DALTON
COMMUNICATION

The first polyoxomolybdenum carbonate compound: Synthesis and crystal structure of $(NH_4)_5[(Mo_2{}^{V}O_4)_3(\mu_6\text{-}CO_3)(\mu\text{-}CO_3)_3(\mu\text{-}OH)_3]\cdot 0.5CH_3OH$ 1

Manolis J. Manos,[a] Anastasios D. Keramidas,[b] J. Derek Woollins,[c] Alexandra M. Z. Slawin *[c] and Themistoklis A. Kabanos *[a]

[a] *Department of Chemistry, Section of Inorganic and Analytical Chemistry, University of Ioannina, 45110 Ioannina, Greece. E-mail: tkampano@cc.uoi.gr*
[b] *Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus. E-mail: akeramid@ucy.ac.cy*
[c] *Department of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY16 9ST. E-mail: jdw3@st-andrews.ac.uk*

Received 17th September 2001, Accepted 30th October 2001
First published as an Advance Article on the web 8th November 2001

The first polyoxomolybdenum carbonate has been synthesized and its single crystal structure as well as its IR, UV-vis and ^{13}C NMR spectra have been determined.

The design and synthesis of polyoxometalates have generated significant interest not only for their molecular and electronic structural diversity, but also because of their significance in quite diverse disciplines, *e.g.* catalysis,[1] medicine,[1] materials science[1] and molecular magnetism.[2] There has been a great deal of research activity aimed at the polyoxomolybdenum-derivatives with inorganic ligands,such as phosphates,[3] arsenates,[4] halides,[5] nitrosyls[5] *etc.* Among these derivatized polyoxomolybdates containing inorganic components, there are no such examples with carbonate as inorganic ligand. This is unexpected since the environmental impact of the industrial CO_2 output has led to a greater interest by environmental chemists, geochemists, oceanographers and biologists in the applied aspects of metal-carbonate chemistry.[6] Herein we describe the synthesis and structural characterization of the first polyoxomolybdenum carbonate compound **1**, containing six molybdenum(V) atoms arranged in a planar circular array with Mo^V–Mo^V single bonds alternating with long Mo^V–Mo^V nonbonding contacts and templated by a μ_6-$CO_3{}^{2-}$ anion.

A saturated aqueous solution (~20 mL, pH ≈ 9) of NH_4HCO_3 (~82 mmol) was added in one portion to a stirred solution of Mo^VCl_5 (1.7 mmol) in ~8 mL (pH ≈ 0) concentrated HCl–H_2O (1 : 2 v/v). Upon addition of NH_4HCO_3 the dark red colour of the solution immediately changed to light red and an orange–brown precipitate was formed and the pH of the solution changed to ≈8. The solution was filtered and red well-shaped hexagonal crystals of **1** suitable for single-crystal X-ray structure analysis were obtained by vapour diffusion of methyl alcohol into the filtrate.† Yield, 0.05 g (15%) based on molybdenum. The electronic spectrum of **1** in H_2O consists of a shoulder in the visible and two peaks and a shoulder in the ultraviolet region, namely: λ_{max}/nm (ε_M/M^{-1} cm^{-1}); 446 (sh) (185), 302 (12950), 218 (sh) (28400), 193 (35100). The infrared spectrum of **1** exhibited bands at 3132s (br), 1540s, 1456s, 1400s, 1328s, 1099s, 966s [ν(Mo=O)], 831m, 730s, 517w, 489m and 396w cm^{-1}. With reference to the vibrational frequencies of the carbonate ion in the free[7a] and coordinated states,[7b] the infrared data suggested that the carbonate groups in **1** were involved in at least two different modes of coordination.

The low yield (15%) in the synthesis of **1** is probably due to the high solubility of **1** in water. However, we succeeded in isolating the crystalline polyoxomolybdenum(V)-carbonate derivative in significantly higher yield (32%) in the presence of high electrolyte concentrations (NaCl ≈ 0.8 M), which presumably reduces drastically the solubility of **1**.[8]

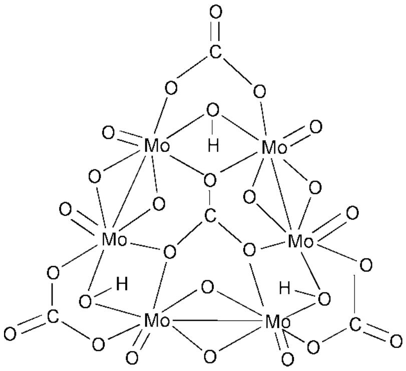

Fig. 1 Molecular drawing of **1**.

