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Acta Cryst. (1999). C**55**, 521-523

$K_2[MoO_3(C_2O_4)]\cdot H_2O$

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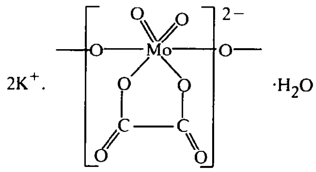
(*Received 9 July 1998; accepted 11 November 1998*)

Abstract

In the title compound, *catena*-poly[dipotassium [[(oxalato-*O*,*O*′)dioxomolybdate]-μ-oxo] monohydrate], oxalate acts as a bidentate ligand coordinating to each Mo atom through the two deprotonated carboxylate groups. The coordination polyhedron of molybdenum is distorted octahedral and there are infinite chains in the structure. Principal dimensions are: Mo—O(terminal) 1.560 (3) and 1.739 (3) Å, Mo—O(bridging) 2.046 (4) and 2.410 (4) Å, and Mo—O(carboxylate) 1.949 (3) and 2.113 (3) Å.

Comment

Oxalate is an important organic ligand, which is coordinated to many metals in complexes exhibiting different structural characteristics, such as $[Cu_2(\mu\text{-ox})_2(\mu\text{-pyz})(pyz)_2]_n$ (pyz is pyrazine; Kitagawa *et al.*, 1995), $[Cu(en)_2][Cu(ox)_2]$ (Oshio & Nagashima, 1992), $(Ph_4P)_2[(VO)_2(H_2O)_2(C_2O_4)_3]\cdot 4H_2O$ and $(Ph_4P)[VOCl(C_2O_4)]$ (Salta *et al.*, 1996), *etc.* In order to further understand the structure of the complexes containing the oxalate ligand, we have decided to turn our attention to molybdenum(VI) oxalate complexes. This is because molybdenum in the V and VI oxidation states forms a considerable number of oxo complexes (Cruywagen *et al.*, 1986). Few of these have been unequivocally characterized structurally, but it is important to do so in many cases. The point of particular interest in such compounds is the different structural arrangements which have an effect on intramolecular bond distances and angles. We report here an infinite-chain molybdenum–oxalate compound, (1).



(1)

It was found that $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$, (2), which was structurally characterized by X-ray diffraction (Cotton *et al.*, 1964), and (1) were considered to have a similar coordination mode for molybdenum. Structure analysis shows that in the anion of (1), the various Mo—O bond lengths and O—Mo—O bond angles vary considerably. The six oxygen ligands of each Mo atom are of three types, namely, terminal, bridging and oxalate, with respective Mo—O bond lengths of 1.560 (3)–1.739 (3), 2.046 (4)–2.410 (4) and 1.949 (3)–2.113 (3) Å, and angles ranging from 164.01 (14) to 76.85 (14)°. A comparison of (1) with (2) showed that one Mo—O(terminal) bond distance [1.560 (3) Å] in (1) is shorter than that in (2) (average 1.69 Å), however, another Mo—O(terminal) bond distance [1.739 (3) Å] is longer than that in (2). Therefore, the Mo—O(bridging) bond distances of (1) are longer than in (2) (1.876 Å), and their corresponding angles are considerably different, in particular, the Mo—O—Mo angle [156.2 (2)°] in (1) is bent, whereas that in (2) is linear. Both K1 and K2 are nine-coordinate, with bond lengths ranging from 2.532 (5) to 3.301 (5) Å. The water molecule is coordinated to two K atoms, with the O*W*···K distances ranging from 2.532 (5) to 3.014 (5) Å. In addition, the shorter Mo—O7 bond distance is probably due to the fact that the K···O7 interaction is weaker than the K···O4 interaction, leading to the Mo—O7 bond being stronger than the Mo—O4 bond, *e.g.* K2···O4^{iv} 2.611 (4), K2···O7^{iv} 3.288 (4) Å *etc.* [symmetry code: (iv) $x-1, y, z$].

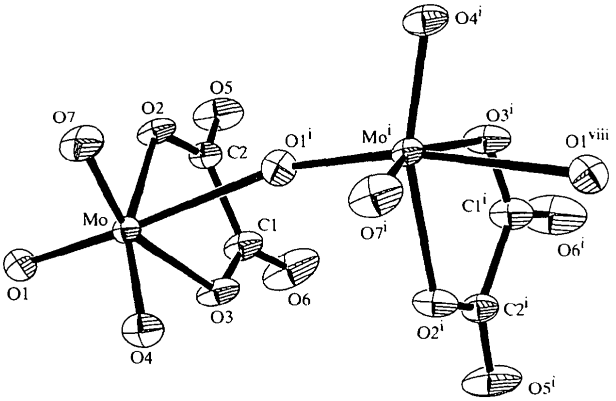


Fig. 1. The structure of the $[MoO_3(C_2O_4)]^{2-}$ infinite chain, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (viii) $x, y, 1+z$.]

