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Polytopal Isomerism of the $[Cd(S\{O\}CPh)_3]^-$ Anion

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Introduction

In recent years, several salts of the thiobenzoato complexes $[M(thb)_3]^-$ (thb = S{O}CPh; M = Zn, Cd, Hg) have been characterized structurally.[1−3] In all cases, the primary metal−ligand bonding is through sulfur, with only secondary bonding to oxygen. An intriguing feature of the structures has been the occurrence and planarity, or near-planarity, of the MS_3 skeleton. For the divalent zinc group elements, clear MS_3 skeletons have otherwise been found only in thiolate complexes, usually[4] with sterically hindered thiolates.[5−9] In these complexes, the skeletons are (near-)planar also.

We report here the structural characterization of $(Ph_4P)[Cd(thb)_3]$ in two modifications, monoclinic (**1**-m) and rhombohedral (**1**-r). The rhombohedral modification exhibits an extraordinary range of geometries for the CdS_3 skeletons in the anions that it contains, from planar through to uniquely pyramidal. Planar-pyramidal isomerism of three-coordinate species is so rare that no stereochemical notation appears to have been developed for it.[10]

Experimental Section

General Procedure. All materials were obtained commercially and used as received except that solvents were dried by standing over 3A molecular sieves. All preparations were carried out under Ar, with solvents that had been sparged with Ar. $(Ph_4P)[Cd(thb)_3]$ was synthesized from Et_3N, PhC{O}SH, $Cd(NO_3)_2{\cdot}4H_2O$, and Ph_4PBr, as described previously.[2] As a precaution, the thiobenzoato complexes were stored under Ar at 5 °C, although they appear to be stable for days at room temperature.

Monoclinic and Rhombohedral $(Ph_4P)[Cd(thb)_3]$ (1-m and 1-r). The crystalline orange-yellow product obtained during the literature synthesis of $(Ph_4P)[Cd(thb)_3]$ proved to be **1**-r, as described below. Paler yellow **1**-m was obtained in crystalline form by layering Et_2O onto a solution of **1**-r in CH_2Cl_2−MeCN and allowing diffusion to occur at room temperature. Anal. Calcd for $C_{45}H_{35}Cd_1O_3P_1S_3$ (mol wt 863.35): C, 62.60; H, 4.09. Found: C, 62.55; H, 3.90.

Table 1. Crystallographic Data for Monoclinic and Rhombohedral $(Ph_4P)[Cd(SCOPh)_3]$ (**1**-m and **1**-r)

	1-m	**1**-r
empirical formula	$C_{45}H_{35}Cd_1P_1O_3S_3$	
formula weight	863.28	
space group	$P2_1/n$	$R3$
temp (°C)	20(2)	21(1)
a (Å)	13.344(2)	35.555(6)
b (Å)	14.776(2)	35.555(6)
c (Å)	20.731(3)	19.643(6)
β (deg)	92.57(1)	90
V (Å^3)	4083.4(10)	21505(8)
Z	4	21
ρ_{calcd} (g cm^{-3}), ρ_{obsd} (g cm^{-3})	1.40, 1.40(5)	1.40
μ(Mo Kα) (cm^{-1})	7.66	7.53
λ(Mo Kα) (Å)	0.710 73	
basis of refinement	F^2	F
$R_1{}^a$	0.060^b	0.072^c
wR$_2$	$0.122^{b,d}$	$0.089^{c,e}$

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $I/\sigma(I) > 2$. [c] $I/\sigma(I) > 3$. [c] $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$, with $w = 1/[\sigma^2(F_o)^2 + (0.0422p)^2 + 9.1125p]$, where $p = (F_o{}^2 + 2F_c{}^2)/3$. [e] $wR_2 = [\sum w(F_o - F_c)^2/\sum wF_o{}^2]^{1/2}$, with $w = 1/\sigma^2(F_o)$. $\sigma(F_o)$ is derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$.

X-ray Structure Determinations. Diffraction experiments for **1**-m and **1**-r were performed with a Siemens P4 diffractometer with the XSCANS software package[11] and an Enraf-Nonius CAD-4 diffractometer, respectively, in $\theta/2\theta$ mode. A summary of the crystallographic details for **1**-m and **1**-r is given in Table 1.

