C(43′)	0.5465 (8)	0.1457 (2)	0.8019 (4)	0.075 (2)
C(44′)	0.4521 (9)	0.1331 (2)	0.7866 (6)	0.089 (3)
C(45′)	0.3912 (7)	0.1296 (2)	0.7134 (6)	0.078 (3)
C(46′)	0.4283 (5)	0.1397 (2)	0.6542 (4)	0.057 (2)
O(1)	1.0282 (3)	0.15141 (12)	0.5952 (2)	0.0491 (10)
O(2)	0.5147 (3)	0.20571 (12)	0.3999 (2)	0.0422 (9)
O(3)	0.7714 (2)	0.17983 (10)	0.4984 (2)	0.0317 (8)
O(4)	0.3430 (7)	0.1593 (3)	0.3842 (10)	0.271 (8)
O(5)	1	0	1	0.17 (3)
O(6)	0.892 (3)	0.0365 (12)	0.936 (2)	0.23 (2)
C	1.147 (3)	0.0236 (12)	0.773 (2)	0.26 (2)
Cl(1)	1.130 (2)	0.0779 (9)	0.7659 (15)	0.487 (14)
Cl(2)	1.250 (2)	0.0233 (9)	0.849 (2)	0.52 (2)

Table 2. *Selected geometric parameters (Å, °)*

Mo(1)—O(1)	1.701 (4)	Mo(2)—O(2)	1.707 (4)
Mo(1)—O(3)	1.947 (3)	Mo(2)—O(3)	1.925 (3)
Mo(1)—N(1)	2.104 (4)	Mo(2)—N(1′)	2.103 (4)
Mo(1)—N(2)	2.095 (4)	Mo(2)—N(2′)	2.090 (4)
Mo(1)—N(3)	2.090 (4)	Mo(2)—N(3′)	2.093 (4)
Mo(1)—N(4)	2.095 (4)	Mo(2)—N(4′)	2.102 (4)
O(1)—Mo(1)—O(3)	176.2 (2)	O(2)—Mo(2)—N(1′)	91.6 (2)
O(1)—Mo(1)—N(1)	91.3 (2)	O(2)—Mo(2)—N(2′)	93.4 (2)
O(1)—Mo(1)—N(2)	93.2 (2)	O(2)—Mo(2)—N(3′)	94.1 (2)
O(1)—Mo(1)—N(3)	94.3 (2)	O(2)—Mo(2)—N(4′)	90.0 (2)
O(1)—Mo(1)—N(4)	90.9 (2)	O(3)—Mo(2)—N(1′)	86.1 (2)
O(3)—Mo(1)—N(1)	86.4 (2)	O(3)—Mo(2)—N(2′)	87.9 (2)
O(3)—Mo(1)—N(2)	89.8 (2)	O(3)—Mo(2)—N(3′)	88.1 (2)
O(3)—Mo(1)—N(3)	87.9 (2)	O(3)—Mo(2)—N(4′)	88.62 (15)
O(3)—Mo(1)—N(4)	86.1 (2)	N(1′)—Mo(2)—N(2′)	90.2 (2)
N(1)—Mo(1)—N(2)	90.1 (2)	N(1′)—Mo(2)—N(3′)	174.2 (2)
N(1)—Mo(1)—N(3)	174.3 (2)	N(1′)—Mo(2)—N(4′)	89.7 (2)
N(1)—Mo(1)—N(4)	89.9 (2)	N(2′)—Mo(2)—N(3′)	89.9 (2)
N(2)—Mo(1)—N(3)	89.1 (2)	N(2′)—Mo(2)—N(4′)	176.5 (2)
N(2)—Mo(1)—N(4)	175.9 (2)	N(3′)—Mo(2)—N(4′)	89.8 (2)
N(3)—Mo(1)—N(4)	90.4 (2)	Mo(1)—O(3)—Mo(2)	178.5 (2)
O(2)—Mo(2)—O(3)	177.4 (2)		

