Synthesis and Characterization of Dithiocarbonate Derivatives of Zinc and Cadmium Bis(dithiocarbamates)†

Ricardo Baggio,[a] **Alicia Frigerio,**[a] **Emilia B. Halac,**[a] **Daniel Vega**[a] **and Mireille Perec** *[,b]
[a] *Division Fisica del Solido, Departamento de Fisica, Comision Nacional de Energia Atomica, Avda del Libertador 8250, 1429 Buenos Aires, Argentina*
[b] *Departamento de Quimica Inorganica, Analitica y Quimica Fisica, Universidad de Buenos Aires, Ciudad Universitaria, Pabellon II, 1428 Buenos Aires, Argentina*

The mixed-ligand complexes $[NBu^n_4][Zn(S_2CNMe_2)_2(S_2COEt)]$ **1**, $[NBu^n_4][Cd(S_2CNEt_2)_2(S_2COEt)]$ **2** and $[PPh_4][Cd(S_2CNEt_2)_2(S_2COEt)]$ **3** have been prepared by direct addition of zinc and cadmium bis(dithiocarbamate) to the tetraalkylammonium or tetraphenylphosphonium dithiocarbonate salt in acetone at room temperature. The compounds were characterized by elemental analysis and infrared, Raman, and ^1H NMR spectroscopy. The crystal structures of **1** and **3** were determined: **1**, orthorhombic, space group *Pbca* (no. 61), $a = 20.140(5)$, $b = 16.570(4)$, $c = 21.453(5)$ Å and $Z = 8$; **3**, orthorhombic, space group $Pna2_1$ (no. 33), $a = 19.027(5)$, $b = 13.829(3)$, $c = 15.938(4)$ Å and $Z = 4$. The environment about zinc is a distorted trigonal bipyramid with a monodentate dithiocarbonate ligand in an equatorial position and the dithiocarbamate ligands spanning one axial and one equatorial position each. The cadmium environment is a distorted six-co-ordinate trigonal prism. The metal–sulfur modes are assigned empirically at 218 (Zn–S) and at 165 cm^{-1} (Cd–S). The thermal degradation of solids **1** and **2** affords ZnS and CdS, respectively.

There has lately been renewed interest in the synthesis and characterization of unusual mononuclear zinc(II)– and cadmium(II)–sulfur co-ordination units as structural models for likely binding sites in certain metalloproteins[1–3] and in photoelectrochemical devices.[4]

Mononuclear tetrathiolate complexes of Zn^{II} and Cd^{II} are scarce and usually distorted tetrahedral,[5–13] although trigonal-planar[1,2] $[Zn(SR)_3]^-$ and $[Cd(SR')_3]^-$, where R = C_6HMe_4-2,3,5,6 and R′ = $C_6H_2Pr^i_3$-2,4,6 and square-planar[3] $[Cd(i\text{-mnt})_2]^{2-}$ (i-mnt = dimercaptomethylenemalononitrile) have recently been reported. Anionic adducts with the versatile dithioacid donors dithiocarbamates ($S_2CNR_2^-$), *O*-ethyl dithiocarbonate (S_2COEt^-) and the phosphorodithioates $[S_2P(OC_6H_4Me\text{-}p)_2]^-$ and $S_2PPh_2^-$ have been extensively studied.[14] Distorted-tetrahedral[15a,b] $[Zn(S_2CNMe_2)_3]^-$ and $[Zn(S_2PR_2)_3]^-$ (R = OC_6H_4Me-*p* or Ph), octahedral or trigonal-prismatic[15c] $[Cd(S_2CNEt_2)_3]^-$ and $[Cd\{S_2P(OPr^i)_2\}_3]^-$ and the unusual square-pyramidal[16] $[Cd(S_2COEt)_3]^-$ geometry have been established by X-ray diffraction.

