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Urea as '*deus ex machina*' in giant molybdenum blue type cluster synthesis: an unusual hybrid compound with perspectives for related nano, supramolecular and extended structures†

Achim Müller,* Soumyajit Roy, Marc Schmidtmann and Hartmut Bögge
Fakultät für Chemie der Universität, Lehrstuhl für Anorganische Chemie I, Postfach 100131, D 33501 Bielefeld, Germany. E-mail: a.mueller@uni-bielefeld.de

Received (in Cambridge, UK) 19th June 2002, Accepted 5th August 2002
First published as an Advance Article on the web 20th August 2002

The reaction of an aqueous solution of ammonium heptamolybdate with sodium dithionite and urea—a glue and cluster hydration shell destructing agent corresponding to its role in inclusion compound chemistry—at low pH value results in the formation of nanosized ring shaped molybdenum–oxide based clusters which in a short time get linked to chains.

The deliberate synthesis of multifunctional nanosized materials from well-defined building blocks which are abundant in a virtual library is one of the most challenging problems in contemporary chemistry. Pertinent targets include the synthesis of materials with especially desirable properties. In solutions of oxoanions of the early transition elements, especially molybdates under reducing conditions, an enormous variety of compounds can be formed by linking together metal–oxide building blocks. Here we report a one day facile synthesis‡ of a related molybdenum–oxide based compound **1**, exhibiting a chain of nanosized ring shaped cluster units with unique receptor properties, which shows perspectives for related nano-, supramolecular- and solid-state chemistry. In this context it should be mentioned that for nearly 200 years it was not possible to obtain pure compounds from the related molybdenum blue solutions mainly due to the high solubility of the abundant species (Fig. 1).[1] Progress in the present case corresponds to the use of urea which forms interesting crystalline supramolecular compounds due to N–H···O=C hydrogen bonding, a property which is used technologically to separate hydrocarbons.[2] Interestingly, urea shows complementary sites for hydrogen bonding comparable to the cluster itself.

Compound $^{1}_{\infty}\{(NH_3CONH_2)_{14}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{68}]\}\cdot xH_2O$ ($x \approx 350$) **1** was obtained by addition of urea