The intensity data were collected at room temperature because of increased reflection breadth at lower temperature. The room temperature data hampered refinement of the diffuse solvent molecules. One water molecule (assigned occupancy 1.0) was within hydrogen-bonding distance (2.8 Å) of the terminal oxo atom O(2) of the dimer. A second water site contained two positions [O(5) and O(6)] 2.0 Å apart that were constrained to have total occupancy of 1.0 (actual total occupancy was 0.5). A third solvent site was partially occupied with one half molecule of CH_2Cl_2. Cell determination and intensity-data collection were performed on an Enraf–Nonius FAST area-detector diffractometer with an Mo rotating-anode source. Our detailed methods and procedures for small-molecule X-ray data collection with the FAST system have been described previously (Scheidt & Turowska-Tyrk, 1994). All reflections were used in least-squares refinement, including negative intensities.

Data collection: *MADNES* (Messerschmitt & Pflugrath, 1987). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

We thank the National Institutes of Health for support of this research under grant GM-38401. Funds for the purchase of the FAST area-detector diffractometer were provided through NIH grant RR-06709. BC also thanks the J. Peter Grace Prize Fellowship through the University of Notre Dame.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1173). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Johnson, J. F. & Scheidt, W. R. (1978). *Inorg. Chem.* **17**, 1280–1287.

Kim, K., Sparapany, J. W. & Ibers, J. A. (1987). *Acta Cryst.* C**43**, 2076–2078.

Ledon, H. J., Bonnet, M. C., Brigandat, Y. & Varescon, F. (1980). *Inorg. Chem.* **19**, 3488–3491.

Messerschmitt, A. & Pflugrath, J. W. (1987). *J. Appl. Cryst.* **20**, 306–315.

Scheidt, W. R. & Turowska-Tyrk, I. (1994). *Inorg. Chem.* **33**, 1314–1318.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1996). C**52**, 835–838

A Trinuclear Cluster of Molybdenum(IV), $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(HC_2O_4)_2(C_2O_4)(H_2O)_3$

F. A. Cotton,[a] Lee M. Daniels,[a] Maoyu Shang,[a] Rosa Llusar[b] and Willi Schwotzer[a]

[a]*Department of Chemistry, Mail Stop 3255, Texas A&M University, College Station, TX 77843, USA, and* [b]*Department of Experimental Sciences, Universitat Jaume I, PO Box 242, Castelló, Spain. E-mail: cotton@tamu.edu*

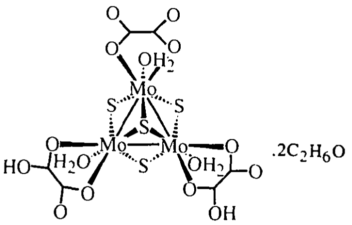
(Received 25 April 1995; accepted 9 October 1995)

Abstract

The three molybdenum centers in triaqua-$1\kappa O$;$2\kappa O$;$3\kappa O$-bis[oxalato(1−)]-$2\kappa^2O,O''$;$3\kappa^2O,O''$-oxalato(2−)-$1\kappa^2O,O''$-μ_3-thio-tri-μ-thio-$1{:}2\kappa^2S$;$1{:}3\kappa^2S$;$2{:}3\kappa^2S$-*triangulo*-trimolybdenum diethanol solvate, $[Mo_3S_4(C_2HO_4)_2(C_2O_4)(H_2O)_3].2C_2H_6O$, form an equilateral triangle with an average Mo—Mo distance of 2.736 (4) Å. Each Mo atom is in a distorted octahedral environment made up of two O atoms of an oxalate ligand, one O atom of a water molecule, one capping-sulfur and two bridging-sulfur ligands. The structure is further stabilized by intermolecular hydrogen bonding between the oxalate and water ligands.