The study of mononuclear five-co-ordinate zinc complexes and its relevance to the catalytic action of zinc metalloenzymes is currently an active area of research. Zinc complexes with N_3O_2 ligand cores have been investigated as model compounds for the carbonic anhydrase catalytic cycle.[17–19] It has been suggested that, in zinc-containing proteins and enzymes, the formation of five-co-ordinate zinc intermediates involving sulfur donors only might also take place.[20] To our knowledge, ZnS_5 units have been achieved only through sulfur bridging in various dimeric[14] $[\{Zn(S_2CNR_2)_2\}_2]$ and more recently in dimeric[20] $[\{Zn[Ph(MeS)C{=}C(S)Ph]_2\}_2]$. Complexes with CdS_5 co-ordination units have been found in more complex polymeric structures.[21]

Herein, we report the reactions leading to two novel dithiocarbamate/dithiocarbonate mixed-ligand complexes of Zn and Cd with two dithiocarbamate and one dithiocarbonate bound to the same metal centre. The results of this study include the X-ray structural determinations of $[NBu^n_4][Zn(S_2CNMe_2)_2(S_2COEt)]$ and $[PPh_4][Cd(S_2CNEt_2)_2(S_2COEt)]$. The zinc adduct is of particular interest as it constitutes the first model compound for a mononuclear ZnS_5 unit.

Results and Discussion

The zinc and cadmium complexes $[NBu^n_4][Zn(S_2CNMe_2)_2(S_2COEt)]$ **1**, $[NBu^n_4][Cd(S_2CNEt_2)_2(S_2COEt)]$ **2** and $[PPh_4][Cd(S_2CNEt_2)_2(S_2COEt)]$ **3** have been prepared in high yield by direct addition of the zinc or cadmium bis(dialkyldithiocarbamate) and tetra-*n*-butylammonium or tetraphenylphosphonium dithiocarbonate in equimolar amounts in acetone solution. The solid compounds are stable when kept in a dry atmosphere and solubility is limited to the more polar solvents such as acetonitrile, dichloromethane, and acetone. While complexes **1** and **2** have been used for the vibrational study and thermolysis, **1** and **3** were used for the X-ray structural analysis. No single crystals suitable for X-ray studies could be obtained for the complexes of Zn and Cd with a common cation.

Description of Structures.—Crystal data for the complexes $[NBu^n_4][Zn(S_2CNMe_2)_2(S_2COEt)]$ **1** and $[PPh_4][Cd(S_2CNEt_2)_2(S_2COEt)]$ **3** are given in Table 1 and final atomic co-ordinates in Table 2. The molecular structures including the atomic numbering schemes are shown in Figs. 1 and 2. Relevant interatomic distances and angles are listed in Table 3. The zinc atom in **1** is co-ordinated to one sulfur atom of the dithiocarbonate ligand and to the four sulfur atoms of the two bidentate dithiocarbamate ligands. The Zn–S bond length for the unidentate dithiocarbonate is 2.316(7) Å and the distance from the Zn atom to the second sulfur dithiocarbonate atom is 4.798(8) Å, evidently a non-interaction. To our knowledge this is the first example of a zinc complex in which the dithiocarbonate ligand is co-ordinated in the unidentate fashion and should be of interest with respect to the reactivity studies of the uncoordinated sulfur atom. The S_2CO group is fairly planar

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

and the C–S bond lengths are 1.71(2) Å for the bonded S atom and 1.64(2) Å for the non-bonded S atom, similar to the values found for the unidentate ligand in $[Cd(S_2COEt)_3]^-$.[16] The dithiocarbamate ligands exhibit a wide range of Zn–S distances with one ligand being more symmetrically bonded than the other [2.366(7)–2.540(7) and 2.301(7)–2.932(7) Å]. The first three values are within the ranges reported for Zn–S bonds in a number of relevant four- and five-co-ordinate complexes with different sulfur donor ligands.[22] However, the long Zn–S bond distance of 2.932(7) Å is the longest so far observed for a Zn–S bond in a mononuclear unit. It is significantly longer than the sum of the covalent radii (2.33 Å) but shorter than the van der Waals distance[23] (3.27 Å), and is certainly indicative of a weak bonding interaction.