The molecular drawing of the anion of **1** as well as its ORTEP plot are shown in Figs. 1 and 2 respectively. The main structural unit in **1** is a $[(Mo_2{}^VO_4)_3(CO_3{}^{2-})_4(OH)_3]^{5-}$ cluster, which has a three-fold axis passing through C(1). The six molybdenum(V) atoms lie in a plane in a pseudo-hexagonal arrangement and display alternating bonding and nonbonding Mo–Mo contacts. There are four carbonate groups in **1**. Three of these carbonate groups are on the periphery of the cluster and each has a terminal oxo-group, while the unique central carbonate group, which defines a plane parallel to and above (0.94 Å) the Mo_6 plane provides three μ-oxygen bridges so as to join each pair of molybdenum(V) centers. There are two crystallographically independent molybdenum atoms in an asymmetrical unit, as shown in Fig. 1. The two molybdenum atoms have identical coordination environments and each is coordinated in a severely distorted octahedral geometry (ignoring the Mo^V–Mo^V interaction), by two μ-O^{2-}, one μ-OH^- and two carbonate (one μ- and one μ_6-) oxygen atoms as well as an oxo group. The carbonate groups (3μ- and one μ_6-) and the three "*syn*" μ-O^{2-} oxygen atoms lie on one side, and the terminal oxo, the three "*anti*" μ-OH^- and the remaining three "*anti*" μ-O^{2-} oxygen atoms on the other, such that the $[(Mo_2{}^VO_4)_3(CO_3{}^{2-})_4(OH)_3]^{5-}$ cluster takes the shape of an adorned crown. The three symmetry related (C_3 axis) H atoms, H(60), H(60A) and H(60B) hydrogen-bond to O(4′), O(4A′) and O(4B′) of an adjacent anion to give a centrosymmetric six-fold hydrogen bonded dimer (Fig. 3).

All the known molybdenum compounds, which contain the hexanuclear planar Mo_6-polyoxo unit, have been synthesized in acidic aqueous media[3,9,10] and hydrothermal techniques were most commonly used to prepare such compounds.[3,9] Thus, the preparation of **1** in alkaline aqueous medium represents the

