Inorg. Chem. **1994,** *33,* 2073–2074

Synthesis and Characterization of an Oxomolybdate–Copper(II) Cluster Containing Coordinatively Bound Schiff-Base Molecules

Athanasios N. Papadopoulos,[†] Antonis G. Hatzidimitriou,[‡] Andre Gourdon,[‡] and Dimitris P. Kessissoglou*[,†]

Laboratory of Inorganic Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece, and CEMES-LOE/CNRS, 31055 Toulouse Cedex, France

Received October 14, 1993

Despite the fact that the coordination chemistry of polymolybdates with organic molecules is of interest in the development of models for the interaction of organic substrates with catalytic oxide surfaces,[1,2] relatively few examples of organic derivatives of polymolybdates have been reported.[3] Furthermore, the antagonistic function of the molybdenum ion with regard to copper in humans and animals[4] has raised the interest in interaction of Cu ions with ligated molybdenum species. Most of the Mo–Cu mixed-metal complexes reported till now[5] employ mainly $[MoS_4]^{2-}$ as the source of the molybdenum component. We have extended this chemistry to the Schiff-base ligands, which form complexes with coordination environments rich in oxygen. The compound reported here is the first example that includes a $[MoO_4]^{2-}$ group, which is the major source for molybdenum in biological systems and the product of the hydrolysis of MoO_2^{2+} species at pH = 7, interacting with Cu(II) ions. This may be considered as a new insight into the metabolic disturbances and diseases in humans and animals caused by deficiency or excess of molybdenum and copper trace elements.[4] In the course of this research, the chemistry of MoO_2(Schiff-base)(solvent) compounds with Cu(II) ions has been studied.[6] Reaction of MoO_2(5-Cl-Hsaladhp)(MeOH) [H_3saladhp = 1,3-dihydroxy-2-methyl-2-(salicylideneamino)propane] with $Cu(CH_3COO)_2$ in methanol/CH_3CN, yielded green crystals of a mixed metal 2Mo(VI)–2Cu(II) cluster having a $Mo_2Cu_2O_4$ cubane like core.[6a]

$$2MoO_2[\text{5-Cl-Hsaladhp}](CH_3OH) + 2Cu(CH_3COO)_2 \xrightarrow{\text{MeOH}} Cu_2Mo_2O_4[\text{5-Cl-saladhp}]_2(CH_3O)_2 + 4CH_3COOH \quad (1)$$

$Cu_2Mo_2O_4$(5-Cl-saladhp)$_2(CH_3O)_2$ (**1**) was refluxed with an excess of bpy(bpy = 2,2′-bipyridine or bipyridyl) in acetonitrile for 2 h. The lightly colored blue solution was cooled to room temperature and left for slow evaporation. Pale blue/green crystals of the formula $CuMo_3O_8$(5-Cl-Hsaladhp)$_2$(bpy)$_2$ (**2**) were deposited over a period of a week. Compound **2** is a 1:1 electrolyte in H_2O, dissociating most likely to $[Cu(bpy)_2]^{2+}$ and $[MoO_4]^{2-}$ or $[Mo_3O_8(\text{Schiff-base})_2]^{2-}$ ions, and is slightly soluble in DMF and DMSO. The IR spectrum of compound **2** exhibits the ν(C=N) and ν(C=O) bands of the Schiff-base ligands at 1620 and 1540 cm^{-1} respectively, which are characteristic of the formation of a chelated ring [e.g. Mo–O(21)–C(201)–C(206)–C(207)–N(201)] (Figure 1). In addition, the molybdenum species displays a complex pattern of bands in the 770–920-cm^{-1} range attributable to ν(Mo=O) modes. The room-temperature powder and the low temperature (T = 95 °C) DMSO-glass X-band EPR spectra of **2** are typical for a Cu(II) ion without showing any interaction with the $[MoO_4]^{2-}$ moiety. The EPR powder spectrum shows only a broad band with $g = 2.12$, while in the EPR DMSO-glass spectrum at 95 K, four copper hyperfine components ($I = {}^3/_2$) appear in the low-field $g_\parallel$ signal, with $g_\parallel = 2.06$, $g_\perp = 2.26$, and $A_\parallel = 165.4 \times 10^4$ cm^{-1}. It clearly shows that the unpaired electron is located on the Cu(II) ion, and the oxidation states for copper and molybdenum are 2+ and 6+, respectively. No superhyperfine structure of the EPR signal has been detected, due to copper–nitrogen interaction.