The constraint at the zinc atom may be conveniently described by the index parameter[24] τ, defined as [S(31)–Zn–S(22) − S(11)–Zn–S(32)/60]. The calculated value of 0.7 describes a type of structure which is 70% along the pathway of distortion from ideal square-pyramidal (τ = 0) toward ideal trigonal-bipyramidal geometry (τ = 1). Ths sulfur atoms S(11), S(21) and S(32) define the equatorial plane, and the Zn atom is 0.253(3) Å above this plane pointing towards S(31). The Zn–S(31) and Zn–S(22) axial bonds show an average deviation of 20° from the normal to the equatorial plane, which may be attributed to the acute bite angles of the spanning dithiocarbamate ligands, 73.6(2) and 67.4(2)°, the larger bite angle corresponding to the less-distorted ligand. The equatorial Zn–S bonds are significantly shorter than the axial bonds, and the resulting shape is a rough trigonal-bipyramid compressed along the equatorial belt. The shortening of the equatorial Zn–S bonds occurs at the expense of the axial bonds, and the dithiocarbamate ligands are forced to become more monodentate in nature. The structure found here for complex **1** supports recent theoretical calculations, showing that five-co-ordinate zinc(II) complexes of the type ML_5 are favoured when the incoming fifth ligand is anionic and located at an equatorial site with short zinc–ligand bonds.[17] An interesting comparison

Table 1 Crystal data for $[NBu^n{}_4][Zn(S_2CNMe_2)_2(S_2COEt)]$ **1** and $[PPh_4][Cd(S_2CNEt_2)_2(S_2COEt)]$ **3**

	1	**3**
Formula	$C_{25}H_{53}N_3OS_6Zn$	$C_{37}H_{45}CdN_2OPS_6$
M	668.4	868.4
Crystal symmetry	Orthorhombic	Orthorhombic
Space group	*Pbca* (no. 61)	$Pna2_1$ (no. 33)
a/Å	20.140(5)	19.027(5)
b/Å	16.570(4)	13.829(3)
c/Å	21.453(5)	15.938(4)
U/Å^3	7159(2)	4194(1)
Z	8	4
D_c/g cm^{-3}	1.240	1.375
F(000)	2864	1792
Crystal dimensions/mm	0.25 × 0.12 × 0.12	0.24 × 0.15 × 0.10
μ(Mo-Kα)/cm^{-1}	18.1	16.8
Total no. reflections	3626	2357
No. unique data	1556 [$I > 3.5\,\sigma(I)$]	1212 [$I > 2.5\,\sigma(I)$]
R	0.089	0.065
R′	0.095	0.067
Weighting scheme	$2.46/[\sigma^2(F) + 0.0034F^2]$	$1.63/[\sigma^2(F) + 0.0014F^2]$

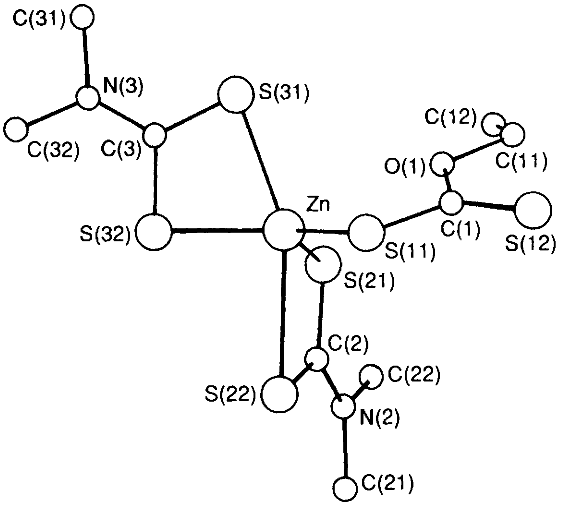

Fig. 1 Structure of the anion $[Zn(S_2CNMe_2)_2(S_2COEt)]^-$ and its numbering scheme

Table 2 Fractional atomic coordinates for $[NBu^n{}_4][Zn(S_2CNMe_2)_2(S_2COEt)]$ **1** and $[PPh_4][Cd(S_2CNEt_2)_2(S_2COEt)]$ **3**

