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# Soccer-playing metal oxide giant spheres: a first step towards patterning structurally well defined nano-object collectives†

**Achim Müller,* Ekkehard Diemann, S. Qaiser Nazir Shah, Christoph Kuhlmann and Matthias C. Letzel**
*Faculty of Chemistry, University of Bielefeld, D-33501 Bielefeld, Germany.*
*E-mail: a.mueller@uni-bielefeld.de*

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**In context with the challenge to assemble giant molecules into patterns with limited size, molybdenum oxide giant spheres (with a molecular mass of about 16 kDa) could be 'kicked out' like soccer balls into the gas phase using matrix assisted laser desorption and ionization (MALDI) and detected by TOF mass spectrometry while cluster collectives ranging from dimers to pentamers were observed.**

The class of nanoscaled reduced molybdenum oxides forming spherical and wheel shaped entities, the largest discrete inorganic systems structurally characterized, has gained much interest not only because of the mere beauty of the compounds but also because of their potential functionality as nanoreactors and as construction units for new materials.[1] We have now succeeded in 'kicking out' such molybdenum oxide giant spheres (with a molecular mass of about 16 kDa) like soccer balls into the gas phase using matrix assisted laser desorption and ionization (MALDI) and detecting them by TOF mass spectrometry. Not only single spheres but also aggregates of 2, 3, 4 and 5 such giant balls, the latter with a mass of more than 75 kDa, have been observed. These findings, confirming the existence of such giant clusters in the gas phase, open a wide field of non-trivial experiments, *i.e.* single molecule spectroscopy of nano-objects or the epitaxial growth of layers of functionalized supramolecules or cluster collectives suitable for electronic devices (quantum-dot cellular automata).[2] In this context it should be noted that it is still an unsolved problem to assemble molecules to patterns of limited size without obtaining crystals.[3]

The compounds studied were $[Mo_{78}Fe_{30}O_{274}(H_2O)_{94}(CH_3COO)_{12}]\cdot ca.\ 150H_2O$ ('$Mo_{78}Fe_{30}$' $\equiv$ $\{(Mo)Mo_5\}_{12}(Mo_6)Fe_{30}$),[4] $[Mo_{102}O_{252}(H_2O)_{78}(CH_3COO)_{12}]\cdot ca.\ 150H_2O$ ('$Mo_{102}$')[5] and $(NH_4)_{42}[Mo_{132}O_{372}(H_2O)_{72}(CH_3COO)_{30}]\cdot ca.\ 300H_2O\cdot ca.\ 10CH_3COONH_4$ ('$Mo_{132}$'),[4] all containing giant spheres (Fig. 1), for which the term *keplerates*‡ has been coined. The first two are uncharged whereas the third carries a rather large negative charge. An interesting topological aspect of the cluster species is that they all have the same $(Pentagon)_{12}(Linker)_{30}$ basic structure, whereas the pentagonal unit $(Mo)Mo_5$, important for all related spherical systems, is formed by a central $MoO_7$ bipyramid sharing edges with five $MoO_6$ octahedra. Suitable for linking are, for instance, dinuclear dumb-bell shaped $\{Mo^V_2\}$ groups (stabilized by a bidentate ligand, *e.g.* an acetate anion in $[Mo^V_2O_4(CH_3COO)]^+$) or mononuclear fragments like $\{Fe^{III}(OH_2)_2\}^{3+}$ and $\{OMo^V(OH_2)\}^{3+}$. The latter two are abundant in the species under study.

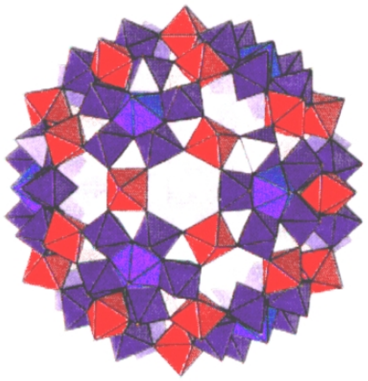

**Fig. 1** Polyhedral representation of the shell of the $Mo_{72}Fe_{30}$ type keplerate, red $FeO_6$ octahedra, purple $(Mo)Mo_5$ units (for details *cf.* ref. 4; the other six Mo atoms are not of the shell type).

