Metal–oxo cluster-supported transition metal complexes: hydrothermal synthesis and characterization of $[\{M(phen)_2\}_2(Mo_8O_{26})]$ (M = Ni or Co)

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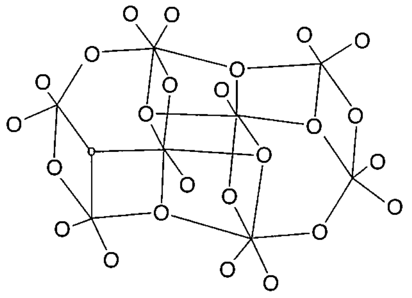
Two new metal–oxo supported transition metal complexes, $[\{M(phen)_2\}_2(Mo_8O_{26})$ (M = Ni or Co; phen = 1,10-phenanthroline) are synthesized by a hydrothermal method and characterized by X-ray crystallography, showing that the octamolybdate possesses a novel unprecedented structure and that $[M(phen)_2]^{2+}$ units are covalently bonded to the $[Mo_8O_{26}]^{4-}$ cluster.

Metal–oxo cluster chemistry has been actively purchased owing to interest in the chemistry itself and its various applications in fields such as catalysis, electric conductivity, magnetism, nonlinear optical properties and medicine.[1] Recently, an important advance in metal oxide cluster chemistry has been study of polyoxoanion-supported inorganic or organometallic complexes. The syntheses and structures of complexes include $[\{Cu(4,4'\text{-bipy})\}_4(Mo_8O_{26})]$,[2] and $[\{Cu(en)_2\}_2(Mo_8O_{26})]$,[3] which possess infinite extended structures, $[\{Zn(2,2'\text{-bipy})_2\}_2(V_4O_{12})]$[4] and $[La(Mo_8O_{26})_2]^{5-}$,[5] which are molecular clusters; and organometallic compounds $[(CO)_3Mn(cis\text{-}Nb_2W_4O_{19})]^{3-}$,[6] and $[\{(\eta\text{-}C_5Me_5)Rh\}(Mo_{13}O_{40})]^{2+}$,[6] which have discrete cluster structures.

We report here the syntheses and characterization of octamolybdate-supported nickel– and cobalt–phenanthroline molecular clusters $[\{Ni(phen)_2\}_2(Mo_8O_{26})]$ **1** and $[\{Co(phen)_2\}_2(Mo_8O_{26})]$ **2**. To date, α-, β- and γ- isomers of octamolybdates have been crystallographically confirmed in several salts, and recently the δ-isomer in $[(\eta\text{-}C_5Me_5Rh)_2(\mu_2S\text{-}Me)_3]_4[Mo_8O_{26}]\cdot 2MeCN$[8] and $[\{Cu(4,4'\text{-bipy})\}_4(Mo_8O_{26})]$,[2] and ε-isomer in $[\{Ni(H_2O)_2(4,4'\text{-bipy})_2\}_2(Mo_8O_{26})]$[2] have also been characterized. The results of structure determination upon $[Mo_8O_{26}]^{4-}$ in both **1** and **2** indicates a novel unprecedented ξ-isomer structural form (Scheme1).

Compounds **1** and **2** were prepared hydrothermally from a mixture of MoO_3, H_2MoO_4, $Ni(OAc)_2\cdot 6H_2O$, 1,10-phenanthroline and H_2O in a mol ratio of 1.0: 1.0: 0.8: 1.6: 450, heated at 170 °C for three days. Purple block crystals of **1** were obtained in *ca.* 35% yield. While bright red tetragonal prismatic crystals of **2** were obtained under the same reaction conditions using $Co(OAc)_2\cdot 4H_2O$. Compounds **1** and **2** were characterized by elemental analyses,† spectroscopic (IR and UV-VIS)‡ and single-crystal X-ray structure analyses.§



Scheme 1 The structure of ξ-$[Mo_8O_{26}]^{4-}$.