	1			**3**		
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*X*/*a*	*Y*/*b*	*Z*/*c*
M	0.138 7(1)	0.089 3(2)	0.158 0(1)	0.159 1(1)	0.054 0(2)	0.000 0
S(11)	0.061 1(3)	0.190 7(4)	0.172 7(3)	0.157 9(3)	−0.118 1(4)	−0.073 4(4)
S(12)	−0.017 2(4)	0.284 9(4)	0.082 0(4)	0.276 7(3)	−0.069 0(4)	0.033 4(4)
S(21)	0.206 2(3)	0.086 6(4)	0.071 5(3)	0.179 0(3)	0.143 3(4)	−0.151 4(4)
S(22)	0.254 9(3)	0.194 6(4)	0.170 6(3)	0.228 5(3)	0.216 4(4)	0.011 2(5)
S(31)	0.078 8(3)	−0.045 6(4)	0.156 3(3)	0.125 3(3)	0.024 1(4)	0.164 1(4)
S(32)	0.167 1(3)	0.022 8(4)	0.251 9(3)	0.026 6(3)	0.086 4(4)	0.036 4(4)
O(1)	0.040 4(9)	0.145(1)	0.062 2(8)	0.257(1)	−0.237(1)	−0.039(1)
N(2)	0.307(1)	0.184(1)	0.058(1)	0.255(1)	0.304(1)	−0.134(1)
N(3)	0.115(1)	−0.124(1)	0.259(1)	−0.008(1)	0.067(1)	0.194(1)
C(1)	0.017(2)	0.207(1)	0.100(1)	0.234(1)	−0.143(1)	−0.028(1)
C(2)	0.260(1)	0.157(1)	0.098(1)	0.222(1)	0.226(1)	−0.097(1)
C(3)	0.118(1)	−0.056(1)	0.225(1)	0.044(1)	0.059(1)	0.140(1)
C(11)	0.017(2)	0.152(2)	−0.002(1)	0.302(2)	−0.309(2)	0.002(2)
C(12)	0.056(2)	0.094(2)	−0.041(2)	0.363(2)	−0.258(2)	−0.038(2)
C(21)	0.355(1)	0.247(2)	0.073(1)	0.321(1)	0.340(3)	−0.097(2)
C(22)				0.277(1)	0.426(2)	−0.073(2)
C(23)	0.314(2)	0.149(2)	−0.005(1)	0.239(1)	0.316(1)	−0.224(1)
C(24)				0.306(1)	0.275(1)	−0.262(1)
C(31)	0.080(1)	−0.195(2)	0.237(1)	0.000(1)	0.023(1)	0.278(1)
C(32)				0.021(2)	0.103(2)	0.336(2)
C(33)	0.148(2)	−0.134(2)	0.319(1)	−0.076(1)	0.117(1)	0.186(2)
C(34)				−0.119(1)	0.033(1)	0.155(2)

Table 3 Relevant interatomic distances (Å) and angles (°) for $[NBu^n_4][Zn(S_2CNMe_2)_2(S_2COEt)]$ **1** and $[PPh_4][Cd(S_2CNEt_2)_2(S_2COEt)]$ **3**