For **1**-m, a total of 6313 reflections were collected ($2\theta_{max} = 46.0°$, $-1 \leq h \leq 14$, $-1 \leq k \leq 16$, $-22 \leq l \leq 22$) and a Gaussian absorption correction was applied to the 5662 independent reflections ($R_{int} = 0.015$). SHELXTL-PC[12] programs were used for data processing, solution, and initial refinements. Final refinements were performed using SHELXL-93[13] software programs. The non-hydrogen atoms in the anion, and the phosphorus atom, were refined anisotropically. Isotropic thermal parameters were refined for the carbon atoms of the cation phenyl rings, to which 2-fold symmetry constraints were applied. Hydrogen atoms were included in calculated positions. In the final least-squares refinement cycles on F^2, the model converged at $R_1 = 0.060$, wR2 = 0.122 for 3657 observations ($I/\sigma(I) \geq 2$), and 358 parameters.

For **1**-r, a total of 6635 data were collected ($2\theta_{max} = 45°$, $-38 \leq h \leq 0$, $0 \leq k \leq 38$, $0 \leq l \leq 21$) and corrected for absorption by an analytical method.[14] Of the observed reflections ($I > 3\sigma(I)$), 4261 were independent ($R_{int} = 0.030$). The structure was determined by direct phasing and Fourier methods. There were 2 $^1/_3$ anions and 2 $^1/_3$ cations in the asymmetric unit, giving a total of 129 non-hydrogen atoms in the asymmetric unit. Phenyl rings of the cations were modeled as planar groups with refineable *mm*2 symmetry. The phenyl and thiocarboxylate carbons of the anions were also considered planar, but there was no restriction on phenyl−C{O}S bond rotation. Each of the 17 rigid groups was refineable for rotation and translation, with thermal motions described by a TL rigid-body model. The remaining atoms were refined with individual anisotropic thermal parameters. Hydrogen atom positions were calculated. In the final least-squares cycle on F, convergence was achieved at $R_1 = 0.072$, $wR_2 = 0.089$ for the 4261

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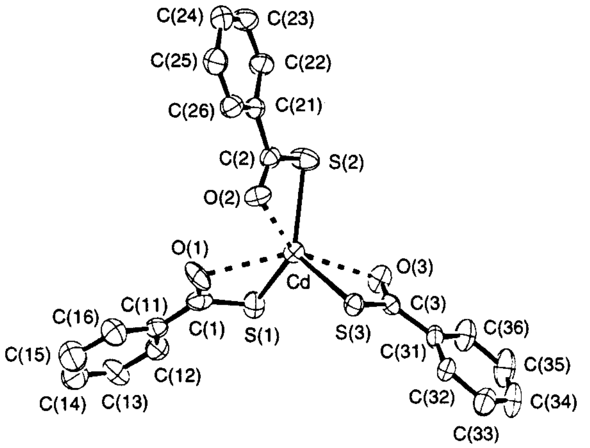

Figure 1. View of the anion in monoclinic $(Ph_4P)[Cd(S\{O\}CPh)_3]$ (**1**-m) showing the numbering scheme used. Atoms are shown as 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Anions in Monoclinic $(Ph_4P)[Cd(S\{O\}CPh)_3]$ (**1**-m)

Bond Distances					
Cd−S1	2.567(3)	Cd−S2	2.527(2)	Cd−S3	2.531(2)
Cd−O1	2.698(6)	Cd−O2	2.567(5)	Cd−O3	2.633(5)

Bond Angles			
S1−Cd−S2	122.14(9)	S1−Cd−O3	86.69(13)
S1−Cd−S3	111.32(7)	S2−Cd−O1	110.2(2)
S2−Cd−S3	120.71(8)	S2−Cd−O2	61.02(13)
O1−Cd−O2	77.6(2)	S2−Cd−O3	97.74(14)
O1−Cd−O3	141.6(2)	S3−Cd−O1	119.97(14)
O2−Cd−O3	140.5(2)	S3−Cd−O2	100.28(13)
S1−Cd−O1	56.41(12)	S3−Cd−O3	60.20(12)
S1−Cd−O2	132.62(13)		

observed reflections and 390 variables. Symmetry-imposed disorder existed for one ring of the PPh_4^+ cation (C) that sits on a 3-fold axis. The choice of space group was not unambiguous. However, possibilities other than R3 require that the anion A, situated at the origin, occupy a site with symmetry higher than that intrinsic in the anion itself, which would be impossible without further disorder. Refinement of the structure to a satisfactory residual confirmed the choice of space group. Atomic scattering factors and anomalous dispersion factors were from a standard reference.[15] Structure solution was by SIR92,[16] and refinement used RAELS92.[17] ORTEP II[18] was used for the structural diagrams.

Additional details are available as Supporting Information.

Results and Discussion

Selected bond distances and angles for **1**-m and **1**-r are given in Tables 2 and 3, respectively.