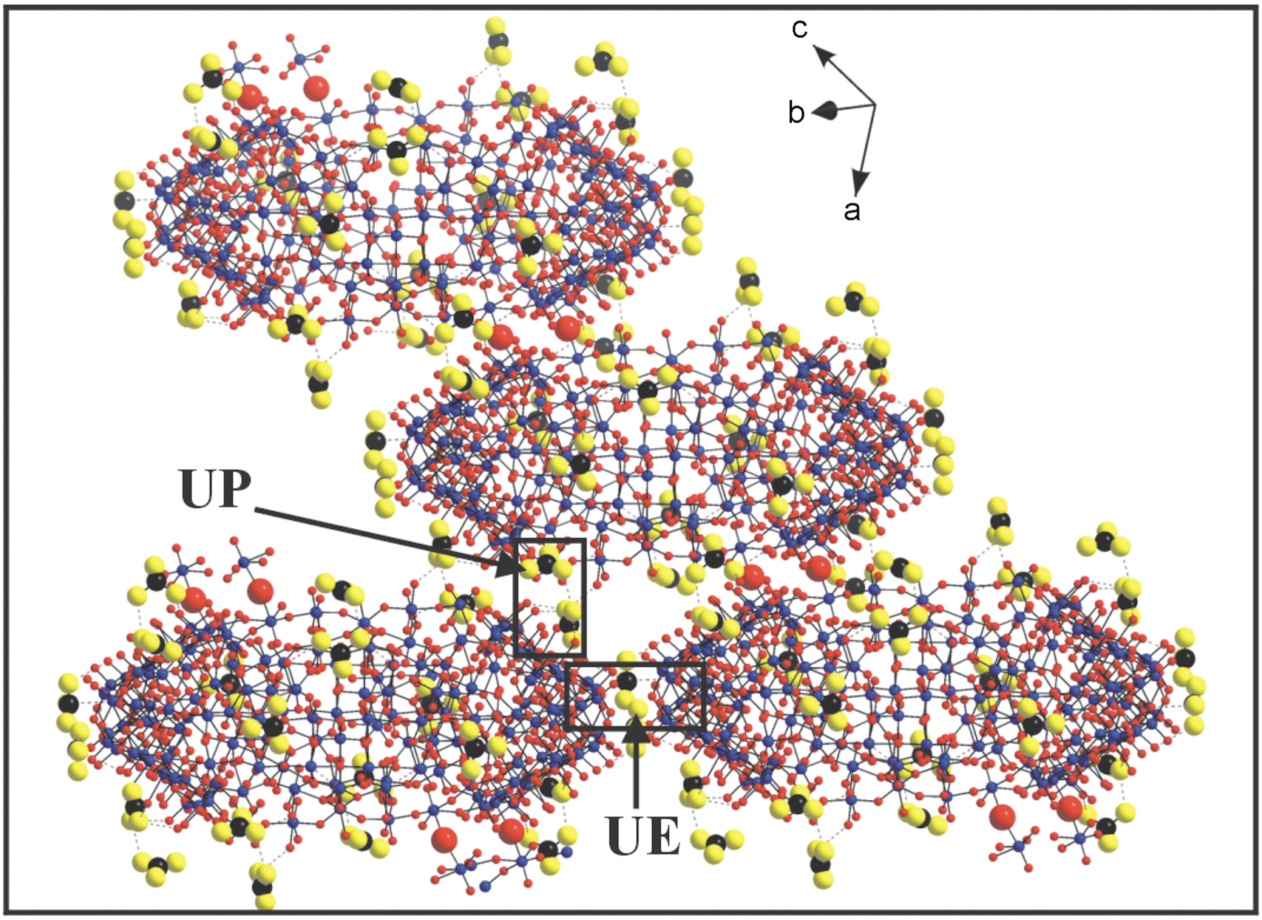

Fig. 1 Ball-and-stick representation of four $\{Mo_{154}\}$ type rings of **1** 'glued' with two types of protonated urea molecules (viz., equatorial UE as well as polar UP; see Fig. 2). Colour code: molybdenum: blue; oxygen: red; carbon: black; nitrogen and oxygen atoms of urea units which could not clearly be distinguished using X-ray crystal structure analysis: yellow. The atoms of the urea (type) units and the oxygen atoms which covalently connect adjacent rings have been enlarged for clarity.

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† Dedicated to Prof. G. Huttner on the occasion of his 65th birthday.

DOI: 10.1039/b205887a

to the reaction mixture from which normally discrete nanosized wheel shaped cluster species§ such as $[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]^{14-} \equiv [\{Mo_9O_{26}(\mu_3\text{-}O)_2H(H_2O)_3\}\{Mo^{VI}_2O_5(H_2O)_2\}]_{14}^{14-} \equiv [\{Mo_1Mo_8\}\{Mo_2\}]_{14}^{14-}$ [1,3] are formed (referred to here as $\{Mo_{154}\}$) and was characterized by elemental analysis, thermogravimetric analysis (to determine the crystal water content), cerimetric titrations [for the determination of the (formal) number of Mo^V centres], bond valence sum (BVS) calculations (to determine the number of H_2O ligands and OH groups as well as the number of Mo^V centres),[3] spectroscopic methods (IR, resonance-Raman, VIS–NIR),¶ solid-state ^{13}C NMR and single crystal X-ray structure analysis.‖

The monoclinic unit cell of **1** (space group *C*2/*m*) shows the abundance of two nanosized ring shaped $\{Mo_{154}\}$ units, which are related by a translation of ½, ½, 0. Along the smaller crystallographic *c*-axis, the rings appear to be arranged like a flight of stairs with protonated urea molecules attached to the surface of each of them (Fig. 1). Every $\{Mo_{154}\}$ ring is connected to its next (chain) neighbours *via* two covalent Mo–O–Mo bonds at $\{Mo_2\}$ type $(H_2O)Mo{=}O$ positions.[3] The urea units—protonated at the pH of the reaction and fixed to the cluster surface—act as counter ions and form a part of the overall supramolecular assembly. The observed protonation is consistent with numerous elemental analyses and with the fact that salts of protonated urea exist.[4]

