nu_{\max}/\mathrm{cm^{-1}}$): 978_{sh}, 959_{s}, 888_{s}, 856_{sh}, 447_{m}, $369_{\mathrm{m\text{-}s}}$, 327_{s} (see Fig. S3); UV-Vis ($\mathrm{H_2O}$; $\lambda_{\max}$/nm): 379 (sh), 340 ($\varepsilon/\mathrm{dm^3\,mol^{-1}\,cm^{-1}} = 3 \times 10^5$); see part 5 in the ESI.‡

‖ Crystal data for **2**: $\mathrm{C_{68}H_{1012}Mo_{60}Na_4N_{68}O_{764}S_{60}W_{72}}$, $M = 36\,022.62$ g mol^{-1}, rhombohedral, space group $R\bar{3}$, $a = 32.687(2)$, $c = 73.762(4)$ Å, $V = 68\,251(7)$ Å^3, $Z = 3$, $\rho = 2.629$ g cm^{-3}, $\mu = 10.106$ mm^{-1}, $F(000) = 50\,580$, crystal size = 0.35 × 0.28 × 0.25 mm^3. A total of 184 856 reflections ($2.20 < \Theta < 27.86°$) were collected of which 34 131 reflections were unique ($R(\mathrm{int}) = 0.0534$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.03. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0624$ for 25 014 reflections with $I > 2\sigma(I)$, $R = 0.0998$ for all reflections; max/min residual electron density 2.134 and −2.127 e Å^3. CCDC 884952 contains the supplementary crystallographic data for this paper. (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen 1997/2001; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001.)

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Zusammenfassung der Ergebnisse

Mit Hilfe der Raman-Spektroskopie konnte gezeigt werden, dass sich das $\{Mo_{132}\}$-Keplerat **1** bei Zugabe vorsynthetisierter $\{Mo_2{}^{V}O_4\}^{2+}$-Einheiten zu einer wässrigen Lösung von Ammoniumheptamolybdat, die in Anwesenheit von Ammoniumacetat mit Essigsäure auf pH = 4 eingestellt wird, spontan nach kurzer Reaktionszeit bildet. Diese Beobachtung lässt den Schluss zu, dass die $\{Mo_2{}^{V}O_4\}^{2+}$-Einheiten die Formierung der zur Kapselbildung notwendigen pentagonalen $\{(Mo)Mo_5\}$-Einheiten aus den in einer (virtuellen) dynamischen Bibliothek vorhandenen Polyoxomolybdat-Spezies lenken.

$(NH_4)_{42}[Mo^{VI}{}_{72}Mo^{V}{}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}] \cdot$ ca. $(300\,H_2O + 10\,CH_3COONH_4)$ $\equiv (NH_4)_{42} \cdot \mathbf{1a} \cdot$ ca. $(300\,H_2O + 10\,CH_3CO_2NH_4) \equiv \mathbf{1}$

Die Ausweitung der Untersuchungen auf Polyoxowolframat-Systeme ergab, dass die Zugabe vorsynthetisierter $\{Mo_2{}^{V}O_4\}^{2+}$-Einheiten zu einer wässrigen Lösung von Natriumwolframat bei hohen Temperaturen zur Bildung einer neuartigen molekularen Kapsel auf Wolframoxid-Basis führt. Die Familie der nanoskaligen Keplerate mit dem allgemeinen Aufbauprinzip $(\text{Pentagon})_{12}(\text{Linker})_{30}$ konnte durch die Synthese des $\{(W)W_5\}_{12}\{Mo_2O_4\}_{30}$-Clusters **2**, in dem 12 $\{(W)(W_5)\}$-Einheiten mit 30 $\{Mo_2{}^{V}O_2(\mu\text{-}O)_2\}^{2+}$ verknüpft sind, erweitert werden. Während die Existenz der pentagonalen $\{(Mo)(Mo_5)\}$-Einheit im $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$-Anion, das sich unter nichtreduzierenden Bedingungen in wässrigen Molybdatlösungen bei niedrigen pH-Werten bildet, seit langer Zeit bekannt ist, ist die analoge $\{(W)(W_5)\}$-Einheit in der Chemie der Polyoxowolframate bislang unbekannt gewesen.