Comment

The $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(HC_2O_4)_2(C_2O_4)(H_2O)_3.2C_2H_5OH$ {triaquabis[oxalato(1−)][oxalato(2−)]-μ_3-thio-tri-μ-thio-*triangulo*-trimolybdenum diethanol solvate, (I)} trinuclear cluster has been structurally characterized as part of a systematic structural study of trinuclear cluster species of molybdenum and tungsten.



(I)

From a structural point of view these compounds have been classified into three categories according to the presence of zero, one or two capping ligands (μ_3-type). The title compound belongs to the second structural type (M_3X_{13}) with one capping ligand. A simplified description of the bonding in the M_3X_{13} cluster (Bursten, Cotton, Hall & Najjar, 1982) indicated three bonding molecular orbitals ($1a_1$, $1e$), one essentially non-bonding ($2a_1$) and five antibonding ($2e$, $3e$, $1a_2$). This implies that these clusters can accommodate six metal–metal bonding electrons. In addition, one or two electrons can enter the $2a_1$ molecular orbital that has little, if any, metal–metal antibonding character.

The Mo_3S_4 units consist of an equilateral triangle of Mo atoms [mean Mo—Mo distance = 2.736 (4) Å] ligated by a triply bridging S atom [mean Mo—μ_3-S distance = 2.322 (1) Å] and three S atoms that bridge pairs of Mo atoms [mean Mo—μ_2-S distance = 2.280 (8) Å]. Ignoring the metal–metal bonds, the coordination sphere around each Mo atom is a slightly distorted octahedron. The outer coordination positions on each Mo atom are occupied by two O atoms of the chelating oxalate (or hydrogen oxalate) ligand [mean Mo—O distance = 2.14 (1) Å] and one O atom of a water molecule [mean Mo—O distance = 2.20 (2) Å]. The water molecules occupy the position *trans* to the μ_3-S atom.

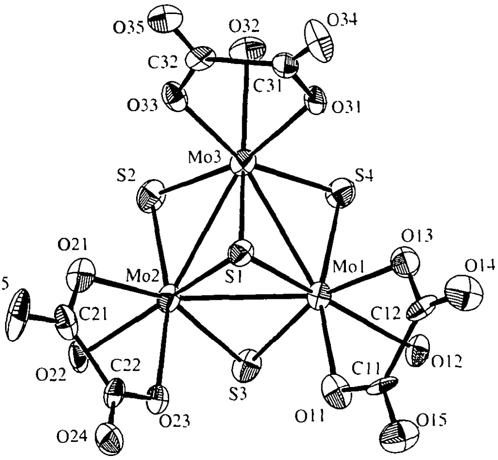


Fig. 1. *ORTEPII* (Johnson, 1971) view of the molecule with atom-numbering scheme. Atoms are represented by anisotropic displacement ellipsoids at the 40% level.

Two interstitial molecules of ethanol are clearly present, but the interatomic distances and displacement parameters for these moieties are not precise enough to allow distinction of the CH_3 end from the OH end. Each terminal atom was therefore modeled as a mixture of C and O, and the ratio allowed to refine. The position occupied by O40/C40 refined to 53 (7)% oxygen (and the other end, O42/C42, to the complementary value). For the other ethanol molecule, O50/C50 refined to 26 (8)% oxygen. The only H atoms included in the entire model were those used in calculated positions on the methylene C atoms of the ethanol molecules.