The structure of **1**-m consists of discrete anions and cations. The cations exhibit no unusual features. A view of the anion is shown in Figure 1. The primary Cd−S distances and secondary Cd···O distances within the anion, 2.527(2)−2.567(3) and 2.567(5)−2.698(6) Å, can be compared with 2.453(2)−2.545(2) and 2.490(4)−3.019(4) Å found[2] for $(Ph_4As)[Cd(thb)_3]$ (**2**). The CdS_3 skeleton is close to planar, as is the CdO_3 skeleton, and the dihedral angle between the S_3 and O_3 planes falls within the literature range for discrete anions $[M(thb)_3]^-$ (M = Zn-Hg) (Table 4). Thus, the O atoms in **1**-m (and **2**) are distributed about both sides of the S_3 plane in the anion. The range of S−Cd−S angles in **1**-m is significantly smaller than that in **2** (Tables 2 and 4), almost certainly because the nearest O atom is 2.08 Å from the S_3 plane of **1**-m, but much closer, 0.27 Å, in **2**. It is, however, much larger than those occurring in the anions of types A and C in **1**-r (see below).

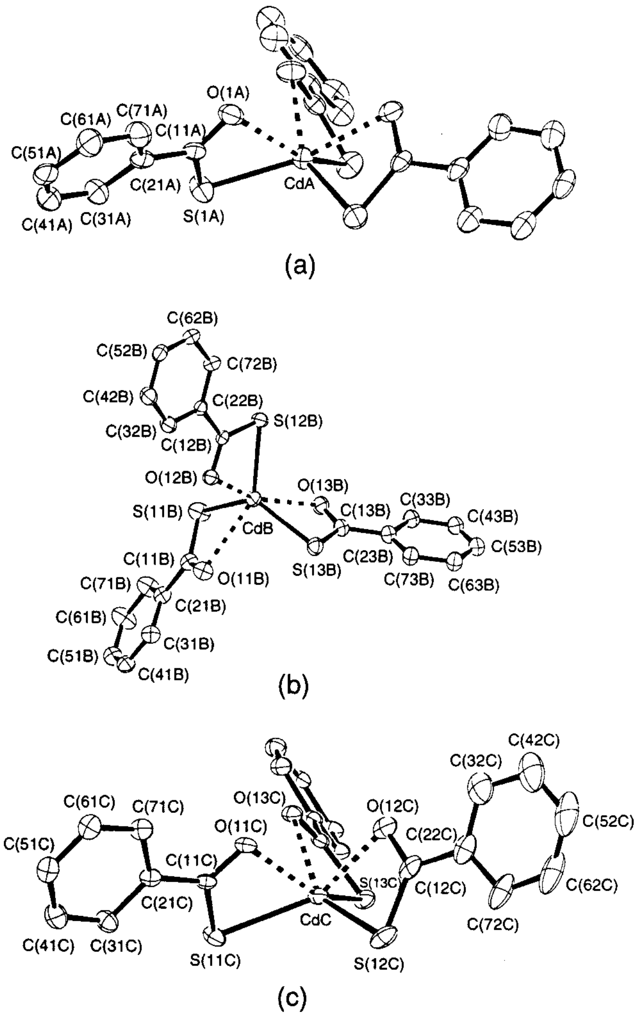

Figure 2. Views of the three crystallographically different anions in **1**-r, showing the numbering scheme used: (a) anion A; (b) anion B; (c) anion C. Atoms are shown as 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

In **2**, where one O atom of the anion is very close to the S_3 plane, the CdS_3O_3 kernel can be described as highly distorted octahedral (cf. ref 3), with the disparate donor atoms in the *mer* configuration. This description is less appropriate for the anion in **1**-m, although the expected near-planarity of the CdS_3 and CdO_3 skeletons is retained. Despite the differences between the two anions, the proportions of the total bond valence[19] (TBV) attributable to primary Cd−S and secondary Cd···O bonding are similar: the ratio of contributions of Cd···O to Cd−S bonding is 0.27 (TBV = 2.00) in **1**-m and 0.25 (TBV = 2.18) in **2**.