The crystal of **1** consists of discrete centrosymmetric heterometallic decanuclear clusters $[\{Ni(phen)_2\}_2(Mo_8O_{26})]$ (Fig. 1). The octamolybdate anion in **1** has a novel unprecedented structure mode denoted ξ- $[Mo_8O_{26}]^{4-}$ composed of a Mo_6O_6 ring capped on opposite faces by MoO_6 octahedra. The characteristic feature of this isomer is that the Mo_6O_6 ring contains two octahedral and four trigonal-bipyramidal Mo^{VI} atoms. In the ring, the linkage between any two MoO_5 trigonal bipyramids is edge-shared, while that between any MoO_6 octahedron and MoO_5 trigonal bipyramid is corner-shared. Each capping MoO_6 octahedron is linked to two MoO_6 octahedra and a trigonal bipyramid in the Mo_6O_6 ring by edge sharing and to another MoO_5 trigonal bipyramid of the ring by corner sharing. Two capping MoO_6 octahedra are attached to each other by edge sharing. The structural features of ξ-$[Mo_8O_{26}]^{4-}$ in **1** are different from those of the α-isomer consisting of six MoO_6 octahedra and two MoO_4 tetrahedra, the β-isomer consisting of eight edge-shared MoO_6 octahedra, the γ-isomer having six MoO_6 octahedra and two MoO_5 trigonal bipyramids, the δ-isomer composed of four MoO_6 octahedra and four MoO_4 tetrahedra[2,8] and the ε-isomer composed of six MoO_5 square pyramids and two MoO_6 octahedra.[2] The structure of the ξ- isomer also differs from that of (α–γ)- or (β–γ)-isomers proposed by Klemperer and Shum,[9] which, as yet has not been synthesized. Although the structure of proposed (α–γ)- or (β–γ)- isomers is also composed of four MoO_6 octahedra and four trigonal bipyramids as found in the ξ-isomer, their arrangement these isomers are different. In (α–γ)- or (β–γ)- isomers, the Mo_6O_6 ring contains four octahedral and two trigonal-bipyramidal Mo^{VI} atoms, and there are two edge-

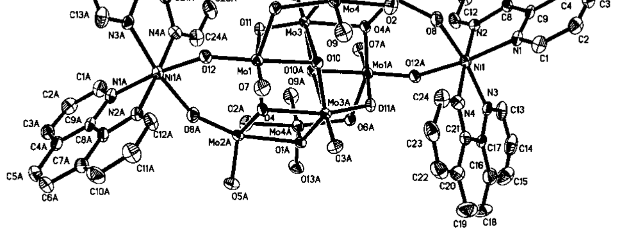


Fig. 1 Molecular drawing of **1** (50% displacement ellipsoids). Symmetry code: i $-x$, $-y$, $-z$. Selected bond lengths (Å): Mo(1)–O(7) 1.711(11), Mo(1)–O(6) 1.876(9), Mo(1)–O(12) 1.740(9), Mo(1)–O(4) 2.032(8), Mo(1)–O(10) 2.146(8), Mo(1)–O(11) 2.341(10), Mo(2)–O(5) 1.687(9), Mo(2)–O(8) 1.731(9), Mo(2)–O(2) 1.830(10), Mo(2)–O(4^i) 1.894(9), Mo(2)–O(1)2.244(8), Mo(3)–O(3)1.694(10), Mo(3)–O(11) 1.734(8), Mo(3)–O(1) 1.892(8), Mo(3)–O(10^i) 1.926(8), Mo(3)–O(4) 2.197(8), Mo(3)–O(10) 1.926(8), Mo(4)–O(13) 1.690(9), Mo(4)–O(9) 1.685(10), Mo(4)–O(2) 2.018(10), Mo(4)–O(6) 1.939(9), Mo(4)–O(1) 2.182(9), Ni(1)–O(8) 2.080(9), Ni(1)–O(12^i) 2.071(9).