The Mo—Mo distances are consistent with the presence of Mo—Mo single bonds and an oxidation state of four for the three metal atoms. According to Cotton's molecular-orbital scheme (Cotton, 1964) for such trinuclear clusters, six *d* electrons occupy the bonding molecular orbitals $(1a_1)^2(1e)^4$. The oxidation states thus suggest that two of the three chelating ligands are hydrogen oxalate ligands, and one is a fully deprotonated oxalate ligand. Since the reaction occurred in an acidic environment (oxalic acid), the retention of some of the protons in the ligated oxalates is a reasonable assumption. No residual Fourier peaks that might be interpreted as H atoms were discernible and the regularity of the C—O distances in the ligands also gives no clues about the location of the H atoms. However, the hydrogen-bond scheme clearly indicates the locations of the oxalate H atoms. As shown in the list of hydrogen-bond contacts below, there are eight hydrogen bonds: six involve the protons from the three water ligand molecules. Analysis of this scheme reveals that the other two H atoms must be bonded to O15 and O25. The ethanol molecules have no close intermolecular contacts with the clusters that might indicate additional hydrogen bonds. Hydrogen bonding contacts: $O12\cdots O35^{i}$ 2.79 (1), $O12\cdots O14^{ii}$ 2.86 (1), $O12\cdots O15^{ii}$ 2.89 (1), $O22\cdots O25^{iii}$ 2.90 (1), $O22\cdots O24^{ii}$ 2.72 (1), $O22\cdots O25^{ii}$ 2.70 (1), $O32\cdots O15^{iv}$ 2.66 (1), $O32\cdots O34^{ii}$ 2.68 (1) Å [symmetry codes: (i) $x, 1-y, \frac{1}{2}+z$; (ii) $x, y-1, z$; (iii) $-x, 1-y, -z$; (iv) $x, 1-y, \frac{1}{2}-z$].

The caesium salt of the (deprotonated) dianion of this molecule is known, and its structure has been reported (Cotton, Dori, Llusar & Schwotzer, 1985).

Experimental

The compound was prepared by reacting $(NH_4)_2Mo_3S_{12}.2H_2O$ with a large excess of oxalic acid under reflux conditions.

Details of the preparation and spectroscopic characterization have been described elsewhere (Cotton, Llusar, Marler, Schwotzer & Dori, 1985). Crystals were obtained by slow evaporation of ethanol/water solutions.

Crystal data

$[Mo_3S_4(C_2HO_4)_2(C_2O_4)(H_2O)_3].2C_2H_6O$
$M_r = 828.32$
Monoclinic
$P2/c$
$a = 19.403\ (5)$ Å
$b = 6.555\ (1)$ Å
$c = 19.512\ (6)$ Å
$\beta = 97.38\ (2)°$
$V = 2461\ (1)$ Å^3
$Z = 4$
$D_x = 2.236$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6.0–11.5°$
$\mu = 1.919$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.2 × 0.2 × 0.1 mm
Dark brown

