Acta Cryst. (1994). C**50**, 196–198

Tetrakis(isopropylammonium) β-Octamolybdate(VI)

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(*Received* 29 *January* 1993; *accepted* 9 *July* 1993)

Abstract

The structural analysis revealed that the title compound, $4[C_3H_{10}N][Mo_8O_{26}]$, contains discrete centrosymmetric polyanions, β-$[Mo_8O_{26}]^{4-}$, linked to isopropylammonium cations through hydrogen bonds. Some of these hydrogen bonds play an important role in the UV-induced photochromism of this compound.

Comment

The paramagnetic Mo^VO_6 site in the polyoxomolybdates has been characterized with the help of electron spin resonance spectroscopy for UV-irradiated single crystals of alkylammonium polyoxomolybdates such as $[NH_3{}^iPr]_6[Mo_8O_{26}(OH)_2]$.$2H_2O$ (Isobe, Marumo, Yamase & Ikawa, 1978; Yamase, 1978; Yamase & Suga, 1989), $[NH_3Pr]_6[Mo_7O_{24}]$.$3H_2O$ (Yamase, 1982), $[NH_3{}^iPr]_6[Mo_7O_{24}]$.$3H_2O$ (Ohashi, Yanagi, Sasada & Yamase, 1982; Yamase, 1986) and $[NH_3Me]_8[Mo_{10}O_{34}]$.$2H_2O$ (Yamase, 1985; Bharadwaj, Ohashi, Sasada, Sasaki & Yamase, 1986; Yamase, 1986). While the photo-induced formation of the paramagnetic site has received considerable attention, the paramagnetic site in β-$[Mo_8O_{26}]^{4-}$ lattices remains uninvestigated. By treatment of $NH_3{}^iPr$ and MoO_3 in aqueous solution, the photosensitive isopropylammonium salt of β-$[Mo_8O_{26}]^{4-}$ was prepared. The compound becomes red–brown in colour upon photoexcitation of the O→Mo charge-transfer bands, as similarly observed for the $[NHEt_3]^+$ salt (Bharadwaj, Ohashi, Sasada & Yamase, 1984), and has a high solubility (7.87 g per 100 ml at 294 K) in water.

The title compound was prepared by the reaction between stoichiometric amounts of MoO_3 (10.07 g, 69.96 mmol) and isopropylamine (3 ml, 34.86 mmol) on reflux at 373 K in aqueous solution (100 ml) for 2 h. Colourless single crystals of $[NH_3{}^iPr]_4[Mo_8O_{26}]$ appeared overnight.

The unit cell is shown in Fig. 2. The β-octamolybdate anions are located at positions $(0,\frac{1}{2},0)$ and $(0,0,\frac{1}{2})$. There are two independent cations per half anion. These cations occupy the vacant sites between the polyanions and are involved in hydrogen bonds with the anions to form a three-dimensional network. The N(2) atom interacts with three O atoms, O(7), O(8) and O(12), in the same y level, forming a hydrogen-bond network along the a axis. Polyanions located at different y levels are connected by N1···O4 and N1···O3 hydrogen bonds.

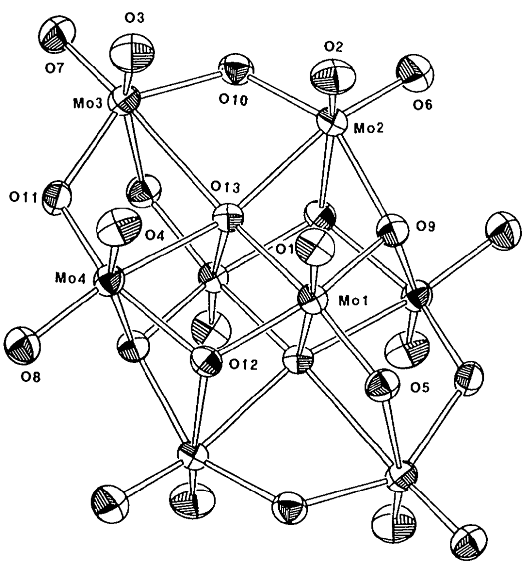

Fig. 1. Thermal ellipsoid plot showing the labelling of the polyanion.

