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The Structure of the Cadmium Tris(methoxyethylxanthato) Anion, Cd($CH_3OCH_2CH_2OCS_2$)$_3^-$, as its Tetraethylammonium Salt

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It has recently been observed [1] that substituting methoxyethyl for ethyl in cadmium bisxanthates results in major structural changes. Thus, whereas approximately tetrahedral geometry is found for the cadmium atom in the polymeric structure of cadmium bis-ethylxanthate, Cd(exa)$_2$, the cadmium atom in the methoxyethylxanthate (moexa) analogue is coordinated, surprisingly, by two chelating xanthate ligands in a planar arrangement and through two longer interactions with sulphur atoms of neighbouring molecules. This results in a tetragonally distorted octahedral environment around the cadmium atom. In the cadmium tris(ethylxanthato) anion, Cd(exa)$_3^-$ [2], the cadmium atom is coordinated by five sulphur atoms, two each from two chelating xanthates and one from the third xanthate ligand; an additional weak Cd–O bond has also been suggested [3]. It was therefore of interest to examine also the effect on the structure of the methoxyethyl groups on the tris(xanthato) anion.

In contrast to Cd(exa)$_3^-$ where the cadmium has five sulphur atoms in its coordination sphere the corresponding methoxyethylxanthate complex, Cd(moexa)$_3^-$, is surrounded by six sulphur atoms from three chelating ligands (see Fig. 1). In fact here the immediate environment of the cadmium atom is very similar to that observed in the cadmium tris(diethyldithiocarbamato) ion, Cd(dedtc)$_3^-$ [3], which has been described as being intermediate between an octahedral and a trigonal prismatic geometry. In Cd(moexa)$_3^-$, the two triangular faces of the prism may be defined by the atoms S(1), S(3) and S(5) and S(2), S(4) and S(6). The two faces are rotated by approximately 25° from the trigonal-prismatic geometry as compared with 17° for Cd(dedtc)$_3^-$. The distortion from octahedral geometry in Cd(dedtc)$_3^-$ has been explained in terms of the restricted bite of the dithiocarbamate ligand. The similarity between the two structures therefore suggests that this may also be the reason for the distortion in the geometry of Cd(moexa)$_3^-$.

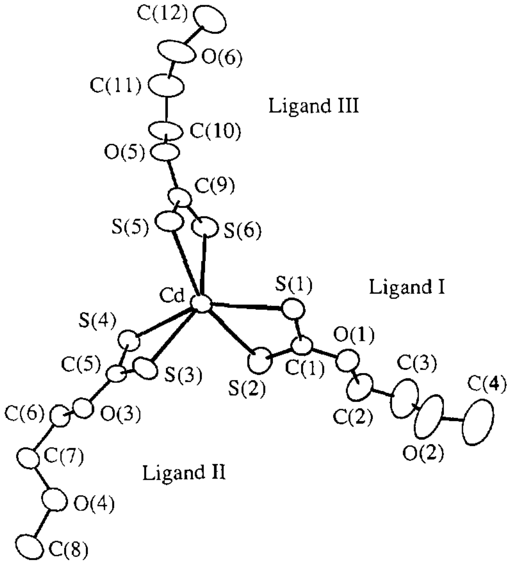

Fig. 1. The structure of the cadmium tris(methoxyethylxanthato) anion.

The Cd–S bond lengths are typical for the coordination of a chelated xanthate to cadmium (Table I). The average Cd–S bond length of 2.700(3) Å is similar to that observed for the chelating xanthate ligands in Cd(exa)$_3^-$ [2] and in the 1,10-phenanthroline adduct of Cd(exa)$_2$ [4], although this distance is a little longer than the 2.63 Å observed in Cd(moexa)$_2$ [1]. Of the three xanthate ligands identified in the diagram, ligands II and III show some degree of asymmetry in their coordination as evidenced by the bond lengths. In contrast, the coordination of ligand I is symmetrical.