DOI: 10.1039/b108430p

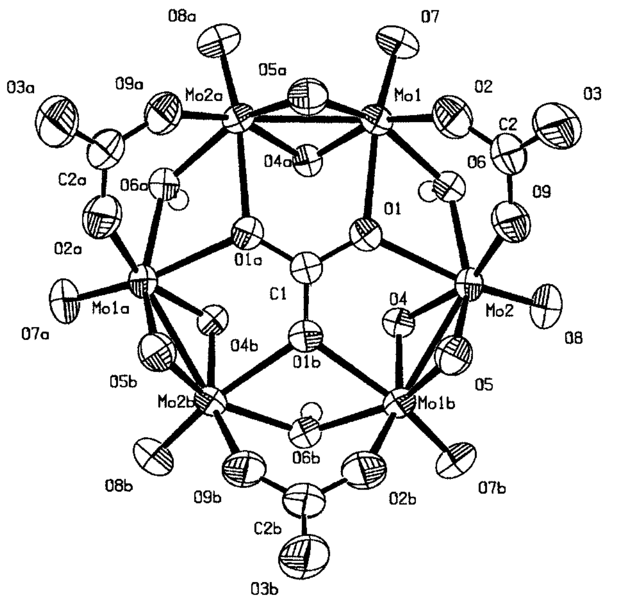

Fig. 2 ORTEP[11] plot of **1**. View down the three-fold axis in the $[(Mo_2{}^{V}O_4)_3(CO_3{}^{2-})_4(OH^-)_3]^{5-}$ anion. The ring of six edge-sharing $Mo^{V}O_6$ octahedra are bridged internally [C(1)] and externally [C(2), C(2A) and C(2B)] by carbonate anions. Displacement ellipsoids are plotted at 50% probability level. Averaged bond lengths (Å): Mo=O, 1.674(4); Mo–O(μ-O^{2-}), 1.948(4); Mo–O(μ-OH^-), 2.094(3); Mo–O(μ-$CO_3{}^{2-}$), 2.070(4); Mo–O(μ_6-$CO_3{}^{2-}$), 2.355(3); Mo(1)–Mo(2), 2.5884(6), Mo(1)–Mo(2B), 3.548(6); C–O(terminal), 1.212(8); C–O(μ-$CO_3{}^{2-}$), 1.301(6); C–O(μ_6-$CO_3{}^{2-}$), 1.284(4).

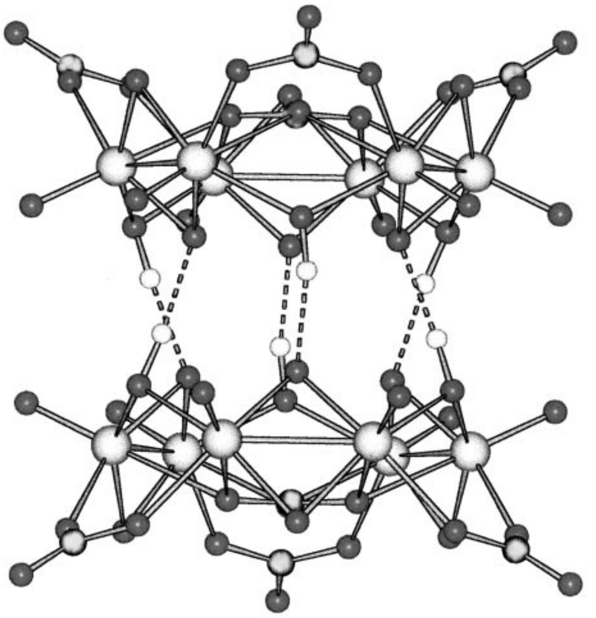

Fig. 3 Drawing of the $\{[(Mo_2{}^{V}O_4)_3(\mu_6\text{-}CO_3{}^{2-})(\mu\text{-}CO_3{}^{2-})_3(\mu\text{-}OH^-)_3]^{5-}\}_2$ dimer. Hydrogen bonds connecting the two anions are shown as broken lines. Mo, light grey; C, grey; O, dark grey; H, white.

first example of isolation of planar $(Mo_2{}^{V}O_4)_3$ polyoxo unit in such an environment and of course under very mild conditions.

Compound **1** is diamagnetic and EPR silent but NMR active. In D_2O solution, the ^{13}C NMR spectrum of **1** showed two major peaks at 160 and 165 ppm with a 1 : 3 intensity ratio, together with three minor resonances at 160.5, 164.5 and 165.5 ppm. The two major peaks were assigned to the μ_6- and μ-bridged carbonates respectively. The minor resonances are tentantively attributed to decomposition products. The ^{13}C NMR spectrum of **1** in D_2O containing eight equivalents of Na_2CO_3 showed that none of the three minor resonances were due to the free carbonate anion and in addition their intensity was substantially reduced compared to the intensity of the two major peaks.

In conclusion, we have prepared, under mild conditions, the first polyoxomolybdenum carbonate compound, by simply mixing $Mo^{V}Cl_5$ with NH_4HCO_3. In marked contrast to all planar $Mo_6{}^{V}$ oxometalates, which were prepared in acidic aqueous solutions, compound **1** was isolated in aqueous alkaline solution. The preparation of **1** further emphasises the great ability of the seemingly pedestrian carbonate anion to act as a template in the self-assembly of metal–anionic aggregates. Efforts to synthesize and characterize various polyoxo-metal carbonate compounds are in progress.

Acknowledgements

We thank Mrs F. Masala for typing this manuscript as well as Dr V. Tangoulis, Dr L. Lalioti and Assistant Professor S. Skoulika for helpful discussions.