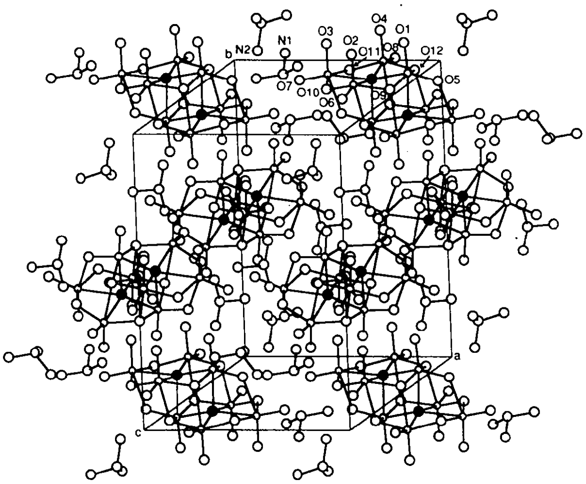

Fig. 2. The unit cell of the title compound with O- and N-atom labelling. Filled circles correspond to the O(13) atom.

Experimental

Crystal data

$4[C_3H_{10}N][Mo_8O_{26}]$
$M_r = 1423.979$
Monoclinic
$P2_1/c$
$a = 11.096\ (2)$ Å
$b = 17.308\ (3)$ Å
$c = 10.526\ (2)$ Å
$\beta = 116.53\ (1)°$
$V = 1808.5\ (9)$ Å^3
$Z = 2$
$D_x = 2.615$ Mg m^{-3}
$D_m = 2.63\ (1)$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 10\text{-}12°$
$\mu = 2.71$ mm^{-1}
$T = 296$ K
Prism
$0.40 \times 0.20 \times 0.20$ mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF
$T_{\min} = 0.93$, $T_{\max} = 1.07$
5691 measured reflections
5264 independent reflections
4621 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.0082$
$\theta_{\max} = 30°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 14$
3 standard reflections monitored every 100 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.0294$
$wR = 0.0329$
$S = 4.820$
4487 reflections
226 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.025$
$\Delta\rho_{\max} = 0.65$ e Å^{-3}
$\Delta\rho_{\min} = -1.17$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

All calculations were carried out using *TEXSAN* (Molecular Structure Corporation, 1989) running on a MicroVAX II computer.

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Mo(1)	0.09562 (4)	0.08582 (3)	0.51062 (5)	1.71 (2)
Mo(2)	−0.08183 (5)	0.08684 (3)	0.67947 (5)	1.94 (2)
Mo(3)	−0.35376 (5)	0.04843 (3)	0.38658 (5)	2.06 (2)
Mo(4)	−0.16770 (5)	0.05252 (3)	0.21882 (5)	1.97 (2)
O(1)	0.0683 (4)	0.1811 (2)	0.4807 (4)	2.7 (2)
O(2)	−0.1056 (4)	0.1818 (2)	0.6404 (4)	3.0 (2)
O(3)	−0.3672 (4)	0.1464 (2)	0.3613 (4)	3.2 (2)
O(4)	−0.1830 (4)	0.1508 (2)	0.2035 (4)	3.1 (2)
O(5)	0.2672 (3)	0.0720 (2)	0.5621 (4)	2.2 (1)
O(6)	−0.0515 (4)	0.0805 (2)	0.8521 (4)	3.0 (2)
O(7)	−0.5127 (4)	0.0181 (2)	0.3421 (4)	2.9 (2)
O(8)	−0.1924 (4)	0.0222 (2)	0.0553 (4)	3.1 (2)
O(9)	0.1027 (3)	0.0756 (2)	0.6979 (4)	1.9 (1)
O(10)	−0.2603 (3)	0.0482 (2)	0.5902 (4)	2.2 (1)
O(11)	−0.3294 (4)	0.0232 (2)	0.2224 (4)	2.3 (1)
O(12)	0.0336 (3)	0.0471 (2)	0.3154 (4)	2.0 (1)
O(13)	−0.1050 (3)	0.0508 (2)	0.4564 (3)	1.8 (1)
N(1)	−0.2369 (5)	0.2063 (3)	0.9020 (6)	3.6 (2)
N(2)	0.2002 (5)	0.0726 (3)	0.1715 (5)	2.6 (2)
C(11)	−0.3573 (6)	0.1568 (3)	0.8108 (6)	2.8 (2)
C(12)	−0.4549 (7)	0.1567 (4)	0.8732 (7)	4.0 (3)
C(13)	−0.4181 (6)	0.1892 (4)	0.6599 (7)	3.8 (3)
C(21)	0.2030 (6)	0.1552 (3)	0.1326 (6)	3.0 (2)
C(22)	0.2919 (7)	0.1644 (4)	0.0599 (8)	4.4 (3)
C(23)	0.2435 (9)	0.2036 (4)	0.2595 (8)	5.1 (4)