The compounds were co-crystallized first with sinapinic acid, a material which has been used successfully as the MALDI matrix in numerous cases before. However, only rather broad, low intensity signals were obtained. The real breakthrough was achieved when the matrix material was changed to 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB).[6] A droplet of an aqueous solution or a water–acetonitrile mixture solution of the keplerates was deposited on a thin layer of DCTB crystallized on the target. After evaporation the residue was covered with a methanolic solution of DCTB. In cases of samples in the water–acetonitrile mixtures, a solution of DCTB in methanol was directly added to achieve an optimized co-crystallization.§

Under these conditions we obtained MALDI spectra of textbook quality for the first two compounds in the DCTB matrix (Fig. 2). Here we observe as main products the single balls $Mo_{72}(Mo_6)Fe_{30}$ (15.93 kDa with all decorations, but without the crystal water) and $Mo_{102}$ (15.94 kDa), singly and doubly charged, and remarkably also oligomers with 2, 3, 4 and 5 balls, again singly and doubly charged. Taking into account the molecular mass of DCTB (250 Da) the mass distribution

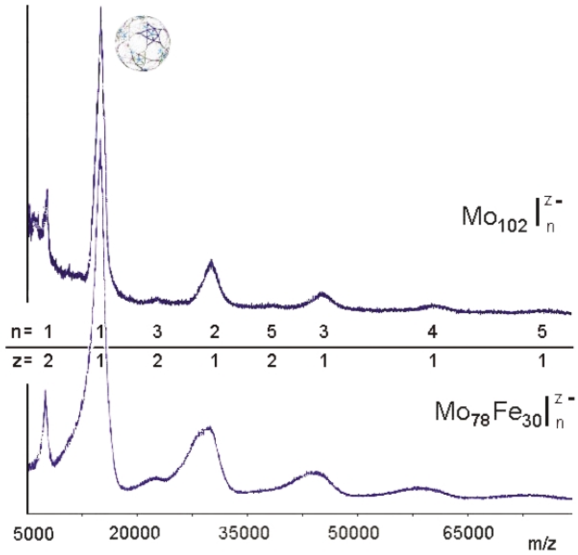

**Fig. 2** MALDI TOF mass spectra of the $Mo_{72}(Mo_6)Fe_{30}$ and $Mo_{102}$ species and their oligomers.

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† Dedicated to Prof. I. Haiduc on the occasion of his 65th birthday.

over the peaks covers the complete range from the fully ligand decorated (together with only a few matrix molecules) down to completely undecorated giant spheres.

The MALDI experiments with the $Mo_{132}$ type compound turned out to be difficult because of interference due to the excess of ammonium acetate in the matrix and probably also because of the high initial charge of the contained giant sphere which has a mass of a little less than 21.7 kDa. Here we observed only a broad signal centered at about 17 kDa, obviously due to a fragment of the sphere, together with a signal at *ca.* 8.5 kDa due to the related doubly charged species. Such a mass may be obtained by removing most of the ligand decorations and, in addition, a $Mo_{16}$ cap from the giant sphere. An interesting related aspect here is that an equilibrium exists in solution between the spherical $Mo_{132}$ cluster and the corresponding basket type species $Mo_{116}$ which can also be isolated as a fragment from the sphere from that solution.[7] The structure of this basket can be derived from that of the closed icosahedral cluster system by removing the cap-like fragment $(Mo)Mo_5\{Mo^V{}_2\}_5 \equiv$ (Pentagon)(Linker)$_5$. It seems reasonable to assume that a corresponding opening of the sphere may occur in the gas phase too.

If DCTB molecules are not to be made primarily responsible for glueing together of the oligomeric assemblies, the question arises as to whether a competing mechanism is present. In fact, in the cases of the $Mo_{72}(Mo_6)Fe_{30}$ cluster a solid state reaction has been observed which leads to crosslinking of the spheres *via* covalent –Fe–O–Fe– bridges,[8] a procedure which might well be operative also in the present cases. A comparable reaction is not yet known for the $Mo_{102}$ entities but linking *via* covalent –Mo–O–Mo– bridges has already been found for related 'giant wheel' systems[3] which interestingly also contain pentagons, but with lower symmetry. Apart from the fascinating observation that giant cluster collectives exist in the gas phase, it might be worthwhile to refer to the fact that these can also be condensed on surfaces with options for electronic devices.[2] In this context it is important to note that the spherical systems can be functionalized, *i.e.* by changing their surface properties as well as their contents – even with the option of encapsulating clusters/quantum dots.[9]

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## Notes and references

‡ A keplerate has, essentially by definition, one central point, its barycentre – whether or not occupied by an atom – and its atoms are organized in one or more spherical shells around this central point while each symmetry class of atoms forms the set of vertices of a Platonic or a (generalized) Archimedean solid.

§ MALDI TOF mass spectra were recorded with a Voyager DE Instrument from PE Biosystems, Weiterstadt, Germany, mounted with a 1.2 m flight tube. Ionization was achieved with a LSI nitrogen laser ($\lambda$ = 337 nm, 3 ns pulse width, 3 Hz, 600 shots for an average scan). The acceleration voltage was 25 kV in the negative ion detection mode. The mass axis was calibrated externally with mixtures of bovine insulin, thioredoxin from *E. coli* and horse apomyoglobin with sinapinic acid on the same target.

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