

Synthesis and X-Ray Structures of Molybdenum(VI) Complexes with Benzamide Oximes. A Rare Linear Tetramolybdenum Compound

$[\text{Mo}_4\text{O}_{11}\{\textit{p}\text{-ToIC}(\text{NH}_2)\text{NHO}\}_2\{\textit{p}\text{-ToIC}(\text{NH})\text{NHO}\}\{\textit{p}\text{-ToIC}(\text{NH})\text{NO}\}]^-$

Valérie Chilou, Pierre Gouzerh, Yves Jeannin,* and Francis Robert

Laboratoire de Chimie des Métaux de Transition, UA-CNRS 419, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France

An asymmetrical dinuclear molybdenum complex $[\text{Mo}_2\text{O}_5(\text{Hbao})_2]$ with benzamide oxime (H_2bao) and a rare linear tetranuclear molybdenum complex $[\text{Mo}_4\text{O}_{11}(\text{H}_2\text{mbao})_2(\text{Hmbao})(\text{mbao})]^-$ with *p*-methylbenzamide oxime (H_2mbao) have been prepared and characterized by X-ray diffraction.

Co-ordination compounds of isopolyoxometallates are currently attracting attention as models for the interaction of substrates with metal oxide surfaces.¹ They are also of interest owing to the possible oxygen transfer between the metal and the ligand.² A variety of polyoxomolybdenum complexes incorporating oxygen and/or nitrogen containing ligands have been reported.³ Investigating the reactions of polyoxometallates with amide oximes we recently reported the syntheses and the X-ray structures of three complexes involving acetamide oxime and containing the new cyclic tetrametallate $[\text{M}_4\text{O}_{12}\{\text{MeC}(\text{NH}_2)\text{NO}\}_2]^{2-}$ with $\text{M} = \text{Mo}, \text{W}$.⁴ Owing to their exceptional structural features, we

explored the reactivity of other amide oximes towards polyoxometallates. We report the reaction of benzamide oxime $[\text{PhC}(\text{NH}_2)\text{NOH} = \text{H}_2\text{bao}]$ and its *p*-methyl derivative $[\textit{p}\text{-MeC}_6\text{H}_4\text{C}(\text{NH}_2)\text{NOH} = \text{H}_2\text{mbao}]$ with $(\text{NBu}_4)_4[\alpha\text{-Mo}_8\text{O}_{26}]$ yielding dinuclear and tetranuclear compounds containing the known $\text{Mo}_2\text{O}_5^{2+}$ core and the exceptional linear $\text{Mo}_4\text{O}_{11}^{2+}$ core.

In a typical experiment a solution of $(\text{NBu}_4)_4[\alpha\text{-Mo}_8\text{O}_{26}]^5$ (2.15 g) and $\text{PhC}(\text{NH}_2)\text{NOH}^6$ (2.45 g) in MeCN (25 ml) was refluxed for 6 h; large yellow–orange crystals (**2**) were deposited after 1–2 days. They are stable when kept in the mother liquor. Looking for more stable crystals, we con-

sidered *p*-methylbenzamide oxime;⁷ yellow–orange crystals (3) were obtained which behaved similarly.

In only one experiment, $[\text{Mo}_2\text{O}_5\{\text{PhC}(\text{NH})\text{NHO}\}_2]$ (1) was deposited from the mother solution as yellow crystals which were stable in air. This compound is more easily prepared from the reaction of $[\text{MoO}_2(\text{acac})_2]$ (Hacac = pentanedione) with $\text{PhC}(\text{NH}_2)\text{NOH}$ in MeOH. Satisfactory analytical results were obtained for (1) and (2), if free of solvent.

In order to identify these compounds, X-ray structure determinations were carried out for (1) and (3). In the case of (3), crystals were kept with a drop of solution in a sealed Lindeman tube.[†]

Compound (1) contains dinuclear complexes $[\text{Mo}_2\text{O}_5\{\text{PhC}(\text{NH})\text{NHO}\}_2]$. Both molybdenum atoms are linked by an oxo-bridge. Each molybdenum is co-ordinated to two doubly-bonded oxygen atoms and to one bidentate $\text{PhC}(\text{NH})\text{NHO}^-$ ligand through the NH nitrogen and the NHO oxygen atoms (Figure 2) so that molybdenum is five-co-ordinate with an approximately trigonal bipyramidal environment. The oxime oxygen atom is pointing towards the second molybdenum but distances are fairly long: Mo(1)–O(16) 3.065(4) and Mo(2)–O(6) 2.693(3) Å. The difference between these distances suggests that this compound could also be described as containing a five-co-ordinate and a six-co-ordinate molybdenum atom. This distinguishes the structure of (1) from that of the molybdenum dinuclear complex with *N*-methylacetamide oxime which displays a face-sharing bioctahedral arrangement⁸ where both bridges are identical and asymmetrical. A dinuclear doubly bridged complex in which one Mo atom is five-co-ordinate while the other is six-co-ordinate, has been recently reported.⁹