Table 2. Mo—O *and* O—O *bond distances* (Å) *and* O—Mo—O *bond angles* (°) *in the* β-$[Mo_8O_{26}]^{4-}$ *polyanion, and hydrogen-bond contacts* (Å)

	Mo(1)	O(1)	O(5)	O(9)	O(12)	O(13)	O(13$^{\rm i}$)
O(1)	1.684 (4)		105.8 (2)	101.6 (2)	100.9 (2)	98.6 (2)	172.9 (2)
O(5)	1.748 (4)	2.736 (5)		97.4 (2)	95.8 (2)	155.5 (2)	81.3 (1)
O(9)	1.945 (3)	2.816 (5)	2.777 (5)		149.7 (1)	79.0 (1)	77.5 (1)
O(12)	1.969 (3)	2.820 (5)	2.763 (5)			77.7 (1)	77.7 (1)
O(13)	2.125 (3)	2.901 (5)		2.593 (5)	2.571 (5)		74.2 (1)
O(13$^{\rm i}$)	2.385 (4)		2.735 (5)	2.732 (5)	2.750 (5)	2.729 (7)	

	Mo(2)	O(2)	O(6)	O(9)	O(10)	O(13)	O(12$^{\rm i}$)
O(2)	1.687 (4)		105.0 (2)	99.3 (2)	102.0 (2)	94.6 (2)	165.1 (2)
O(6)	1.697 (4)	2.684 (6)		100.8 (2)	99.9 (2)	160.3 (2)	88.7 (2)
O(9)	1.978 (3)	2.800 (5)	2.837 (5)		145.2 (1)	73.5 (1)	71.9 (1)
O(10)	1.895 (4)	2.787 (5)	2.752 (5)			77.6 (1)	80.9 (1)
O(13)	2.330 (3)	2.984 (5)		2.593 (5)	2.669 (5)		71.5 (1)
O(12$^{\rm i}$)	2.375 (4)		2.889 (5)	2.575 (5)	2.794 (5)	2.750 (5)	

	Mo(3)	O(3)	O(7)	O(10)	O(11)	O(13)	O(5$^{\rm i}$)
O(3)	1.712 (4)		104.9 (2)	98.2 (2)	97.1 (2)	92.2 (2)	161.8 (2)
O(7)	1.694 (4)	2.700 (6)		106.5 (2)	103.2 (2)	162.9 (2)	93.4 (2)
O(10)	1.919 (4)	2.747 (5)	2.898 (5)		141.6 (1)	72.5 (1)	76.7 (1)
O(11)	1.914 (4)	2.721 (5)	2.832 (5)			71.9 (1)	77.8(1)
O(13)	2.519 (3)	3.099 (5)		2.669 (5)	2.649 (5)		69.6 (1)
O(5$^{\rm i}$)	2.330 (3)		2.900 (5)	2.605 (5)	2.634 (5)	2.735 (5)	

	Mo(4)	O(4)	O(8)	O(11)	O(12)	O(13)	O(9$^{\rm i}$)
O(4)	1.710 (4)		104.3 (2)	102.4 (2)	97.8 (2)	94.9 (2)	164.7 (2)
O(8)	1.700 (4)	2.692 (6)		102.3 (2)	98.0 (2)	160.0 (2)	88.3 (2)
O(11)	1.882 (4)	2.802 (5)	2.792 (5)		146.7 (1)	78.5 (1)	82.9 (1)
O(12)	2.000 (4)	2.802 (5)	2.799 (5)			73.6 (1)	71.5 (1)
O(13)	2.277 (3)	2.963 (5)		2.649 (5)	2.571 (5)		
O(9$^{\rm i}$)	2.376 (4)		2.881 (5)	2.842 (5)	2.575 (5)	2.732 (5)	

Hydrogen-bond contacts

N(1)···O(2$^{\rm i}$)	2.984 (7)	N(2)···O(7$^{\rm iv}$)	3.025 (6)
N(1)···O(3$^{\rm i}$)	2.868 (7)	N(2)···O(8$^{\rm v}$)	2.867 (6)
N(1)···O(4$^{\rm ii}$)	3.107 (7)	N(2)···O(10$^{\rm iii}$)	3.100 (6)
N(1)···O(6)	3.195 (6)	N(2)···O(12)	2.901 (6)
N(2)···O(6$^{\rm iii}$)	3.073 (6)		

Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, y, 1 + z$; (iii) $-x, -y, 1 - z$; (iv) $1 + x, y, z$; (v) $-x, -y, -z$.