Data collection

Syntex $P3$ equivalent diffractometer
$2\theta/\omega$ scans
Absorption correction: none
3294 measured reflections
3194 independent reflections
1712 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0743$
$\theta_{\rm max} = 22.5°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 7$
$l = -20 \rightarrow 20$
3 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0514$
$wR(F^2) = 0.0931$
$S = 1.096$
3190 reflections
309 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.011$
$\Delta\rho_{\rm max} = 0.8\ (1)$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.7\ (1)$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	Occupancy	x	y	z	$U_{\rm eq}$
Mo1	1.00	0.28279 (5)	0.3287 (2)	0.17576 (5)	0.0226 (3)
Mo2	1.00	0.15388 (5)	0.3210 (2)	0.09954 (5)	0.0234 (3)
Mo3	1.00	0.27097 (5)	0.3084 (2)	0.03494 (5)	0.0244 (3)
S1	1.00	0.2360 (2)	0.5785 (5)	0.09911 (15)	0.0237 (8)
S2	1.00	0.1772 (2)	0.0994 (5)	0.0153 (2)	0.0308 (9)
S3	1.00	0.1921 (2)	0.1233 (5)	0.1940 (2)	0.0287 (9)
S4	1.00	0.3396 (2)	0.1103 (5)	0.1116 (2)	0.0301 (9)
O11	1.00	0.2621 (4)	0.5355 (13)	0.2544 (4)	0.029 (2)
O12	1.00	0.3437 (3)	0.1941 (13)	0.2696 (3)	0.024 (2)
O13	1.00	0.3711 (4)	0.5360 (14)	0.1919 (4)	0.033 (2)
O14	1.00	0.4115 (4)	0.8220 (15)	0.2413 (4)	0.040 (2)
O15	1.00	0.3001 (4)	0.8030 (15)	0.3173 (4)	0.041 (2)
O21	1.00	0.0896 (4)	0.5171 (12)	0.0335 (4)	0.027 (2)
O22	1.00	0.0522 (3)	0.1782 (13)	0.0985 (4)	0.026 (2)
O23	1.00	0.1062 (4)	0.5227 (14)	0.1671 (4)	0.030 (2)
O24	1.00	0.0519 (4)	0.8195 (15)	0.1682 (4)	0.034 (2)
O25	1.00	0.0232 (4)	0.7933 (14)	0.0273 (4)	0.047 (3)
O31	1.00	0.3587 (4)	0.5090 (13)	0.0223 (4)	0.025 (2)
O32	1.00	0.3177 (4)	0.1502 (13)	−0.0461 (4)	0.035 (2)
O33	1.00	0.2405 (4)	0.4913 (12)	−0.0534 (4)	0.026 (2)
O34	1.00	0.3878 (4)	0.7991 (16)	−0.0251 (5)	0.042 (2)
O35	1.00	0.2657 (4)	0.7469 (12)	−0.1213 (4)	0.033 (2)
C11	1.00	0.3045 (6)	0.674 (2)	0.2719 (5)	0.024 (3)
C12	1.00	0.3687 (6)	0.688 (2)	0.2331 (6)	0.027 (3)
C21	1.00	0.0601 (6)	0.670 (2)	0.0594 (6)	0.028 (3)
C22	1.00	0.0734 (6)	0.672 (2)	0.1381 (6)	0.028 (3)
C31	1.00	0.3488 (6)	0.656 (3)	−0.0221 (6)	0.032 (3)
C32	1.00	0.2791 (6)	0.6365 (18)	−0.0711 (6)	0.024 (3)
O40	0.47 (7)	0.5189 (8)	0.112 (3)	0.5929 (8)	0.122 (10)
C40	0.53 (7)	0.5189 (8)	0.112 (3)	0.5929 (8)	0.122 (10)
C41	1.00	0.4783 (5)	0.285 (2)	0.6170 (6)	0.021 (3)
O42	0.53 (7)	0.5116 (9)	0.489 (3)	0.6205 (9)	0.119 (9)
C42	0.47 (7)	0.5116 (9)	0.489 (3)	0.6205 (9)	0.119 (9)
O50	0.26 (8)	0.8783 (8)	0.276 (3)	0.6655 (7)	0.093 (9)
C50	0.74 (8)	0.8783 (8)	0.276 (3)	0.6655 (7)	0.093 (9)
C51	1.00	0.8666 (6)	0.495 (2)	0.6859 (6)	0.027 (4)
O52	0.74 (8)	0.9155 (9)	0.644 (4)	0.6632 (9)	0.173 (11)
C52	0.26 (8)	0.9155 (9)	0.644 (4)	0.6632 (9)	0.173 (11)

Table 2. *Selected geometric parameters* (Å, °)