$[(CH_3)_2NH_2]_{48}[\{(W^{VI})W^{VI}{}_5O_{21}(H_2O)_5(CH_3COO)_{0.5}\}_{12}\{Mo^{V}{}_2O_4(CH_3COO)\}_{30}] \cdot$ ca. $\{270\,H_2O + 7\,CH_3COO^- + 7\,(CH_3)_2NH_2{}^+\} \equiv [(CH_3)_2NH_2]_{48} \cdot \mathbf{2a} \cdot$ ca. $\{270\,H_2O + 7\,CH_3COO^- + 7\,(CH_3)_2NH_2{}^+\} \equiv \mathbf{2}$

Infolge der Entdeckung dieses Clusters war es möglich, weitere sphärische Cluster mit $\{(W)(W_5)\}$-Einheiten verknüpft durch $\{Mo_2{}^{V}O_2(\mu\text{-}O)(\mu\text{-}S)\}^{2+}$- und $\{Mo_2{}^{V}O_2(\mu\text{-}S)_2\}^{2+}$-Einheiten zu synthetisieren (Verbindungen **3**, **4** und **5**). Keplerat **5** wurde durch Austausch der an die Mo^{V}-Zentren koordinierenden Acetat- gegen Sulfat-Liganden erhalten und zeigt die prinzipielle Möglichkeit zur Modifikation des Kapselinneren auf, die bereits beim $\{Mo_{132}\}$-Keplerat bekannt ist.

$Co_{12}[\{W^{VI}{}_6O_{21}(H_2O)_6\}_{11}\{W^{VI}{}_6O_{21}(H_2O)(H_2Mo_2O_8(H_2O))\}\{Mo^{V}{}_2O_2S_2(CH_3COO)\}_{10}$
$\{Mo^{V}{}_2O_2S_2(H_2O)_2\}_{20}] \cdot$ ca. $\{11\,[(CH_3)_4N]^+ + 8\,Na^+ + 11\,CH_3COO^- + 4\,SO_4{}^{2-} +$
$_{350}\,H_2O\} \equiv Co_{12} \cdot$ **3a** $\cdot$ Gitterbestandteile $\equiv$ **3**

$Na_{42}[\{W^{VI}{}_6O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_3S(CH_3COO)\}_{30}] \cdot$ ca. $250\,H_2O \cdot$ ca. $15\,CH_3COONa$
$\equiv Na_{42} \cdot$ **4a** $\cdot$ ca. $250\,H_2O \cdot$ ca. $15\,CH_3COONa \equiv$ **4**

$Na_4(CH_3NH_3)_{68}[\{W^{VI}{}_6O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_3S(SO_4)\}_{30}] \cdot$ ca. $230\,H_2O \cdot$ ca. $250\,H_2O$
$\equiv Na_4(CH_3NH_3)_{68} \cdot$ **5a** $\cdot\ 230\,H_2O \equiv$ **5**

Die Stabilität der wasserlöslichen Kapseln **2**, **3** und **5** konnte durch die Raman-Spektroskopie belegt werden. Wie zu erwarten weisen die Spektren aller neuen Kapseln auf Grund ihrer hohen Symmetrie nur wenige intensive Banden auf, liefern aber wichtige Informationen über die Veränderung der Oberflächeneigenschaften, die auf die Substitution der 72 Mo^{VI}-Zentren durch W^{VI}-Zentren zurückzuführen ist. So fallen beim Vergleich der Spektren der $\{(W^{VI})(W_5{}^{VI})\}_{12}\{Mo_2{}^{V}O_2X_2\}_{30}$-Keplerate (X = O, S) mit dem Spektrum des bekannten $\{(Mo^{VI})(Mo_5{}^{VI})\}_{12}\{Mo_2{}^{V}O_4\}_{30}$-Keplerats Unterschiede im Bereich zwischen 900 – 1000 cm^{-1}auf: Die der $\nu(W{=}O_{term})$ A_g-Schwingung zuzuordnende Bande, ist deutlich intensiver und tritt bei einer höheren Wellenzahl auf als die entsprechende $\nu(Mo{=}O_{term})$-Bande des $\{Mo_{132}\}$-Keplerats. Diese Beobachtung ist durch die höhere Polarisierbarkeit und die höhere Bindungsstärke der terminalen W=O-Bindungen zu erklären. Die höhere Bindungsstärke der W=O-Bindungen senkt die Elektronendichte an den entsprechenden Sauerstoffatomen.