The unit cell of **1**-r contains 21 formula units. The discrete anions and cations occur in three crystallographically different forms, A, B, and C, as shown in a projection down c

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Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for the Anions in Rhombohedral $(Ph_4P)[Cd(S\{O\}CPh)_3]$ (**1**-r)

anion A		anion B		anion C	
		Bond Distances			
CdA−S1A	2.512(7)	CdB−S11B	2.469(6)	CdC−S11C	2.535(6)
		CdB−S12B	2.555(5)	CdC−S12C	2.564(7)
		CdB−S13B	2.592(6)	CdC−S13C	2.519(5)
CdA−O1A	2.640(15)	CdB−O11B	2.669(13)	CdC−O11C	2.503(12)
		CdB−O12B	2.516(11)	CdC−O12C	2.459(18)
		CdB−O13B	2.494(12)	CdC−O13C	2.615(12)
		Bond Angles			
S1A−CdA−S1A[a]	111.1(2)	S11B−CdB−S12B	117.0(2)	S11C−CdC−S12C	113.1(2)
		S11B−CdB−S13B	133.8(2)	S11C−CdC−S13C	114.2(2)
		S12B−CdB−S13B	108.7(2)	S12C−CdC−S13C	114.0(2)
O1A−CdA−O1A[a]	93.1(4)	O11B−CdB−O12B	83.9(4)	O11C−CdC−O12C	81.0(4)
		O11B−CdB−O13B	115.3(4)	O11C−CdC−O13C	85.1(3)
		O12B−CdB−O13B	154.0(4)	O12C−CdC−O13C	90.5(4)
S1A−CdA−O1A	61.4(4)	S11B−CdB−O11B	59.1(3)	S11C−CdC−O11C	61.8(3)
S1A−CdA−O1A[a]	153.6(3)	S11B−CdB−O12B	106.1(3)	S11C−CdC−O12C	142.0(3)
S1A−CdA−O1A[b]	94.8(4)	S11B−CdB−O13B	99.1(4)	S11C−CdC−O13C	93.4(3)
		S12B−CdB−O11B	143.3(3)	S12C−CdC−O11C	96.9(3)
		S12B−CdB−O12B	61.4(3)	S12C−CdC−O12C	61.6(4)
		S12B−CdB−O13B	101.4(3)	S12C−CdC−O13C	151.0(3)
		S13B−CdB−O11B	88.3(3)	S13C−CdC−O11C	145.8(2)
		S13B−CdB−O12B	101.4(3)	S13C−CdC−O12C	100.6(3)
		S13B−CdB−O13B	63.9(3)	S13C−CdC−O13C	60.8(3)

[a] Symmetry operators: $1 - y, -1 + x - y, z$. [b] Symmetry operators: $2 - x + y, 1 - x, z$.

Table 4. Selected Structural Features of $[M(S\{O\}CPh)_3]^-$ (M = Zn, Cd, Hg) in Some Salts

cation, M	range of S−M−S angles (deg)	∑S−M−S (deg)	distance of M from S_3 plane (Å)	distance of M from O_3 plane (Å)	dihedral angle between S_3 and O_3 planes (deg)	ref
Ph_4P^+, Zn	110.96(6)−132.50(6)	359.8(1)	0.06	0.38	75.2	2
Ph_4As^+, Cd	108.50(6)−136.31(5)	360.0(1)	0.01	0.39	71.9	2
Me_4N^+, Cd[a]	114.73(8)−125.85(8)	355.0(1)	0.33	2.03	3.3[b]	1
Ph_4P^+, Cd (monoclinic, **1**-m)	111.32(7)−122.14(9)	354.2(1)	0.36	0.08	69.5	c
Ph_4P^+, Cd (rhombohedral, **1**-r)	111.1(2)[d]	333.3(6)[d]	0.77[d]	1.44[d]	0.0[d,e]	c
	108.7(2)−133.8(2)[f]	359.5(3)[f]	0.11[f]	0.32[f]	74.6[f]	
	113.1(2)−114.2(2)[g]	341.3(3)[g]	0.65[g]	1.56[g]	1.8[g,h]	
Ph_4P^+, Hg	101.59(8)−131.48(7)	359.9(1)	0.05	0.35	58.4	2
Me_4N^+, Hg	109.06(12)−137.98(12)	359.5(2)	0.10	0.41	66.8	3

[a] In $(Me_4N)[Na(Cd(S\{O\}CPh)_3)_2]$. [b] Twist angle, $\phi = 22(3)°$. [c] Present work. [d] Type A anion (see text). [e] Twist angle, $\phi = 36.5°$. [f] Type B anion (see text). [g] Type C anion (see text). [h] Twist angles $\phi = 29.3−35.5°$ (mean 33.0°).

(Supplementary Information). The ratio A:B:C = 3:9:9. Type C cations and type A anions are situated on 3-fold axes. Thus, type C cations are necessarily disordered,[20] but the cations are otherwise unexceptional.