The structure of (3) consists of non-symmetrical linear tetranuclear anions $[\text{Mo}_4\text{O}_{11}(\text{H}_2\text{mbao})_2(\text{Hmbao})(\text{mbao})]^-$. This anion can be viewed as two dissimilar dinuclear units $[\text{Mo}_2\text{O}_5(\text{H}_2\text{mbao})(\text{mbao})]$ and $[\text{Mo}_2\text{O}_5(\text{H}_2\text{mbao})(\text{Hmbao})]^+$ linked by one slightly bent μ -oxo bridge (Figure 1). The identification of the ligand with different protonation contents, *i.e.* zwitterionic *p*-tolC(NH₂)NHO, singly deprotonated *p*-tolC(NH)NHO⁻, and doubly deprotonated *p*-tolC(NH)NO²⁻, is based upon hydrogen atom location on difference Fourier maps. These three forms have already been found in complexes with the parent benzamide oxime ligand: zwitterionic H₂L in a uranyl complex,¹⁰ singly deprotonated

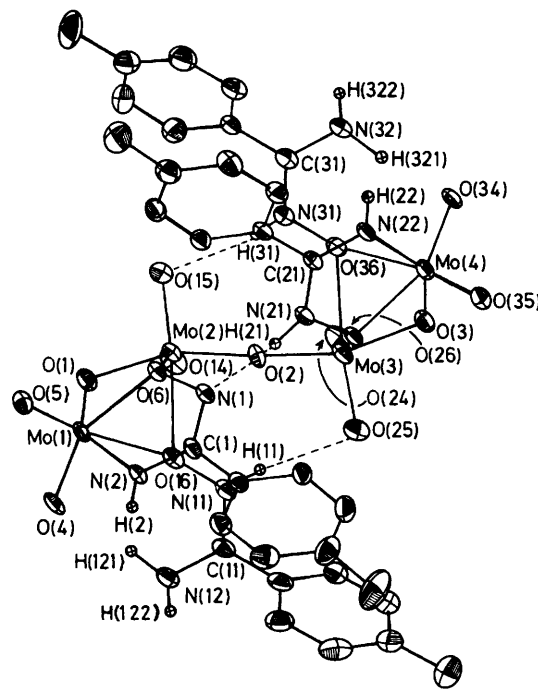


Figure 1. View of the tetranuclear anion (3) $[\text{Mo}_4\text{O}_{11}(\text{H}_2\text{mbao})_2(\text{Hmbao})(\text{mbao})]^-$. Selected bond distances (Å) and angles ($^\circ$) are given for the $[\text{Mo}(1), \text{Mo}(2)]$ moiety, the other one being similar: Mo(1)–O(1) 1.878(4), Mo(1)–O(4) 1.726(4), Mo(1)–O(5) 1.692(4), Mo(1)–O(6) 2.118(3), Mo(1)–N(2) 2.029(5), Mo(1)–O(16) 2.587(4), Mo(2)–O(1) 1.946(4), Mo(2)–O(2) 1.901(4), Mo(2)–O(14) 1.694(4), Mo(2)–O(15) 1.703(4), Mo(2)–O(6) 2.336(4), Mo(2)–O(16) 2.287(4), O(6)–N(1) 1.399(6), N(1)–C(1) 1.299(7), N(2)–C(1) 1.340(6), O(16)–N(11) 1.356(6), N(11)–C(11) 1.303(7), N(12)–C(11) 1.342(7); O(4)–Mo(1)–O(6) 149.7(2), O(1)–Mo(1)–N(2) 140.1(2), O(5)–Mo(1)–O(16) 170.7(2), O(1)–Mo(2)–O(2) 147.1(2), O(6)–Mo(2)–O(14) 162.2(2), O(15)–Mo(2)–O(16) 163.7(2), Mo(1)–O(1)–Mo(2) 112.9(2), Mo(1)–O(6)–Mo(2) 91.3(2), Mo(1)–O(16)–Mo(2) 81.4(2), Mo(2)–O(2)–Mo(3) 150.0(2).