Crystal data: $C_{42}H_{40}Cl_2CuMo_3N_6O_{14}\cdot H_2O\cdot {}^1/_2CH_3CN$ (**2**), M_r = 1313.62, triclinic, a = 13.381(3) Å, b = 14.355(3) Å, c = 14.463(2) Å, α = 77.82(2)°, β = 68.00(2)°, γ = 73.72(2)°, V = 2455(17) Å^3, space group $P\bar{1}$, Z = 2, D = 1.78 g·cm^{-3}, 6117 reflections of 9050 collected were used in the structural analysis (Mo Kα radiation, R = 0.036 and R_w = 0.0364). The X-ray structure of **2** confirms the presence of a trinuclear unit $[Mo_3O_8]^{2-}$ coordinatively bound to the $[Cu(bpy)]^{2+}$ ion. The molybdenum part of the structure may be described in terms of three oxo-bridged molybdenum centers, alternating one tetraoxomolybdate center $[MoO_4]^{2-}$, and two six co-ordinated $[MoO_2$(Schiff-base)] moieties. The two oxo groups of the capping $[MoO_4]^{2-}$ unit O(12) and O(13) bridge the tetrahedral molybdenum [Mo(1)] with the two six coordinated Mo atoms [Mo(2), Mo(3)] at an average distance of 2.22 Å. The third oxo group of the tripodal $[MoO_4]^{2-}$ tetrahedron bridges the $[Mo_3O_8]^{2-}$ unit with the $[Cu(bpy)]^{2+}$ ion, possessing one site in the equatorial plane of the trigonal bipyramidal Cu^{2+} coordination environment. The Mo–O(alkoxy), 1.915 Å, Mo–O(phenoxy), 1.971 Å (average), and Mo–N, 2.229 Å (average) distances of the bound Schiff-bases are consistent with the Mo–O and Mo–N distances in the MoO_2(5-Cl-Hsaladhp)(MeOH) monomer analogue.[6b] It is noticeable that the sum of the trans Mo–O distances of the $[MoO_2$(5-Cl-Hsaladhp)] units are almost identical (3.876–3.998 Å) with an average value of 3.933 Å. While the octahedrons around each molybdenum units shows a strong *cis*-distortion, the lack of any elongation or depression along one of the axes of the octahedron is a strong evidence that Mo keeps a d^0 configuration with a Mo(VI) oxidation state. The coordination mode of the Schiff-base is also quite interesting. In the starting material, MoO_2(5-Cl-Hsaladhp)(MeOH), it acts as tridentate ligand possessing three sites in the equatorial plane of the molybdenum octahedron. In compound **1** the Schiff-base is transferred from the molyb-

---

[†] Aristotle University of Thessaloniki.

[‡] CEMES-LOE/CNRS.

(1) Day, V. W.; Frederick, M. F.; Klemperer, G. K.; Liu, R.-S. *J. Am. Chem. Soc.* **1979**, *101*, 491.

(2) McCarron, E. M.; Staley, R. H.; Sleight, A. W. *Inorg. Chem.* **1984**, *23*, 1043.

(3) (a) McCarron, E. M.; Harlow, R. C. *J. Am. Chem. Soc.* **1983**, *105*, 6179. (b) McCarron, R. M.; Whitney, J. F.; Chase, D. B. *Inorg. Chem.* **1984**, *23*, 3275. (c) Hsich, T. C.; Zubieta, J. *Inorg. Chem.* **1985**, *24*, 1287. (d) Shaikh, S. N.; Zubieta, J. *Inorg. Chem.* **1986**, *25*, 4613. (e) Hsich, T. C.; Shaikh, S.N.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 4079.