Mo1—Mo2	2.741 (2)	Mo2—S3	2.297 (3)
Mo1—Mo3	2.731 (2)	Mo2—O21	2.112 (7)
Mo2—Mo3	2.737 (2)	Mo2—O22	2.182 (7)
Mo1—S1	2.323 (3)	Mo2—O23	2.157 (8)
Mo1—S3	2.279 (3)	Mo3—S1	2.320 (3)
Mo1—S4	2.277 (3)	Mo3—S2	2.271 (3)
Mo1—O11	2.124 (9)	Mo3—S4	2.277 (3)
Mo1—O12	2.229 (7)	Mo3—O31	2.190 (8)
Mo1—O13	2.178 (9)	Mo3—O32	2.183 (7)
Mo2—S1	2.322 (3)	Mo3—O33	2.121 (8)
Mo2—S2	2.281 (4)		
Mo3—Mo1—Mo2	60.03 (4)	S2—Mo2—S3	98.36 (13)
Mo3—Mo2—Mo1	59.80 (4)	O21—Mo2—S1	84.7 (2)
Mo1—Mo3—Mo2	60.17 (4)	O23—Mo2—S1	84.5 (2)
O11—Mo1—O13	73.5 (3)	O22—Mo2—S1	158.7 (2)
O11—Mo1—O12	77.8 (3)	S2—Mo2—S1	105.1 (1)
O13—Mo1—O12	78.7 (3)	S3—Mo2—S1	105.2 (1)
O11—Mo1—S4	161.5 (2)	O33—Mo3—O32	77.2 (3)
O13—Mo1—S4	92.6 (3)	O33—Mo3—O31	73.1 (3)
O12—Mo1—S4	87.7 (2)	O32—Mo3—O31	78.6 (3)
O11—Mo1—S3	92.4 (2)	O33—Mo3—S2	94.0 (2)
O13—Mo1—S3	162.6 (2)	O32—Mo3—S2	89.4 (2)
O12—Mo1—S3	88.6 (2)	O31—Mo3—S2	164.0 (2)
S4—Mo1—S3	98.8 (1)	O33—Mo3—S4	159.2 (2)
O11—Mo1—S1	85.5 (2)	O32—Mo3—S4	86.7 (2)
O13—Mo1—S1	83.6 (2)	O31—Mo3—S4	91.1 (2)
O12—Mo1—S1	158.4 (2)	S2—Mo3—S4	98.9 (1)
S4—Mo1—S1	105.4 (1)	O33—Mo3—S1	86.4 (2)
S3—Mo1—S1	105.8 (1)	O32—Mo3—S1	158.6 (2)
O21—Mo2—O23	74.6 (3)	O31—Mo3—S1	83.6 (2)
O21—Mo2—O22	78.0 (3)	S2—Mo3—S1	105.5 (1)
O23—Mo2—O22	79.1 (3)	S4—Mo3—S1	105.5 (1)
O21—Mo2—S2	96.0 (2)	Mo3—S1—Mo2	72.3 (1)
O23—Mo2—S2	166.0 (2)	Mo3—S1—Mo1	72.1 (3)
O22—Mo2—S2	89.0 (2)	Mo2—S1—Mo1	72.3 (1)
O21—Mo2—S3	159.7 (2)	Mo3—S2—Mo2	73.9 (1)
O23—Mo2—S3	88.6 (2)	Mo1—S3—Mo2	73.6 (1)
O22—Mo2—S3	87.9 (2)	Mo3—S4—Mo1	73.7 (1)

Finding a crystal exhibiting no macroscopic twinning proved hopeless. Axial photographs of the selected crystal revealed a secondary orientation very slightly rotated from the major orientation. The contribution of this second orientation to the total diffraction pattern was visually estimated to be less than 10%, but caused highly asymmetric backgrounds on many weak reflections, leading to higher than expected $\sigma(F_o^2)$ values. The unreasonable anisotropic displacement parameters for C11 and C12 are possibly indicative of a slight disorder, or perhaps due to the lack of any absorption correction, but most likely are artifacts of the inaccuracies in many of the intensities due to the slight twinning problem.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bursten, B. E., Cotton, F. A., Hall, M. B. & Najjar, R. C. (1982). *Inorg. Chem.* **21**, 302–307.

Cotton, F. A. (1964). *Inorg. Chem.* **3**, 1217–1220.

Cotton, F. A., Dori, Z., Llusar, R. & Schwotzer, W. (1985). *J. Am. Chem. Soc.* **107**, 6734–6735.

