Acta Cryst. (1991). C**47**, 306–308

Structure of *cis*-Aquadioxo[2-(α-oxidobenzylidenehydrazonomethyl)-phenolate]molybdenum(IV)

BY H. SUR

Department of Physics, B. N. Mahavidyalaya, Itachuna, Hooghly – 712 147, *West Bengal, India*

R. GHOSH

Department of Physics, University College of Science, 92, *Acharya Prafulla Chandra Road,*
Calcutta – 700009, *India*

AND S. ROYCHOWDHURI AND S. SETH*

Department of Physics, X-ray Laboratory, Presidency College, College Street, Calcutta 700 073,
West Bengal, India

(*Received* 26 *September* 1989; *accepted* 2 *July* 1990)

Abstract. [Mo(O)$_2$(C$_{14}$H$_{10}$N$_2$O$_2$)(H$_2$O)], $M_r = 384{\cdot}2$, monoclinic, $P2_1/n$, $a = 10{\cdot}457$ (3), $b = 9{\cdot}704$ (3), $c = 14{\cdot}844$ (3) Å, $\beta = 105{\cdot}00$ (2)°, $V = 1455{\cdot}0$ (7) Å^3, $D_m = 1{\cdot}78$ (by flotation in bromoform/xylene), $D_x = 1{\cdot}75$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·90 mm^{-1}, $Z = 4$, λ(Mo $K\alpha$) = 0·71069 Å, $F(000) = 768$, $T = 294$ K, final $R = 0{\cdot}033$ and $wR = 0{\cdot}038$ for 2408 independent reflections with $I \geq 2\sigma(I)$. In the complex the metal is surrounded by five O atoms and one azo N atom in a distorted octahedron. The donor atoms of the terdentate O$_2$N-donor ligand are meridional with the O atoms *trans* [O(2)—Mo—O(4) = 150·2 (1)°]. The azo N atom and the O atom of the water molecule are *cis* [N(1)—Mo—O(5) = 77·0 (1)°].

Introduction. Recently, Dutta & Pal (1983) synthesized the title compound. Its crystal structure had been determined to establish the metal coordination and the nature of the bonding.

Table 1. *Final fractional atomic coordinates* ($\times 10^4$, $\times 10^5$ *for* Mo) *and equivalent values of the anisotropic temperature-factor coefficients* (Å$^2 \times 10^4$) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mo	118653 (3)	18724 (3)	19991 (2)	264 (1)
O(1)	13085 (3)	1225 (4)	2892 (2)	423 (10)
O(2)	10447 (3)	491 (3)	2039 (2)	334 (8)
O(3)	11180 (3)	3186 (3)	2465 (2)	426 (10)
O(4)	12850 (3)	2893 (3)	1312 (2)	369 (10)
O(5)	12478 (3)	32 (3)	1185 (2)	377 (10)
N(1)	10319 (3)	1923 (3)	616 (2)	228 (8)
N(2)	9229 (3)	1043 (3)	536 (2)	252 (9)
C(1)	13449 (4)	4801 (4)	533 (3)	393 (15)
C(2)	13177 (5)	5723 (4)	−198 (3)	411 (17)
C(3)	11970 (5)	5676 (5)	−877 (3)	403 (14)
C(4)	11048 (4)	4687 (4)	−829 (3)	339 (14)
C(5)	11293 (4)	3740 (4)	−92 (2)	250 (11)
C(6)	12522 (4)	3798 (4)	595 (3)	295 (12)
C(7)	10262 (4)	2755 (4)	−75 (2)	259 (11)
C(8)	9384 (4)	368 (4)	1325 (2)	252 (11)
C(9)	8376 (4)	−611 (4)	1456 (3)	303 (12)
C(10)	7063 (4)	−509 (5)	940 (3)	423 (14)
C(11)	6125 (5)	−1448 (7)	1071 (4)	610 (20)
C(12)	6519 (6)	−2510 (6)	1710 (4)	604 (22)
C(13)	7805 (6)	−2611 (5)	2211 (4)	520 (18)
C(14)	8751 (5)	−1674 (4)	2105 (3)	387 (15)