The urea (type) units associated with the chain of **1** may be classified into two groups: those (four) found along the equatorial region of every $\{Mo_{154}\}$ ring (UE) and those (eight) found along the polar region (UP) on the upper and lower rims of the ring. The UE units glue the rings along the equator while the UP units 'link' the polar parts of two $\{Mo_{154}\}$ units of different neighbouring chains as shown in Fig. 1 and 2. Interestingly, the latter (UP) also show pairwise hydrogen bonding type interactions. The two other lattice urea cations, being not coordinated and therefore disordered, could not be located.¶ The nitrogen and oxygen atoms of the UE units lie within a distance of 2.9–3.2 Å from the equatorial oxygen atoms of the metal–oxide backbones of two $\{Mo_{154}\}$ units of two neighbouring chains (Fig. 2(a)). The polar UP units are also located within similar distances from the surface atoms of the same $\{Mo_{154}\}$. (The disorder in the system prevents a clear distinction between N and O atoms of urea, see Fig. 2(b)). The given distances lie within the limits of 'moderate' hydrogen bonds.[5,6] (Note, that the negative charge density on the ring units is rather small.) The UP units 'fit into' the specific $\{(Mo_6O_6)_{ring}\}$ hexagonal sites,[7] thereby indicating the possibility for these sites to act as a type of receptor (Fig. 2(b)). Another particularly important feature of **1** is that the surface of the respective cluster ring has in principle the same 'positive or negative' complementary hydrogen bonding sites as urea. Note the unique ability of urea to form remarkable cage structures with encapsulated alkanone, alkanedione, diaminoalkane and many other molecules (this can be used for separating hydrocarbons).[2,8] The observation of related extensive hydrogen bond formation by urea in the present compound is in accordance with the ability of urea to form four hydrogen bonds by two lone pairs of electrons on carbonyl oxygen, as was observed much earlier by Pauling.[9]

The reaction leading to the formation of crystalline **1** shows the following features: (1) the 'coordination' of protonated urea destroys the cluster hydration shell (responsible for the high solubility and difficulty to precipitate the clusters) and simultaneously accelerates chain formation (see ref. 10) by decreasing the negative charge density of the $\{Mo_{154}\}$ type constituent units thereby facilitating Mo–O–Mo bond formation. (2) The subsequent condensation reaction at two $\{Mo_2\}$ type $(H_2O)Mo{=}O$ groups favours an entropy driven reaction with subsequent release of hydration shell and coordinated cluster water molecules into 'liquid bulk water'. To summarize, urea acts as a 'glue' in the formation of the crystalline compound while drastically reducing the crystallization time (*one day*).

The general perspective from the obtained results may be the possibility to investigate a variety of reactions at different sites of a structurally well-defined nanoobject, which can regarding different functionalities (including complementary sites for hydrogen bonding) be considered as a nanostructured landscape. Furthermore, the special situation of specific receptors