HL⁻ in a nickel complex,¹¹ and doubly deprotonated L²⁻ in a platinum complex.¹² The title compound seems to be the first case where these three forms occur simultaneously.

In each dinuclear moiety, *i.e.* $[\text{Mo}(1), \text{Mo}(2)]$ and $[\text{Mo}(3), \text{Mo}(4)]$, the molybdenum atoms are linked by three oxygen bridges, one μ -oxo and two amide oximes, one of which is chelating one molybdenum. Chelating Hmbao⁻ and mbao²⁻ give more symmetrical Mo–O–Mo bridges than in (1). The zwitterionic H₂mbao bridges are asymmetrical [2.287(4) and 2.587(4); 2.316(4) and 2.510(4) Å]. Linear tetranuclear oxo-bridged molybdenum compounds are very rare. To the best of our knowledge the only other one was described a long time ago with the malate anion as a ligand.¹³ In the title compound both moieties are also bound by three intramolecular hydrogen bonds, two N–H \cdots O and one N–H \cdots N; the latter is the strongest with N(1)–N(21) 2.693(6) Å and arises from the dissymmetry of the tetranuclear complex. The cation is NBU_4^+ . The structure was refined with 9 molecules per unit cell of MeCN which are distributed over 16 sites.

It remains to be discussed whether compound (3) results from the degradation of $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$ and then (1) is formed, or conversely (1) is the degradation product of the polyanion and it then yields (3) by condensation. The behaviour of acetamide oxime and benzamide oxime towards polyoxometallates shows that amide oximes are versatile ligands

[†] Data collection: Determination of cell constants and data collection were carried out at room temperature with Mo- K_α radiation with a Nonius CAD-4 diffractometer for (3) and a Philips PW1100 for (1), both equipped with a graphite monochromator. Unit cell dimensions were obtained by a least-squares fit of 25 reflections in the range $15^\circ < \theta < 16^\circ$. Data were recorded by a θ – 2θ scan in the range $1 < \theta < 25^\circ$ and were corrected for Lorentz-polarization effects; an empirical absorption correction based upon a Ψ scan was applied only for (3). All calculations were performed with CRYSTALS.¹⁴ Hydrogen atoms in both cases were found on difference Fourier maps.

Crystal data: (1), $\text{C}_{14}\text{H}_{14}\text{Mo}_2\text{N}_4\text{O}_7$, $M = 542.17$, triclinic, space group $P\bar{1}$, $a = 7.567(2)$, $b = 10.861(1)$, $c = 11.002(2)$ Å, $\alpha = 88.34(1)$, $\beta = 75.48(2)$, $\gamma = 85.60(2)^\circ$, $U = 872.7$ Å³, $Z = 2$, $D_c = 2.06$ g cm⁻³; $\mu = 14.48$ cm⁻¹; $F(000) = 532$; 2967 independent reflections measured, 2541 with $F_o > 10.0$ used in refinement, $R = 0.025$, $R_w = 0.031$ with $w = 1$.

(3), $\text{C}_{48}\text{H}_{73}\text{Mo}_4\text{N}_9\text{O}_{15}$, with *ca.* 4.5 MeCN, $M = 1399.92$ without solvent, triclinic, space group $P\bar{1}$, $a = 14.048(4)$, $b = 15.021(5)$, $c = 18.938(7)$ Å, $\alpha = 83.42(3)$, $\beta = 77.75(3)$, $\gamma = 70.91(3)^\circ$, $U = 3686$ Å³, $Z = 2$, $D_c = 1.42$ g cm⁻³; $\mu = 7.12$ cm⁻¹; 10 167 independent reflections measured, 7933 with $I > 3\sigma(I)$ used in refinement, $R = 0.035$, $R_w = 0.041$ with $w = 1$.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Laboratory Data Centre. See Notice to Authors, Issue No. 1.