Experimental. The title compound was synthesized from the reaction of bis(acetylacetonato)(*cis*-dioxo)-molybdenum(VI) with salicylidenebenzoylhydrazine. Thin plate-shaped orange-yellow crystals obtained by slow evaporation of a solution in a mixture of acetone and alcohol at room temperature. Approximate lattice constants from rotation and Weissenberg photographs, accurate values by least-squares treatment of 25 randomly chosen reflections with $11{\cdot}5 < \theta < 12{\cdot}5°$, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Crystal *ca* 0·3 × 0·1 × 0·3 mm; intensity measurements for reflections with $4{\cdot}0 \leq 2\theta \leq 52{\cdot}0°$, index range $-13 \leq h \leq 12$, $0 \leq k \leq 12$, $0 \leq l \leq 19$, ω–2θ scans; three standard reflections monitored periodically did not vary significantly during data collection; 3362 independent reflections were recorded, 2408 [$I \geq 2\sigma(I)$] employed for the structure determination. Lorentz–polarization correction but no absorption correction; approximate position of the Mo atom from unsharpened three-dimensional Patterson map, positions of remaining non-H atoms from successive weighted Fourier syntheses. Full-matrix least-squares refinement, anisotropic thermal parameters for C, N, O and Mo atoms; H atoms

---

* To whom correspondence should be addressed.

0108-2701/91/020306-03$03.00

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°) *involving non*-H *atoms with e.s.d.'s in parentheses*

Mo—O(1)	1·704 (3)	Mo—O(4)	1·904 (3)
Mo—O(2)	2·011 (3)	Mo—O(5)	2·337 (3)
Mo—O(3)	1·695 (3)	Mo—N(1)	2·261 (3)
O(2)—C(8)	1·328 (4)	O(4)—C(6)	1·354 (5)
N(1)—N(2)	1·404 (4)	N(1)—C(7)	1·295 (5)
N(2)—C(8)	1·315 (4)	C(1)—C(2)	1·378 (6)
C(1)—C(6)	1·393 (6)	C(2)—C(3)	1·397 (6)
C(3)—C(4)	1·375 (7)	C(4)—C(5)	1·401 (5)
C(5)—C(6)	1·420 (5)	C(5)—C(7)	1·446 (6)
C(8)—C(9)	1·469 (6)	C(9)—C(10)	1·392 (5)
C(9)—C(14)	1·397 (6)	C(10)—C(11)	1·389 (8)
C(11)—C(12)	1·389 (8)	C(12)—C(13)	1·361 (8)
C(13)—C(14)	1·382 (8)		
O(5)—Mo—N(1)	77·0 (1)	O(4)—Mo—N(1)	82·0 (1)
O(4)—Mo—O(5)	82·1 (1)	O(3)—Mo—N(1)	94·3 (1)
O(3)—Mo—O(5)	170·8 (1)	O(3)—Mo—O(4)	99·9 (1)
O(2)—Mo—N(1)	71·5 (1)	O(2)—Mo—O(5)	79·0 (1)
O(2)—Mo—O(4)	150·2 (1)	O(2)—Mo—O(3)	95·5 (2)
O(1)—Mo—N(1)	158·4 (2)	O(1)—Mo—O(5)	82·6 (1)
O(1)—Mo—O(4)	102·0 (2)	O(1)—Mo—O(2)	98·1 (2)
O(1)—Mo—O(3)	105·7 (2)		
N(2)—N(1)—C(7)	116·3 (3)	N(1)—N(2)—C(8)	108·5 (3)
C(2)—C(1)—C(6)	120·0 (4)	C(1)—C(2)—C(3)	120·7 (4)
C(2)—C(3)—C(4)	120·0 (4)	C(3)—C(4)—C(5)	120·6 (4)
C(4)—C(5)—C(7)	117·4 (3)	C(4)—C(5)—C(6)	118·9 (4)
C(6)—C(5)—C(7)	123·6 (3)	C(1)—C(6)—C(5)	119·7 (4)
O(4)—C(6)—C(5)	122·5 (4)	O(4)—C(6)—C(1)	117·8 (4)
N(1)—C(7)—C(5)	123·0 (3)	O(2)—C(8)—N(2)	123·4 (4)
N(2)—C(8)—C(9)	120·9 (3)	O(2)—C(8)—C(9)	115·7 (3)
C(8)—C(9)—C(14)	119·1 (4)	C(8)—C(9)—C(10)	121·4 (4)
C(10)—C(9)—C(14)	119·5 (4)	C(9)—C(10)—C(11)	120·5 (4)
C(10)—C(11)—C(12)	119·1 (5)	C(11)—C(12)—C(13)	120·2 (5)
C(12)—C(13)—C(14)	121·7 (5)	C(9)—C(14)—C(13)	118·9 (4)