The structures of the three distinct anions in **1**-r vary remarkably. The principal features of the anions are shown in Figure 2. All involve primary Cd−S bonding, at distances of 2.512(7) Å in anion A, 2.469(6)−2.592(6) Å in anion B and 2.519(5)−2.564(7) Å in anion C, and secondary Cd···O bonding, at distances of 2.640(15), 2.494(12)−2.669(13), and 2.459(18)−2.615(12) Å. The ratio of contributions of Cd···O to Cd−S bonding to the TBV is 0.19 (TBV = 2.12) in anion A, 0.24 (TBV = 2.13) in anion B, and 0.26 (TBV = 2.16) in anion C.

The structure of anion B is very similar to that of the anion in **1**-m (Figures 1 and 2b and Tables 2−4). It has a planar CdS_3 skeleton. In contrast, the CdS_3 skeletons of anions A and C are definitely pyramidal, as indicated by the sums of their S−Cd−S angles, 333.3(6) and 341.3(3)°.[21] On the basis of the different geometries of their primary, CdS_3, skeletons, we believe that anions A−C provide a new example of polytopal isomerism.[22,23]

The range of S−Cd−S angles in anion B lies between the ranges of the anions in **1**-m and **2** (Table 4). This presumably reflects the intermediate distance, 1.69 Å, of the nearest oxygen from the S_3 plane. In anions A and C, the $Cd_AS_3O_3$ and $Cd_CS_3O_3$ kernels have distorted *fac*-octahedral geometry. For anion A, symmetry dictates that the S_3 and O_3 planes are parallel, but the dihedral angle between the normals to the S_3 and O_3 planes is very small for anion C also (Table 4). Likewise, the twist angles, ϕ, between the S_3 and O_3 faces are similar for anions A and C and in both these anions the Cd atoms are closer to the S_3 face than to the O_3 face (Table 4) . The range of the S−Cd−S angles for anion C is very small by comparison with the ranges found in all previously reported discrete[21] $[M(thb)_3]^-$ (M = Zn-Cd) (Table 4). (Anion A has C_3 symmetry.) The

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(20) Disorder of Ph_4P^+ cations is rare. These cations are commonly locked into place by specific cation−cation interactions. See, for example: Dance, I. G.; Scudder, M. L. *J. Chem. Soc., Dalton Trans.* **1996**, 3755.

(21) The geometry of $[Cd(thb)_3]^-$ moieties found[1] in the trimetallic anion of $(Me_4N)(Na[Cd(thb)_3]_2)$ is closely related to those of anions A and C. Again the Cd lies between the S_3 and O_3 planes, although the Cd lies closer to the S_3 plane than in A and C, a difference attributable to bonding of the O atoms to Na^+.

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(23) Alternatively, the anions of different geometry can be described as *allogons*, while the single salt that contains them can be called an *interallogon*: Harrowfield, J. MacB.; Wild, S. B. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 1, Chapter 5, p 206ff.

small variation, and the overall pseudo-C_3 symmetry of the anion, probably reflect the minimalization of interligand S···O interactions when the S_3 and O_3 faces are separated by the intervening Cd atom (Figure 2c).

The structure of **1**-r shows that the $[Cd(thb)_3]^-$ anion has the extraordinary deformability or plasticity that has been termed *fictile*.[24] Fictility of cadmium complexes has been proposed earlier,[25] based on the range of Cd−S distances (2.475−2.537 Å) that is observed in $(Ph_4P)_2$[Cd(*trans*-1,2-S_2-cyclohexane$)_2$]·4H_2O.

The factors influencing the geometry of $[M(thb)_3]^-$ (M = Zn-Hg) remain a topic of considerable interest at UWO. What is clear from the present and previous results is that geometry change is not related simply to the *extent* of secondary M···O bonding, at least when M = Cd. Comparing the CdS_3 skeletons of the anion of **2** and the type A anion in **1**-r, for instance, the first is near-planar, while the second is definitely pyramidal. However, the contribution of Cd···O bonding to the TBV in these two anions is not significantly different (20 vs 19%). Whether the degree of pyramidalization of the MS_3 skeleton in $[M(tbt)_3]^-$ is related to the *directions* of the secondary MO interactions is an open question. Of the discrete anions,[21] only anions A and C of 1-r have distinctly pyramidal CdS_3 skeletons and only these two have all their O atoms restricted to one side of the S_3 plane. However, this might be an effect, rather than a cause, of the pyramidalization.

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Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, complete bond distances and angles, anisotropic thermal parameters, calculated hydrogen atom coordinates, least squares planes and deviations from them, and selected dihedral angles and close non-bonded contacts and a projection down *c* of the structure of rhombohedral $(Ph_4P)[Cd(S\{O\}CPh)_3]$ (**1**-r) (24 pages). Ordering information is given on any current masthead page.

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