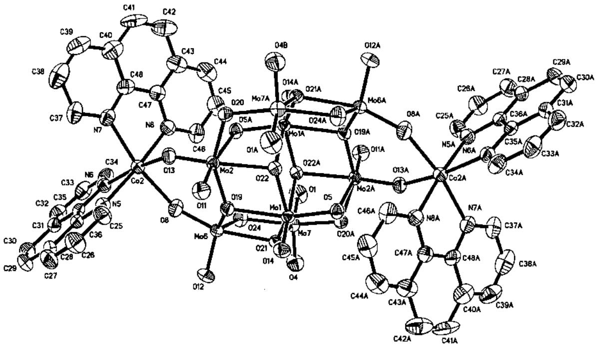


Fig. 2 Perspective drawing of one of the two crystallographically independent [{Co(phen)$_2$}$_2$(Mo$_8$O$_{26}$)] molecules in **2** (50% displacement ellipsoids). Symmetry code: i $-x + 2$, $-y + 2$, $-z$. Selected bond lengths (Å): Mo(1)–O(14) 1.688(3), Mo(1)–O(5) 1.740(3), Mo(1)–O(19) 2.190(3), Mo(1)–O(21) 1.897(3), Mo(1)–O(22) 1.911(3), Mo(1)–O(22^{i}) 2.504(3), Mo(2)–O(11) 1.688(3), Mo(2)–O(13) 1.736(3), Mo(2)–O(20) 1.866(3), Mo(2)–O(5^{i}) 2.337(3), Mo(2)–O(19) 2.024(3), Mo(2)–O(22) 2.149(3), Mo(6)–O(12) 1.696(3), Mo(6)–O(8) 1.733(3), Mo(6)–O(24) 1.831(4), Mo(6)–O(19) 1.900(3), Mo(6)–O(21) 2.236(3), Mo(7)–O(4) 1.693(4), Mo(7)–O(1) 1.685(4), Mo(7)–O(20^{i}) 1.947(3), Mo(7)–O(24) 2.002(4), Mo(7)–O(21) 2.159(3), Co(2)–O(8) 2.092(4), Co(2)–O(13) 2.107(4) (bond lengths in the other independent molecule are very close to the corresponding bonds above).

shared MoO$_5$ trigonal bipyramids in the cavity enclosed by polyhedra in the ring. More specifically, ξ-[Mo$_8$O$_{26}$]$^{4-}$ contains six O(μ$_3$), six O(μ$_2$) and fourteen O(t) atoms, while (α–γ)- or (β–γ)-[Mo$_8$O$_{26}$]$^{4-}$ contain two O(μ$_4$), two O(μ$_3$), eight O(μ$_2$) and fourteen O(t) atoms.

Each ξ-[Mo$_8$O$_{26}$]$^{4-}$ unit forms strong covalent interactions to two [Ni(phen)$_2$]$^{2+}$ units through terminal oxo groups of octahedral and trigonal-bipyramidal Mo sites in the Mo$_6$O$_6$ ring with Ni–O distances of 2.071(9) and 2.080(9) Å. Since the terminal oxo groups of fully oxidized polyoxomolybdate (all Mo sites in the VI oxidation state) are non-basic and unreactive, the formation of **1** reveals the oxophilicity of the [Ni(phen)$_2$]$^{2+}$ group and the structural flexibility of the octamolybdate core in adopting the ξ-structure. In the [Ni(phen)$_2$]$^{2-}$ unit, Ni is coordinated to four N donors of 1,10-phenanthroline ligands besides two terminal oxygen atoms of the octamolybdate cluster, forming a distorted octahedron with one relatively long Ni–N distance of 2.094(12) Å and three Ni–N distances in the range 2.055–2.065 Å. Compound **1** has three kinds of Mo–O bonds: 1.685(10)–1.711(11) Å for Mo–O(t), 1.731(9)–2.341(10) Å for Mo–O(μ$_2$) and 1.892(8)–2.244(8) Å for Mo–O(μ$_3$) bonds, respectively. The average Mo–O bond lengths of Mo(2), Mo(3) and Mo(4) are very similar (1.877–1.903 Å) whereas for Mo(1) Ni(phen)$_2$ this is longer (1.975 Å). It is found for Mo(2), Mo(3) and Mo(4) sites that Mo–O distances increase with increasing coordination number of oxygen (*i.e.* one < two < three), only for the Mo(1) site is this trend is not completely met, with Mo(1)–O(11)(μ$_2$)[2.341(10) Å] being obviously longer than Mo(1)–O(4)(μ$_3$) [2.042(8) Å] and Mo(1)–O(10) (μ$_3$)[2.146(8) Å], respectively.