(4) (a) Mills, C. F. *Chem. Br.* **1979**, *15*, 512. (b) Mills, C. F. *Philos. Trans. R. Soc. London, Ser. B* **1979**, *B288*, 1. (c) Bailar, J. C.; Emeleus, H. J.; R. Nyholm, R. N.; Trotman-Dickenson, X. In *Comprehensive Inorganic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1973; Vol. 3, Chapter 36. (d) da Silva, Frausto; Williams, R. J. P. *The Biological Chemistry of the Elements;* Clarendon Press: Oxford, England, 1991; pp 417, 540.

(5) (a) Muller, A.; Bogge, H.; Schimanski, U. *Inorg. Chim. Acta* **1983**, *69*, 5. (b) Muller, A.; Bogge, H.; Schimanski, U. *J. Chem. Soc., Chem. Commun.* **1980**, 91. (c) Xintao, W.; Shaofeng, L.; Lianyong, Z.; Ojangjin, W.; Jiaxi, L. *Inorg. Chim. Acta* **1987**, *133*, 39. (d) Shihabara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1988**, *110*, 3313. (e) Minelli, M.; Enemark, J. H.; Nicholson, J. R.; Garner, C. D. *Inorg. Chem.* **1984**, *23*, 4386.

(6) (a) Kessissoglou, D. P.; Raptopoulou, C. P.; Bakalbasis, E. G.; Terzis, A.; Mrozinski, J. *Inorg. Chem.* **1992**, *31*, 4339. (b) Kessissoglou, D. P.; Papadopoulos, A. N.; Raptopoulou, C. P.; Terzis, A.; Hatzidimitriou, A. G.; Courdon, A. Manuscript in prepapation.