Cotton, F. A., Llusar, R., Marler, D. O., Schwotzer, W. & Dori, Z. (1985). *Inorg. Chim. Acta*, **102**, L25–27.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 838-840

(*meso*-4,8-Diaza-3,9-dimethyl-6,6-trimethyleneundecane-2,10-dione dioximato-*N*,*N*′,*N*″,*N*‴)oxotechnetium(V), $[TcO(C_{14}H_{25}N_4O_2)]$

CHANG-SHU TSAI,[a] TIAN-HUEY LU,[b]* JANNE-YI DUH[a] AND SI-JUNG YEH[a]

[a]*Institute of Nuclear Science, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China, and* [b]*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300*

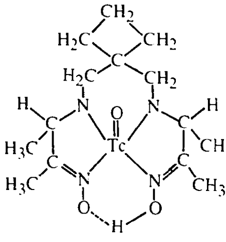
(*Received 12 June 1995; accepted 12 October 1995*)

Abstract

The title compound was synthesized and analyzed by X-ray diffraction, in addition to IR, NMR, visible–UV and mass spectral studies. The coordination geometry about the Tc^V atom is five-coordinate square pyramidal, with four N atoms in equatorial positions and an O atom in the axial position. The Tc=O double-bond distance is 1.664 (5) Å. The two amide Tc—N bond lengths are shorter than the two oxime Tc—N bond lengths. The central six-membered ring has a boat conformation with the Tc-bonded O atom 'hanging' above. The intramolecular hydrogen-bond length between the two O atoms of the oxime groups is 2.432 (9) Å. The cyclobutyl C atoms are, more or less, in a square plane.

Comment

A large number of ^{99}TcO–tetradentate amine oxime complexes have been shown to be neutral, lipophilic and able to cross the intact blood–brain barrier (Troutner, Volkert, Hoffman & Holmes, 1984; Volkert, Hoffman, Seger, Troutner & Holmes, 1984; Jurisson *et al.*, 1986, 1987). Of these, HM-PAO (3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime), the main component of Ceretec^{TM} (Amersham Inc., England), has been used widely in nuclear medicine for efficacious cerebral perfusion imaging. However, it has been realized that there is a vital defect regarding *in vitro* instability (Hung, Corlija, Volkert & Holmes, 1988). Recently, another potential brain-imaging agent, CB-PAO (4,8-diaza-3,9-dimethyl-6,6-trimethyleneundecane-2,10-dione dioxime) was proposed (Colombo *et al.*, 1989). ^{99m}Tc–CB-PAO showed higher *in vitro* stability and lipophilicity than ^{99m}Tc-HM-PAO (Bacciottini *et al.*, 1990). For a better understanding of these facts, it is of great interest to study the coordination pattern of the ^{99}Tc–CB-PAO crystal structure. This is the first time that a single crystal of a Tc complex of the *meso*-CB-PAO isomer, (I), has been isolated and the chemical bonding of Tc with CB-PAO examined.



(I)

X-ray crystallographic analysis showed the title crystal to consist of a mononuclear Tc complex. By referring to the N—Tc—N and O—Tc—N angles in Table 2, it can be seen that the coordination geometry about the Tc^V ion is five-coordinate distorted square pyramidal, with an O atom at the apex and four N atoms in the basal plane. The geometric parameters of TcN_4O in the present structure are comparable with those in $[Tc^VO(pnao\text{-}3H)]$ [pnao-3H is 3,3′-(1,3-propanediyldiimino)bis(3-methyl-2-butanone oximato) (Fair, Troutner, Schlemper, Murmann & Hoppe, 1984)]. The Tc=O bond distance of 1.664 (5) Å is somewhat shorter, compared with the values 1.670 (4)–1.682 (5) Å for mono(oxo)technetium(V)–tetradentate propylene amine oxime derivatives (Fair *et al.*, 1984; Jurisson *et al.*, 1986, 1987). The IR spectrum showed the Tc=O stretch at 931 cm^{-1}. This is at the high energy end of the