There are two crystallographically independent [{Co(phen)$_2$}$_2$(Mo$_8$O$_{26}$)] molecules (Fig. 2) in the unit cell of **2** and both possess rigorous C_i symmetry in the solid state: their non-hydrogen atoms are symmetrically disposed about crystallographic inversion centers at (0,0,0) and (−1/2,1/2,−1/2), respectively. Both molecules contain a ξ-[Mo$_8$O$_{26}$]$^{4-}$ unit, with Mo–O(t) in the range 1.685(3)–1.696(3) Å [1.673(4)–1.690(4) Å second molecule]; Mo–O(μ$_2$) 1.733(3)–2.337(3) Å [1.734(3)–2.329(3) Å] and Mo–O(μ$_3$)1.897(3)–2.504(3) Å [1.903(3)–2.493(3) Å]. Average Mo–O bond lengths in molybdenum coordination polyhedra are as follows: for Mo atoms with coordination number of six, Mo(1)–O = 1.988 Å (av.) and Mo(2)–O = 1.967 Å (av.) [Mo(3)–O = 1.989 Å (av.) and Mo(4)–O = 1.964 Å (av)]; for Mo atoms with a coordination number of five, Mo(6)–O = 1.879 Å (av) and Mo(7)–O = 1.897 Å (av.) [Mo(5)–O = 1.881 Å (av.) and Mo(8)–O = 1.893 Å (av.)]. Thus average Mo–O bond lengths in five- and six-coordinated molybdenum polyhedra are very similar but the latter are significantly longer.

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Notes and references

† Anal: Calc. for **1** C$_{48}$H$_{32}$N$_8$Ni$_2$Mo$_8$O$_{26}$: C, 28.49; H, 1.58; N, 5.53; Ni, 5.83; Mo, 37.96. Found: C, 28.44; H, 1.52; N, 5.47; Ni, 5.76; Mo, 37.12%. Calc. for **2** C$_{48}$H$_{32}$N$_8$Co$_2$Mo$_8$O$_{26}$:C, 28.48; H, 1.58; N, 5.53; Co, 5.82; Mo, 37.95. Found: C, 28.24; H, 1.50; N, 5.23; Co, 5.78; Mo, 37.44%.

‡ *Spectroscopic data*: for **1**: IR (KBr pellet ν/cm^{-1}): Mo–O stretching region, 945, 885, 850, 705. UV–VIS (DMF solution), λ_{max} (ε/dm^3 mol^{-1} cm^{-1}): 322 (1.05 × 10^3), 340 (6.0 × 10^2), 585 (2.15 × 10^2).

For **2**: IR (KBr pellet ν/cm^{-1}): Mo–O stretching region, 960, 890, 850, 720. UV–VIS (DMF solution), λ_{max} (ε/dm^3 mol^{-1} cm^{-1}): 312 (1.1 × 10^3), 340 (1.3 × 10^3), 580 (2.06 × 10^2).

§ *Crystal data*: **1**: [{Ni(phen)$_2$}$_2$(Mo$_8$O$_{26}$)], M = 2021.76, monoclinic, space group P2$_1$/n, a = 12.952(2), b = 16.659(10), c = 13.956(12) Å, β = 106.273(8)°, V = 2890(5) Å^3, Z = 2, D_c = 2.323 g cm^{-3}, F(000) = 1952, T = 293 K. λ(Mo-Kα) = 0.71073 Å, θ range 1.90–26°. Bruker P4 four-circle diffractometer. ω-2θ scan. 5604 reflections are unique, 5604 reflections with $I > 2\sigma(I)$ were used in the refinement and the calculation of R_1 and wR_2. The last successful full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged to R_1 = 0.0414, wR_2 = 0.0815. The positions of hydrogen atoms were calculated in ideal positions and not refined. The structure was solved by direct methods.

2: [{Co(phen)$_2$}$_2$(Mo$_8$O$_{26}$)], M = 2022.20, triclinic, space group $P\bar{1}$, a = 12.913(3), b = 14.021(3), c = 16.687(3) Å, α = 90.14(3), β = 90.13(3), γ = 106.26(3)°, V = 2900.4(10) Å^3, Z = 2, D_c = 2.316 g cm^{-3}, F(000) = 1948, T = 293 K. λ(Mo-Kα) = 0.71073 Å, θ range 1.51–23°. Bruker P4 four-circle diffractometer. ω–2θ scan. 8029 reflections are unique, 8029 reflections with $I > 2\sigma(I)$ were used in the refinement and the calculation of R_1 and wR_2. Least-squares refinement as above converged to R_1 = 0.026, wR_2 = 0.0615. Other details as above.

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