Durch die Verwendung von dinuklearen Molybdänkomplexen, in denen die Mo^{V}-Zentren durch zwei Sulfid-Liganden bzw. einen Sulfid- und einen Oxid-Liganden verbrückt sind, konnten neben den $\{W_3Mo_6O_9\}$-Poren des $\{(W)W_5\}_{12}\{Mo_2O_4\}_{30}$-Clusters **2** die drei neuen Porentypen $\{W_3Mo_6O_6S_3\}$, $\{W_3Mo_6O_7S_2\}$ und $\{W_3Mo_6O_8S\}$ erhalten werden. Die im Vergleich zu den $\{Mo_9O_9\}$- und $\{W_3Mo_6O_9\}$-Poren kleinere Porengröße, die aus dem Vorhandensein von Sulfid-Liganden resultiert, führt zu Veränderungen der Poren-Flexibiltät und -Reaktivität. Die Interaktion dieser Poren mit verschiedenen (harten) Metall-Kationen sowie die Tendenz der über Wasserstoffbrücken gebundenen Gäste (z.B. Guanidinium- oder Formamidiniumkationen), die Poren zu verschließen wird dadurch geschwächt.

Im Innenraum des Keplerats **3** konnte ein neuartiger Trennungs/Segregations-Effekt zwischen der im wesentlich hydrophoben, durch Acetat/Wasser-Liganden aufgespannten inneren Kapselwand und den eingekapselten Wassermolekülen entdeckt werden.

Etwa 20 Wassermoleküle werden von der hydrophoben Kapselinnenfläche abgestoßen und bilden eine ungewöhnlich kugelförmige Schale.

Das wesentliche Ergebnis dieser Arbeit ist die Erkenntnis, dass die *gezielte* Synthese von $\{Mo_{132}\}$ und $\{W_{72}Mo_{60}\}$-Kepleraten möglich ist. Die Zugabe dinuklearer $\{Mo_2^V\}$-Baueinheiten zu einer (virtuellen) dynamischen Bibliothek von „Molybdaten“ oder „Wolframaten“ führt über die Bildung der komplementären pentagonalen transferierbaren $\{(M)M_5\}$-Baugruppe (M = Mo^{VI}, W^{VI}) in einem spontan ablaufenden Selbstorganisationsprozess zu den sphärischen Metall-Sauerstoff-Clustern. Im „Wolframat“-Reaktionssystem verläuft dieser Prozess allerdings vermutlich auf Grund der im Vergleich zum Molybdän festeren W–O-Bindung langsamer und erst bei höheren Temperaturen. Bislang war die Möglichkeit der Direktsynthese nur bei den kleineren Kepleraten des Typs $\{Mo_{72}M_{30}\}$ (M = Fe^{III}, V^{IV}, Cr^{III}) bekannt, allerdings unter deutlich saureren Bedingungen (pH = 2). Auch wenn die Reaktionswege, die zur Bildung der $\{Mo_{132}\}$ und der neuen $\{W_{72}Mo_{60}\}$-Keplerate nicht genau bekannt sind, so lässt sich anhand der erhaltenen Ergebnisse dennoch vermuten, dass die vorsynthetisierten $\{Mo_2^VO_2X_2\}^{2+}$-Baueinheiten (X = O, S) die Formierung der komplementären $\{(M)M_5\}$-Baugruppen steuern, während die Triebkraft der Reaktion – wie bereits angenommen – die hohe Bildungstendenz sphärischer Cluster ist.

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