Crystal data: $C_{20}H_{41}CdNO_6S_6$, $M = 696.3$, monoclinic, $a = 8.326(2)$, $b = 21.717(4)$, $c = 17.698(3)$ Å, $\beta = 92.28(2)°$, $U = 3197.5$ Å^3, $D_m = 1.45$ Mg m^{-3}, $Z = 4$, $D_c = 1.447$ Mg m^{-3}, $F(000) = 1440$, space group, $P2_1/n$ (variant of $P2_1/c$, No. 14), $\mu = 10.54$ cm^{-1}.

Intensity data were collected at room temperature using an Enraf-Nonius CAD-4F diffractometer fitted with Mo Kα radiation, 0.71069 Å. The ω:2θ scan technique was employed to measure 8807 reflections to a maximum Bragg angle of 27.5°. Of the 7308 reflections which were unique 4209 satisfied the $I \geqslant 2.5\sigma(I)$ criterion and were used in the subsequent analysis. No decomposition of the crystal occurred during the data collection. Corrections were applied for Lorentz and polarization effects and for absorption [5].

The structure was solved by normal heavy atom methods and refined by a full-matrix least-squares

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TABLE I. Bond Lengths (Å) and Angles (°)

Cd–S(1)	2.696(2)	Cd–S(2)	2.692(3)	Cd–S(3)	2.642(2)
Cd–S(4)	2.774(2)	Cd–S(5)	2.654(2)	Cd–S(6)	2.743(2)
S(1)–C(1)	1.660(7)	S(2)–C(1)	1.689(8)	C(1)–O(1)	1.335(10)
O(1)–C(2)	1.438(10)	S(3)–C(5)	1.698(6)	S(4)–C(5)	1.672(6)
C(5)–O(3)	1.334(7)	O(3)–C(6)	1.463(7)	S(5)–C(9)	1.674(8)
S(6)–C(9)	1.672(9)	C(9)–O(5)	1.342(9)	O(5)–C(10)	1.496(11)
S(1)–Cd–S(2)	66.5(1)	S(1)–Cd–S(3)	106.4(1)	S(1)–Cd–S(4)	151.0(1)
S(1)–Cd–S(5)	98.9(1)	S(1)–Cd–S(6)	104.1(1)	S(2)–Cd–S(3)	101.2(1)
S(2)–Cd–S(4)	86.8(1)	S(2)–Cd–S(5)	157.6(1)	S(2)–Cd–S(6)	99.4(1)
S(3)–Cd–S(4)	66.4(1)	S(3)–Cd–S(5)	99.2(1)	S(3)–Cd–S(6)	148.1(1)
S(4)–Cd–S(5)	109.9(1)	S(4)–Cd–S(6)	90.8(1)	S(5)–Cd–S(6)	66.6(1)
S(1)–C(1)–S(2)	123.8(5)	S(3)–C(5)–S(4)	123.6(4)	S(5)–C(9)–S(6)	124.7(5)

procedure in which the function $\Sigma w\Delta^2$ was minimized where $\Delta = ||F_o| - |F_c||$ and w was the weight applied to each reflection [5]. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were not included in the model due to disorder. Owing to the high thermal motion of terminal atoms, the C–C, C–O and O–C bond lengths of the xanthate ligands and the C–C bond lengths of the tetraethylammonium cation were constrained to values of 1.55, 1.41, 1.50 and 1.55 Å respectively in the final refinement cycles. A weighting scheme of the form $w = k[\sigma^2(F) + gF^2]^{-1}$, was included in each refinement. At convergence the values of k, g, R and R_w were 0.36, 0.0127, 0.071 and 0.092 respectively. The analysis of variance showed no special features.

Scattering factors for atomic Cd (corrected for $\Delta f'$ and $\Delta f''$) were taken from ref. 6 and those for the remaining atoms were those incorporated in SHELX-76 [5]. Calculations were performed on a VAX 11/780 computer with SHELX-76 and the diagram was drawn using the program ORTEP [7].

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