Experimental

The title compound was separated as light-red prismatic crystals from a reaction system of $(NH_4)_2MoS_4/K_2C_2O_4\cdot H_2O$ (molar ratio 1:2), which was used in an attempt to prepare a bridging sulfur–molybdenum–oxalate compound in a solution of water and MeOH at room temperature under a nitrogen atmosphere.

Crystal data

$K_2[MoO_3(C_2O_4)]\cdot H_2O$
$M_r = 328.18$
Monoclinic
$P2_1/c$
$a = 7.5130 (10)$ Å
$b = 12.740 (2)$ Å
$c = 8.6800 (10)$ Å
$\beta = 95.67 (2)°$
$V = 826.7 (2)$ Å^3
$Z = 4$
$D_x = 2.637$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 2.72–28.97°$
$\mu = 2.605$ mm^{-1}
$T = 293 (2)$ K
Prism
0.36 × 0.22 × 0.08 mm
Light red

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
$T_{min} = 0.564$, $T_{max} = 0.812$
2047 measured reflections
1454 independent reflections
1361 reflections with $I > 2\sigma(I)$

$R_{int} = 0.035$
$\theta_{max} = 28.97°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 1$
$l = -1 \rightarrow 8$
3 standard reflections every 97 reflections intensity decay: 1.5%

Refinement

Refinement on F^2
$R(F) = 0.036$
$wR(F^2) = 0.103$
$S = 1.123$
1454 reflections
119 parameters
H atoms not located
$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 1.6151P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.039$

$\Delta\rho_{max} = 1.196$ e Å^{-3}
$\Delta\rho_{min} = -0.953$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0123 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mo—O7	1.560 (3)	K1···O2^{i}	3.104 (4)
Mo—O4	1.739 (3)	K1···O5^{i}	3.109 (5)
Mo—O3	1.949 (3)	K1···O4^{ii}	3.301 (4)
Mo—O1	2.046 (4)	K2···O4^{iv}	2.611 (4)
Mo—O2	2.113 (3)	K2···O5^{i}	2.639 (4)
Mo—O1^{i}	2.410 (4)	K2···O5^{v}	2.862 (4)
K1···O*W*	2.532 (5)	K2···O6	2.865 (5)
K1···O4	2.648 (3)	K2···O7^{vi}	2.888 (4)
K1···O1^{ii}	2.804 (4)	K2···O*W*	3.014 (5)
K1···O3	2.826 (3)	K2···O6^{i}	3.157 (6)
K1···O7^{iii}	2.935 (4)	K2···O7^{iv}	3.288 (4)
K1···O2^{iii}	2.973 (4)		
O7—Mo—O4	109.3 (2)	O3—Mo—O2	79.51 (12)
O7—Mo—O3	156.2 (2)	O1—Mo—O2	86.32 (14)
O4—Mo—O3	82.15 (14)	O7—Mo—O1^{i}	82.7 (2)
O7—Mo—O1	102.2 (2)	O4—Mo—O1^{i}	87.88 (15)
O4—Mo—O1	104.5 (2)	O3—Mo—O1^{i}	76.85 (14)
O3—Mo—O1	94.55 (15)	O1—Mo—O1^{i}	164.01 (14)
O7—Mo—O2	84.8 (2)	O2—Mo—O1^{i}	78.93 (13)
O4—Mo—O2	159.41 (14)	Mo—O1—Mo^{vii}	156.2 (2)

Symmetry codes: (i) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (ii) $1-x, 2-y, -z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $x-1, y, z$; (v) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $x-1, \frac{3}{2}-y, \frac{1}{2}+z$; (vii) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. The non-H atoms were refined anisotropically to convergence.

Data collection: *P*4 (Siemens, 1994*a*). Cell refinement: *P*4 and *XSCANS* (Siemens, 1994*b*). Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

This work was supported by grants from the Natural Science Foundation of China and the State Key Laboratory of Structural Chemistry.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1220). Services for accessing these data are described at the back of the journal.