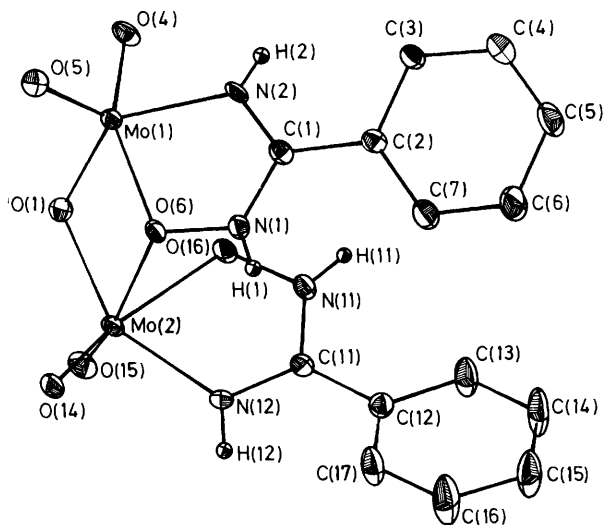


Figure 2. View of the dinuclear complex (1) $[\text{Mo}_2\text{O}_5\{\text{PhC}(\text{NH})\text{NHO}\}_2]$. Selected bond distances (Å) and angles ($^\circ$) are: Mo(1)–O(1) 1.893(3), Mo(1)–O(4) 1.716(3), Mo(1)–O(5) 1.686(4), Mo(1)–O(6) 2.107(3), Mo(1)–N(2) 2.057(4), Mo(1) \cdots O(16) 3.065(4), O(6)–N(1) 1.371(5), N(1)–C(1) 1.308(6), C(1)–N(2) 1.328(6), Mo(2)–O(1) 1.913(3), Mo(2)–O(14) 1.716(3), Mo(2)–O(15) 1.695(4), Mo(2)–O(16) 2.110(3), Mo(2)–N(12) 2.060(4), Mo(2)–O(6) 2.692(3), O(16)–N(11) 1.371(5), N(11)–C(11) 1.309(6), C(11)–N(12) 1.323(6); O(5)–Mo(1)–O(1) 107.4(2), N(2)–Mo(1)–O(1) 135.7(2), N(2)–Mo(1)–O(5) 111.0(2), O(6)–Mo(1)–O(4) 153.3(2), O(15)–Mo(2)–O(1) 104.3(2), N(12)–Mo(2)–O(1) 144.4(2), N(12)–Mo(2)–O(15) 104.6(2), O(16)–Mo(2)–O(14) 150.8(1), Mo(2)–O(1)–Mo(1) 120.1(2), Mo(2)–O(6)–Mo(1) 85.9(1).

which can stabilize various molybdenum stereochemistries and oxomolybdenum cores.

Received, 5th April 1988; Com. 8/01308J

References

- 1 M. T. Pope, in 'Heteropoly and Isopoly Oxometalates,' Springer, New York, 1983.
- 2 R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401.
- 3 S. Liu, S. N. Shaikh, and J. Zubieta, *Inorg. Chem.*, 1987, **26**, 4305, and references therein.
- 4 V. Chidou, P. Gouzerh, Y. Jeannin, and F. Robert, *J. Chem. Soc., Chem. Commun.*, 1987, 1469.
- 5 M. Filowitz, R. K. C. Ho, W. G. Klemperer, and W. Shum, *Inorg. Chem.*, 1979, **18**, 93.
- 6 J. Armand, *C.R. Acad. Sci., Ser. C.*, 1966, **262**, 592.
- 7 K. Clarke, *J. Chem. Soc.*, 1954, 4251.
- 8 K. Wieghardt, W. Holzbach, E. Hofer, and J. Weiss, *Chem. Ber.*, 1981, **114**, 2700.
- 9 B. Piggott, S. F. Wong, and M. V. Capparelli, *Inorg. Chim. Acta*, 1986, **141**, 281.
- 10 E. G. Witte, K. S. Schwochau, G. Henkel, and B. Krebs, *Inorg. Chim. Acta*, 1984, **94**, 323.
- 11 L. Malatesta, G. La Monica, M. Monassero, and M. Sansoni, *Gazz. Chim. Ital.*, 1980, **110**, 113.
- 12 P. L. Bellon, S. Cenini, F. Demartin, M. Monassero, M. Pizzotti, and F. Porta, *J. Chem. Soc., Dalton Trans.*, 1980, 2060.
- 13 M. A. Porai-Koshitz, L. A. Aslanov, G. V. Ivanova, and T. N. Polynova, *J. Struct. Chem. (USSR)*, 1968, **9**, 401.
- 14 D. J. Watkin, J. Carruthers, and P. W. Betteridge, 'CRYSTALS user guide,' Chemical Crystallography Laboratory, University of Oxford, Oxford, 1987.