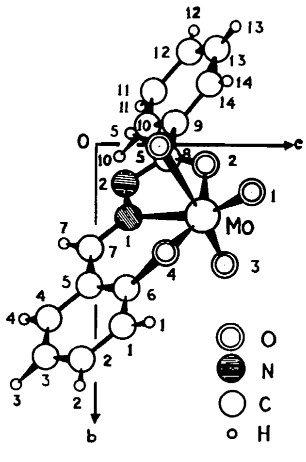

Fig. 1. View of the molecule projected onto the (100) plane showing the atom-numbering scheme.

(excluding one water H atom) included from difference Fourier map and kept fixed during the refinement; each H atom given the isotropic temperature factor of its associated non-H atom. Refinement discontinued when all parameter shifts < σ. Final $R = 0{\cdot}033$ and $wR = 0{\cdot}038$ for 2408 reflections only; function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = [1/\sigma(F_o)]^2$ (from counting statistics). No correction for secondary extinction as $|F_o| - |F_c|$ values for strong low-order reflections were randomly positive and negative. One water H atom could not be located and was not included in the final structure-factor calculation. Final difference map was featureless, with function values between 0·3 and $-0{\cdot}4$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 72–80, 149–150). Structure solution, refinement and geometry calculations were all performed with the *SHELX* system of programs (Sheldrick, 1976) at Calcutta.

Discussion. The final atomic coordinates are given in Table 1* and bond lengths and angles in Table 2. The asymmetric unit, consisting of one molecule, is shown in Fig. 1.

The Mo atom has distorted octahedral coordination: O(2), O(4) and N(1) donor atoms of the terdentate ligand occupy meridional sites [O(2)—Mo—O(4) = 150·2 (1)°] and N(1) is *cis* to the O atom of the water molecule [N(1)—Mo—O(5) = 77·0 (1)°]. The Mo—N distance [2·261 (3) Å] is normal (for a recent review of such distances see Bart & Ragaini, 1980) and, in particular, is similar to values of 2·237–2·272 Å found in the complex [Mo_2(L-histidine)$_2$-O_2S_2].$1\frac{1}{2}H_2O$ (Spivack & Dori, 1975). The Mo—O(2) and Mo—O(4) distances are 2·011 (3) and 1·904 (3) Å; the relative shortness of these bonds could be due to constraints involved in chelate ring

---

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, torsion angles and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53360 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

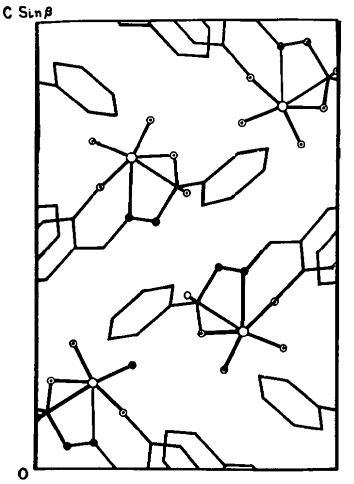

Fig. 2. Molecular packing viewed down **a**. H atoms have been omitted for clarity.

formation. The Mo—O(water) distance, for example, is appreciably longer at 2·337 (3) Å. The distances between the Mo and the terminal O atoms [1·704 (3) and 1·695 (3) Å] are in good agreement with those in bis(μ-ethoxycarbonylimido)-bis[(η-cyclopentadienyl)oxomolybdenum] and μ-ethoxycarbonylimido-μ-oxo-bis[(η-cyclopentadienyl)oxomolybdenum] (Korswagen, Weidenhammer & Ziegler, 1979) and show that the bonds have at least partial double-bond character.