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Siemens (1994*b*). *XSCANS. X-ray Single Crystal Analysis System.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). C**55**, 523–531

Coordination complexes of triphenyltin coumarin-3-carboxylate with *O*-donor ligands: (coumarin-3-carboxylato)triphenyltin–*L* (*L* = ethanol, diphenylcyclopropenone and quinoline *N*-oxide) and bis[(coumarin-3-carboxylato)triphenyltin]–*L* (*L* = triphenylphosphine oxide and triphenylarsine oxide)

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(*Received 29 July 1998; accepted 13 November 1998*)

Abstract

The Sn atoms in (coumarin-3-carboxylato-O^3)(ethanol-O)triphenyltin, $[\mathrm{Sn}(\mathrm{C_6H_5})_3(\mathrm{C_{10}H_5O_4})(\mathrm{C_2H_6O})]$, (coumarin-3-carboxylato-O^3)(1,2-diphenylcyclopropenone-O)triphenyltin, $[\mathrm{Sn}(\mathrm{C_6H_5})_3(\mathrm{C_{10}H_5O_4})(\mathrm{C_{15}H_{10}O})]$, and (coumarin-3-carboxylato-O^3)triphenyl(quinoline N-oxide-O)tin, $[\mathrm{Sn}(\mathrm{C_6H_5})_3(\mathrm{C_{10}H_5O_4})(\mathrm{C_9H_7NO})]$, are five-coordinated with *trans*-$\mathrm{C_3SnO_2}$ trigonal-bipyramidal geometries. In the ethanol adduct, a hydrogen bond links adjacent molecules into a helical chain along the *b* axis. The molecular 1,2-diphenylcyclopropenone and quinoline *N*-oxide adducts were synthesized by condensing triphenyltin hydroxide with coumarin-3-carboxylic acid in ethanol in the presence of an equimolar quantity of the *O*-donor ligand. With triphenylphosphine oxide as the Lewis base, the condensation yields μ-(coumarin-3-carboxylato)-$1\kappa O^3{:}2\kappa O^{3'}$-(coumarin-3-carboxylato)-$1\kappa O^3$-hexaphenyl-$1\kappa^3 C,2\kappa^3 C$-(triphenylphosphine oxide)-$2\kappa O$-ditin, $[\mathrm{Sn_2}(\mathrm{C_6H_5})_6(\mathrm{C_{10}H_5O_4})_2\{\mathrm{PO}(\mathrm{C_6H_5})_3\}]$; this dinuclear complex consists of a dimeric carboxylate-bridged bis[(coumarin-3-carboxylato)triphenyltin] entity that is coordinated by the phosphine oxide. μ-(Coumarin-3-carboxylato)-$1\kappa O^3{:}2\kappa O^{3'}$-(coumarin-3-carboxylato)-$1\kappa O^3$-hexaphenyl-$1\kappa^3 C,2\kappa^3 C$-(triphenylarsine oxide)-$2\kappa O$-ditin, $[\mathrm{Sn_2}(\mathrm{C_6H_5})_6(\mathrm{C_{10}H_5O_4})_2\{\mathrm{AsO}(\mathrm{C_6H_5})_3\}]$, is isomorphous with the phosphine oxide. The carboxylate bridge is longer than the dative Sn—O_L bond in both dinuclear compounds.

Comment

Unlike triorganotin halides and pseudohalides that yield a plethora of 1/1 adducts with 'pointed' (Ng *et al.*, 1982) *O*-donor ligands, triorganotin carboxylates rarely furnish such molecular complexes because the carboxylates are themselves either only weak Lewis acids (as with triphenyltin arylcarboxylates) or are already saturated with respect to coordination through carboxylate bridging (as with triphenyltin alkanoates) (Ng *et al.*, 1988). Complexes of triphenyltin carboxylates with water (Kumar Das *et al.*, 1977; Ng, 1996; Ng & Kumar Das, 1995*a*; Ng *et al.*, 1996) and methanol (Alcock & Roe, 1989) have been isolated, albeit serendipitously; these adducts are held together in the crystal structure by hydrogen bonds involving the solvate molecules. [Bis(*N*,*N*-dimethylthiocarbamoylthio)acetato]triphenyltin is an unusual example of a triorganotin carboxylate showing Lewis acidity; the compound forms 1/1 complexes with hexamethylphosphoramide, triphenylphosphine oxide (Ng, 1995*b*) and quinoline *N*-oxide (Ng, 1997). The Lewis acidity of this carboxylate can be attributed to the electron-withdrawing capacity of the dimethylthiocarbamoylthiolyl units in the anionic group; in fact, the compound is so Lewis acidic that even ethanol can coordinate to it (Ng & Kumar Das, 1991). On the other hand, bis(triphenyltin) succinate, which yields isolable adducts with several *O*-donor ligands (Ng, 1998*a*), represents an anomaly, as the succinato group is not normally considered a strongly basic entity.

Although the coumarin-3-carboxylate anion does not appear to be able to endow the triphenyltin derivative with enhanced Lewis acidity, triphenyltin coumarin-3-carboxylate accepts a coumarin-3-carboxylate anion to form the bis(coumarin-3-carboxylato)triphenylstannate anion, which has been structurally characterized as its tetramethylammonium salt (Ng & Kumar Das, 1997*b*).

Acta Crystallographica Section C
ISSN 0108-2701 © 1999