Notes and references

‡ Crystal data for **1**: $(NH_4)_5[(Mo_2{}^{V}O_4)_3(CO_3{}^{2-})_4(OH^-)_3]\cdot 0.5CH_3OH$: $C_{4.5}H_{25}Mo_6N_5O_{27.5}$, M_r = 1164.94, rhombohedral, space, $R\bar{3}$, a = 21.9946(4), c = 12.4171(4) Å, V = 5202.1(2) Å^3, Z = 6, ρ_{calc} = 2.231 g cm^{-3}, T = 293(2) K. Of the 7650 reflections collected, 1654 symmetry-independent reflections were used to solve the structure. Based on all these data and 142 refined parameters $R1$ = 0.0560 (all data), $wR2$ = 0.1831, and goodness-of-fit on F^2 is 1.059. Data were collected on a Siemens SMART system. A crystal of dimensions 0.10 × 0.10 × 0.10 mm^3 was sealed in a glass capillary with the mother liquor to avoid decomposition. CCDC reference number 171184. See http://www.rsc.org/suppdata/dt/b1/b108430p/ for crystallographic data in CIF or other electronic format.

1 (*a*) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, New York, 1983; (*b*) M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34; (*c*) M. T. Pope and A. Müller, eds., *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1994 .

2 A. Müller, F. Peters, M. T. Pope and D. Gatteschi, *Chem. Rev.*, 1998, **98**, 239.

3 (*a*) R. C. Haushalter and F. W. Lai, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 743; (*b*) R. C. Haushalter and F. W. Lai, *Inorg. Chem.*, 1989, **28**, 2905; (*c*) P. Lightfoot and D. Masson, *Acta Crystallogr., Sect. C*, 1996, **52**, 1077; (*d*) L. M. Mundi and R. C. Haushalter, *Inorg. Chem.*, 1992, **31**, 3050.

4 (*a*) G. Huan, M. A. Greaney and A. J. Jakobson, *J. Chem. Soc., Chem. Commun.*, 1991, 260; (*b*) K.-F. Hsu and S.-L. Wang, *Inorg. Chem.*, 1997, **36**, 3049; (*c*) S.-L. Wang, K.-F. Hsu and Y.-P. Nieh, *J. Chem. Soc., Dalton. Trans.*, 1994, 1681.

5 P. Gouzerh and A. Proust, *Chem. Rev.*, 1998, **98**, 77 and references therein.

6 (*a*) D. A. Palmer and R. Van Eldik, *Chem. Rev.*, 1983, **83**, 651; (*b*) N. Kitajima, S. Hikichi, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.*, 1993, **115**, 5496; (*c*) G. A. Van Albada, I. Mutikainan, O. S. Roubeau, U. Turpeinen and J. Reedijk, *Eur. J. Inorg. Chem.*, 2000, 2179.

7 (*a*) G. Herzeberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand-Reinhold, New York, 1945, p. 178; (*b*) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., Wiley, New York, 1978, p. 252.

8 (*a*) A. Müller, P. Kögeler and C. Kuhlman, *Chem. Commun.*, 1999, 1347; (*b*) A. Müller, H. Bögge and P. Kögeler, *Struct. Bonding (Berlin)*, 2000, **96**, 203; (*c*) A. Müller, C. Kuhlmann, H. Bögge, M. Schmidtmann, M. Baumann and E. Krickenmeyer, *Eur. J. Inorg. Chem.*, 2001, 2271.

9 (*a*) M. I. Khan, Q. Chen and J. Zubieta, *Inorg. Chim. Acta*, 1993, **206**, 131; (*b*) G. Cao, R. C. Haushalter and K. G. Strohmaier, *Inorg. Chem.*, 1993, **32**, 127.

10 (*a*) C. Livage, E. Dumas, C. Marchal-Roch and G. Herve, *C. R. Acad. Sci., Ser. IIc: Chim.*, 2000, **3**, 95; (*b*) E. Cadot, A. Dolbecq, B. Salignac and F. Secheresse, *Chem. Eur. J.*, 1999, **5**, 2396; (*c*) E. Dumas, C. Livage, D. Riou and G. Hervé, *Eur. J. Solid State Inorg. Chem.*, 1997, **34**, 151.

11 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976 .