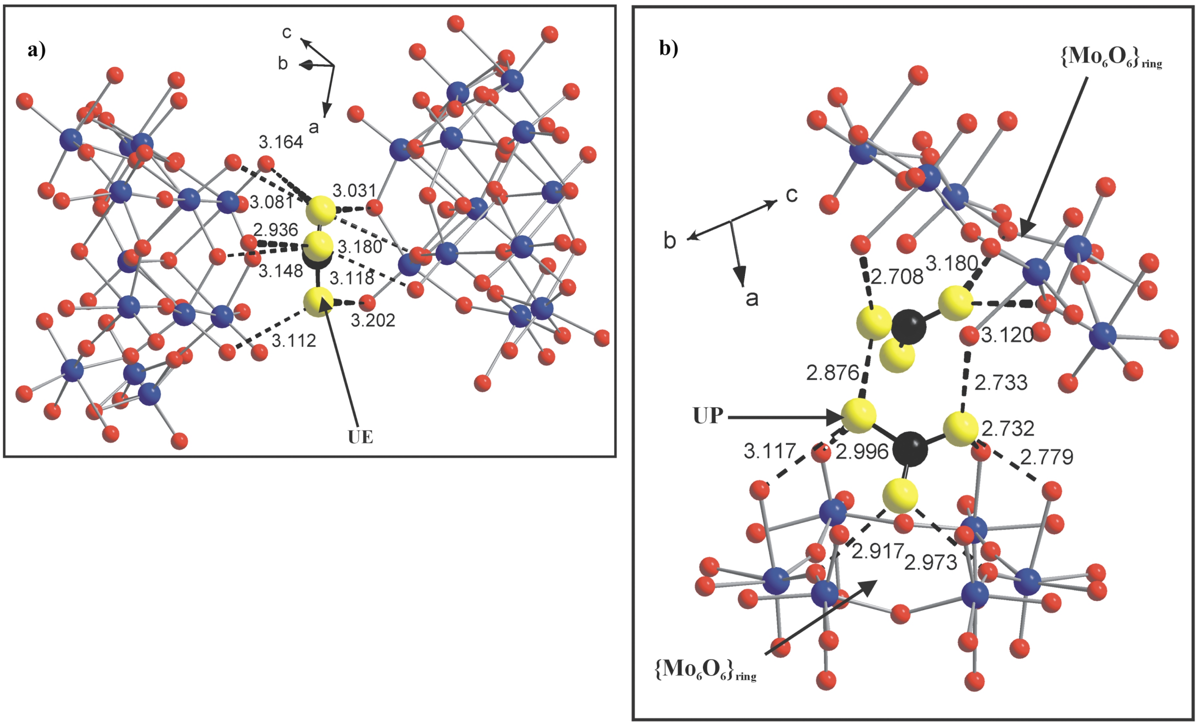

Fig. 2 (a) Representation of ring atoms showing interaction with UE type urea units between two rings of two adjacent chains illustrating the glue function of the latter. (b) Interaction between UP type units among themselves as well as with oxygen atoms of two hexagonal $[\{Mo_6O_6\}]$ ring sites with the potential receptor property of **1**. The difficulty to distinguish exactly between O and N atoms of UP is caused by a $O{=}Mo{-}H_2O$ disorder at the cluster surface (see *e.g.*, A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, S. K. Das and F. Peters, *Chem. Eur. J.*, 1999, **5**, 1496).

opens up new related avenues in host–guest *i.e.*, supramolecular chemistry. Additionally, the option of improving the synthetic routes for extended structures built up from the urea–anionic cluster type aggregates is obvious (see ref. 10).

The authors thank Dr. L. Allouche (Bielefeld) and Professor F. Taulelle (Strasbourg, France) for the measurement of the solid-state NMR spectrum. Financial support of the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the European Commission is gratefully acknowledged. S. R. thanks the Graduiertenkolleg ‘Strukturbildungsprozesse’, Universität Bielefeld, for a fellowship.

Notes and references

‡ To a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1.00 g, 0.809 mmol) and $(NH_2)_2CO$ (0.6 g, 10 mmol) in 40 ml distilled water in a 100 ml closed Erlenmeyer flask, $Na_2S_2O_4$ (0.1 g, 0.574 mmol) was added with constant stirring while the colour of the solution turned green. It was immediately acidified with 30 ml 1 M HCl (colour change to blue) and the solution was heated on a hot plate (60 °C) for 1 h under closed conditions. After 1 day while keeping the solution at 20 °C the precipitated dark blue stick shaped crystals of **1** were filtered off, washed quickly with a small volume of cold water and were dried at room temperature. Yield: 0.63 g (60% based on Mo) (Note: the crystals should be separated from the reaction mixture after 1 day, so as to avoid the coprecipitation of amorphous materials as an after effect.) Anal. Calc. for **1** (M = 29665.8): C 0.49; H 2.91; N 1.43; Mo^V 9.4. Found: C 0.5; H 2.2; N 1.4; Mo^V 9.5%. The value of the crystal water corresponds to the remaining volume of the unit cell. Due to the fast loss of crystal water from this type of compound all the analytical calculations were done taking a loss of *ca.* 50 water molecules into consideration. This explains the difference in the M value used for analytical calculations and that obtained from the single crystal X-ray diffraction experiments. The used reducing agent gives the best results in spite of its instability in an acidic medium.[11]