The atoms of the five-membered chelate ring are coplanar within 0·030 (4) Å whereas those of the six-membered ring deviate more appreciably from planarity [maximum displacement 0·235 (3) Å for O(4)]. The angle between these two planes is 7·2 (1)°. The bite angles of the five- and six-membered chelate rings differ significantly, introducing a considerable distortion into the octahedron. The other two six-membered rings are planar to within ±0·01 Å and are almost parallel to each other [dihedral angle 13·9 (1)°].

The N—N distance [1·403 (4) Å] is intermediate between single- and double-bond lengths indicating that the azo group is involved in resonance. The C—N bond lengths [1·295 (5) and 1·315 (4) Å] and C(8)—C(9) length [1·469 (6) Å] also suggest delocalization. The strained structure of the rings resulting from the steric conditions for complex formation, evident from some distorted angles, may influence both the resonance and the bond lengths.

Fig. 2 shows the contents of the unit cell projected on the (100) plane. The closest intermolecular non-H atom contact is O(1)···C(4) ($x+\frac{1}{2}$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$), 3·308 (5) Å. The shortest intermolecular O···H distance [O(1)···H(4) ($x+\frac{1}{2}$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$), 2·304 (3) Å] is too long to be considered a hydrogen-bonding interaction (Hamilton & Ibers, 1968). The packing of the molecules is thus determined by van der Waals forces. The molecules are packed in layers, but are displaced with respect to one another to relieve short intermolecular contacts, so that packing forces are unlikely to influence the geometry of the molecule to any appreciable extent.

The authors thank Dr William L. Duax, IUCr CSM Secretary, and Dr I. D. Brown, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada, for the collection of diffractometer data and Dr P. Roychowdhury, Science College, and Dr S. Chakraborty, Burdwan University, for their valuable suggestions. Thanks are also due to Professor R. L. Dutta, Department of Chemsitry, University of Burdwan, for providing the sample. Financial assistance from the University Grants Commission, New Delhi, is gratefully acknowledged.

References

Bart, J. C. J. & Ragaini, V. (1980). *Acta Cryst.* **B36**, 1351–1354.
Dutta, R. L. & Pal, A. K. (1983). *Indian J. Chem.* **22A**, 871–874.
Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids*, p. 16. New York: Benjamin.
Korswagen, R., Weidenhammer, K. & Ziegler, M. L. (1979). *Acta Cryst.* **B35**, 2554–2558.
Sheldrick, B. (1976). *Acta Cryst.* **B32**, 2884–2886.
Spivack, B. & Dori, Z. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1977–1980.

Acta Cryst. (1991). C**47**, 308–310

Structure of Aquacarbonato(di-2-pyridylamine)copper(II) Dihydrate

Pervaiz Akhter, Paul Fitzsimmons and Brian Hathaway*
Chemistry Department, University College, Cork, Ireland

(*Received* 26 *September* 1989; *accepted* 2 *July* 1990)

Abstract. (I) $[Cu(CO_3)(H_2O)(C_{10}H_9N_3)].2H_2O$, M_r = 348·79, monoclinic, $P2_1/c$, $Z = 4$, $a = 9{\cdot}345$ (3), $b = 20{\cdot}158$ (5), $c = 7{\cdot}812$ (2) Å, $\beta = 107{\cdot}27$ (4)°, $V = 1405{\cdot}25$ Å^3, D_m(flotation) = 1·66 (5), D_x = 1·648 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 153·7 mm^{-1}, $T = 298$ K, $F(000) = 716$. $R = 0{\cdot}044$ for 1898 unique reflections. The CuN_2O_2O' chromophore involves a distorted square based pyramidal structure, with nearly symmetrically bonded bidentate di-2-pyridylamine (dpyam) and carbonate groups, in the basal plane, from which the Cu atom is displaced 0·328 (4) Å towards the apical O(4) atom [Cu—O(4) = 2·202 (3) Å]. The dpyam ligand has a bite angle of 92·2 (1)° at the Cu atom and the $[CO_3]^{2-}$ anion one of 66·5 (1)°. The dihedral angle between the mean planes of the dpyam and the carbonate ligands is 50·3°.

Introduction. From a preparative solution, methanol/water, containing $Cu(NO_3)_2.3H_2O$, KPF_6, $NaHCO_3$

---

* To whom correspondence should be addressed.