0020-1669/94/1333-2073$04.50/0

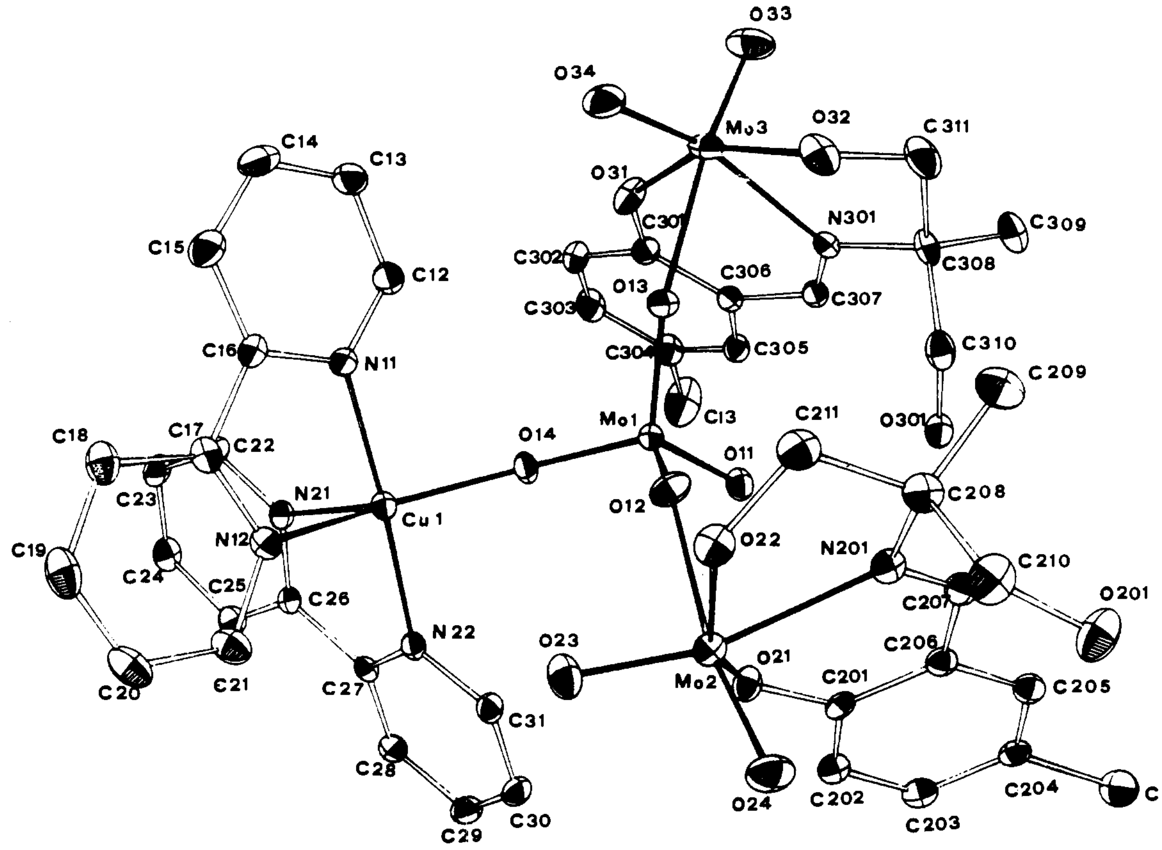

Figure 1. ORTEP view of $CuMo_3O_8(5\text{-}Cl\text{-}Hsaladhp)_2(bpy)_2$ (**2**) showing the atom labeling scheme. Selected bond lenghts (Å) and angles (deg): Mo(1)–O(11) = 1.720(4), Mo(1)–O(12) = 1.748(4), Mo(1)–O(13) = 1.742(4), Mo(1)–O(14) = 1.770(3), Mo(2)–O(12) = 2.239(4), Mo(2)–O(21) = 1.961(4), Mo(2)–O(22) = 1.915(4), Mo(2)–O(23) = 1.704(4), Mo(2)–O(24) = 1.695(4), Mo(2)–N(201) = 2.287(5), Cu(1)–O(14) = 1.942(3), Cu(1)–N(11) = 1.978(4), Cu(1)–N(12) = 2.047(4), Cu(1)–N(21) = 2.161(4), Cu(1)–N(22) = 1.990(4); O(13)–Mo(1)–O(11) = 109.7(2), O(12)–Mo(1)–O(11) = 110.5(2), O(12)–Mo(1)–O(13) = 107.8(2), O(14)–Mo(1)–O(11) = 108.3(2), O(14)–Mo(1)–O(13) = 109.2(2), O(14)–Mo(1)–O(12) = 111.3(2), O(22)–Mo(2)–O(21) = 152.1(2), O(23)–Mo(2)–N(201) = 165.2(2), O(24)–Mo(2)–O(12) = 168.0(2), O(24)–Mo(2)–O(23) = 104.5(2), N(21)–Cu(1)–O(14) = 116.2(2), N(21)–Cu(1)–N(12) = 95.7(2), N(22)–Cu(1)–N(11) = 175.0(2). Parameters for Mo(3) are similar to those for Mo(2).

denum to copper ion and acts as tetradentate ligand with two oxygens and one nitrogen bound to Cu^{2+} ion, occupying the three sites in the basal plane of the square pyramid and one oxygen bound to Mo(VI) ion, while in compound **2** the Schiff-base returns to the Mo atom acting again as tridentate ligand and possessing the three sites in the equatorial plane of the molybdenum octahedron (Figure 1). The cyclic voltammetry of compound **2** in H_2O shows a reversible wave at $E_{1/2} = -209$ mV which may be assigned to the $[Cu(bpy)_2]^{2+} \Leftrightarrow [Cu(bpy)_2]^+$ reduction process. The cathodic potential indicates that the Cu(II) oxidation state is stabilized by the bpy ligands.

Acknowledgment. This work was supported by the Greek Ministry of Industry, Energy and Technology, General Secretariat of Research and Technology.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (13 pages). Ordering information is given on any current masthead page.