§ The description in terms of the building blocks of **1** corresponds to that of the discrete $\{Mo_{154}\}$ type units having the formula $[\{Mo_9O_{26}(\mu_3\text{-}O)_2H(H_2O)_3\}\{Mo^{VI}_2O_5(H_2O)_2\}]_{14}^{14-}$.[1] The charge value for **1** is in accordance with numerous elemental analyses and also the BVS values for the μ_3-O atoms of the equatorial $(\mu_3\text{-}O)\cdots H\cdots(\mu_3\text{-}O)$ linkages between $\{Mo_5O_6\}$ compartments.[1] In all known tetradecameric $\{Mo_{154}\}$ ring type cluster systems without defects, the charge of 14- corresponds to the difference between the (formal) number of Mo^V centres and the number of protons at equatorial μ_3-O atoms (For further details on the structure of $\{Mo_{154}\}$ ring type species, refer to ref. 1).

¶ *Characteristic spectroscopic data* for **1**: IR: ν/cm^{-1} (KBr disk, some characteristic bands 1700–400 cm^{-1}): *ca.* 1700(sh) [ν(C=O)], 1624s [δ(H$_2$O)], *ca* 1400w [δ(N–H)], 1153w, *ca.* 995(sh), 975s, 908m [ν(Mo=O)], *ca.* 633s, 559s. Resonance-Raman: ν/cm^{-1} (solid, KBr dilution, λ_e = 1064 nm): 802s, 535m, 462s, 326s, 215s. VIS–NIR: λ_{max}/nm (solid state reflectance with cellulose as white standard): 700.

Due to the size of the object, the complexity of the structure, the quality of the measurement and the crystals, and the disorder in the system, it is reasonable to expect that the given formula has a (small) error limit regarding cation composition. It cannot be excluded that one or both of the given protonated urea molecules which were not found by the X-ray diffraction experiments might be replaced by two NH_4^+ cations as these are also present in the reaction mixture. For further details on error limits of ring type molybdenum blue complexes refer to ref. 1 and 3.

‖ *Crystal data* for **1**: $C_{14}H_{920}Mo_{154}N_{28}O_{894}$, M = 30566.54 g mol^{-1}, monoclinic, space group $C2/m$, a = 33.4470(13), b = 53.320(2), c = 27.0643(10) Å, β = 107.532(1)°, U = 46024(3) Å^3, Z = 2, D_c = 2.206 g cm^{-3}, μ = 2.139 mm^{-1}, $F(000)$ = 29640, crystal size = 0.40 × 0.20 × 0.10 mm. Crystals of **1** were removed from the mother-liquor and immediately cooled to 183(2) K on a Bruker AXS SMART diffractometer (three circle goniometer with 1K CCD detector, Mo-Kα radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435 and 230 frames (ϕ = 0, 88 and 180°) at a detector distance of 5 cm). A total of 136742 reflections ($0.74 < \theta < 27.03°$) were collected of which 50307 reflections were unique (R(int) = 0.0487). 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-93 to R = 0.0523 for 34050 reflections with $I > 2\sigma(I)$, R = 0.0940 for all reflections; max./min. residual electron density 2.218 and −1.299 e Å^{-3} (SHELXS/L, SADABS-2.03 from G. M. Sheldrick, University of Göttingen; structure graphics with DIAMOND 2.1 from K.Brandenburg, Crystal Impact GbR, 2001).

CCDC 185870. See http://www.rsc.org/suppdata/cc/b2/b205887a/ for crystallographic data in CIF or other electronic format.

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