JMGZ acknowledges support through the Japan Society for the Promotion of Science Fellowship Program.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71489 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1037]

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Acta Cryst. (1994). C**50**, 198–200

Bridged Bis(dicarbadodecaborane)cobalt(III)

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(*Received* 28 *September* 1992; *accepted* 5 *July* 1993)

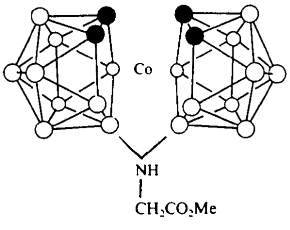
Abstract

The molecule of 8,8′-μ-(methoxycarbonylmethylamino)-3,3′-*commo*-bis[1,2-dicarba-3-cobalta-*closo*-dodecaborane(11)], $[Co(C_7H_{26}B_{18}NO_2)]$, comprises two dicarbaborane ligands coordinated to the Co atom to form a 'sandwich' compound linked by pentagonal faces. The ligands are also linked by a monoatomic nitrogen bridge to which a methoxycarbonylmethyl group is bound, B—N bond lengths being 1.577 (4) and 1.563 (4) Å.

Comment

The present study reports the results of the X-ray investigation of 8,8′-CH_3OCOCH_2NH-3-Co-(1,2-$C_2B_9H_{10})_2$ and forms part of our continuing study of the structure of metallocarbaboranes prepared at the Institute of Inorganic Chemistry of the Czech Academy of Sciences (Janoušek, Plešek, Heřmánek & Baše, 1981).

The significant feature of the title molecule (Fig. 1) is the angle between the open pentagonal faces of the dicarbaborane ligands, *i.e.* the angle, φ, between the best plane through the atoms C(1), C(2), B(4), B(7), B(8) and that through C(1′), C(2′), B(4′), B(7′), B(8′) is 26.0 (1)°. In Table 3, the title compound (III) is compared with analogous compounds $Co(C_2B_9H_{11})_2^-$ (I) (Borodinsky, Sinn & Grimes, 1982) and $Co(C_2B_9H_{10})_2SCH_2COOCH_3$ (II) (Císařová & Petříček, 1986). The geometric parameters derived from our molecule are in good agreement with the conclusion inferred from a previous paper by Císařová & Petříček (1986) that the increasing angle affects the position of the Co atom, which moves towards the bridge. Moreover, with the increase in Co—C distances the C—C distance tends to become shorter. The molecules are dimeric, connected by two symmetrically related hydrogen bonds (through inversion). The interatomic distances N···O(1^i) 2.885 (4) and H(N)···O(1^i) 2.05 (4) Å, and angle N—H···O(1^i) 160 (3)°, are close to the mean values for this type of hydrogen bond in organic compounds (Taylor, Kennard & Versichel, 1984).



(III)

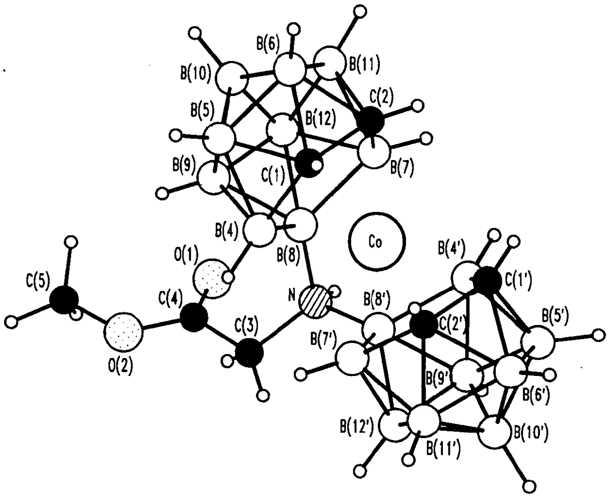


Fig. 1. View of the title molecule with the atom-numbering scheme.

Experimental

Crystal data

$[Co(C_7H_{26}B_{18}NO_2)]$
M_r = 409.80
Tetragonal
$I4_1/a$ (origin at -1 on glide plane *b*)
a = 23.971 (2) Å
c = 14.398 (2) Å

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32 reflections
θ = 10.8–19.0°
μ = 0.8308 mm^{-1}
T = 293 K