	1	**3**		**1**	**3**
M–S(11)	2.316(7)	2.653(6)	C(2)–S(22)	1.69(2)	1.73(2)
M–S(12)	4.798(8)	2.861(6)	C(3)–S(31)	1.69(2)	1.67(2)
M–S(21)	2.301(7)	2.737(6)	C(3)–S(32)	1.74(2)	1.73(2)
M–S(22)	2.932(7)	2.611(5)	O(1)–C(11)	1.47(3)	1.47(4)
M–S(31)	2.540(7)	2.725(6)	C(11)–C(12)	1.50(5)	1.51(5)
M–S(32)	2.366(7)	2.625(6)	N(2)–C(21)	1.46(3)	1.47(3)
M–O(1)	2.992(7)		C(21)–C(22)		1.50(4)
C(1)–O(1)	1.33(3)	1.38(2)	N(2)–C(23)	1.48(4)	1.48(2)
C(2)–N(2)	1.35(4)	1.39(2)	C(23)–C(24)		1.51(4)
C(3)–N(3)	1.34(4)	1.32(3)	N(3)–C(31)	1.46(3)	1.48(2)
C(1)–S(11)	1.71(2)	1.65(2)	C(31)–C(32)		1.50(4)
C(1)–S(12)	1.64(2)	1.63(2)	N(3)–C(33)	1.46(4)	1.47(2)
C(2)–S(21)	1.70(2)	1.65(2)	C(33)–C(34)		1.50(3)
S(11)–M–S(12)		63.6(3)	C(11)–O(1)–C(1)	117(2)	141(3)
S(11)–M–S(21)	121.6(3)	91.0(3)	C(21)–N(2)–C(2)	125(3)	119(2)
S(11)–M–S(22)	95.4(2)	143.7(2)	C(23)–N(2)–C(2)	121(2)	114(2)
S(11)–M–S(31)	108.6(2)	106.6(2)	C(31)–N(3)–C(3)	122(3)	119(2)
S(11)–M–S(32)	112.6(2)	104.0(2)	C(33)–N(3)–C(3)	124(2)	131(2)
S(12)–M–S(21)		108.9(2)	S(11)–C(1)–O(1)	112(2)	115(1)
S(12)–M–S(22)		95.9(2)	S(12)–C(1)–O(1)	124(2)	121(1)
S(12)–M–S(31)		85.2(2)	S(21)–C(2)–N(2)	118(2)	123(3)
S(12)–M–S(32)		144.2(2)	S(22)–C(2)–N(2)	121(2)	116(3)
S(21)–M–S(22)	67.4(2)	66.6(2)	S(31)–C(3)–N(3)	123(2)	125(2)
S(21)–M–S(31)	104.6(2)	161.3(2)	S(32)–C(3)–N(3)	118(2)	118(2)
S(21)–M–S(32)	122.3(2)	104.5(2)	C(21)–N(2)–C(23)	115(2)	122(2)
S(22)–M–S(31)	154.8(2)	100.6(2)	C(31)–N(3)–C(33)	115(3)	111(2)
S(22)–M–S(32)	90.3(3)	108.9(2)	O(1)–C(11)–C(12)	108(2)	87(2)
S(31)–M–S(32)	73.6(2)	65.6(2)	N(2)–C(21)–C(22)		84(2)
S(11)–C(1)–S(12)	124(1)	125(2)	N(2)–C(23)–C(24)		100(2)
S(21)–C(2)–S(22)	122(1)	120(2)	N(3)–C(31)–C(32)		106(2)
S(31)–C(3)–S(32)	119(1)	118(1)	N(3)–C(33)–C(34)		98(2)

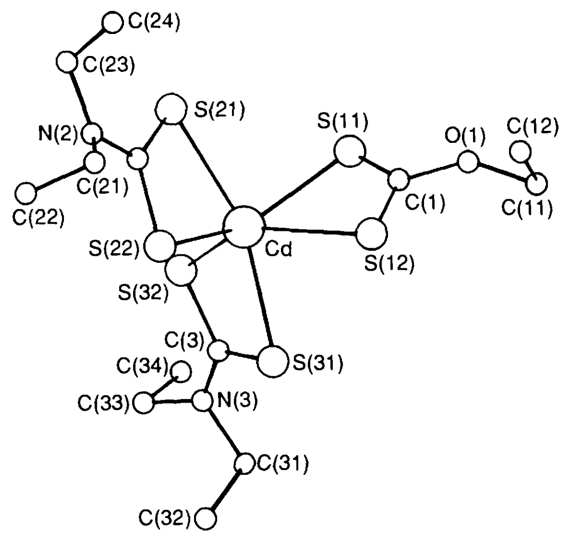

Fig. 2 Structure of the anion $[Cd(S_2CNEt_2)_2(S_2COEt)]^-$ and its numbering scheme

can be made with the structure of the related $[Zn(S_2CNMe_2)_3]^-$,[15a] where only one ligand is allowed to remain bidentate [2.422(2)–2.457(2) Å] and the other two adopt formally unidentate co-ordination [2.299(2) and 2.312(2) Å]. Although other factors cannot be excluded, the different binding of the dithiocarbonate compared with the dithiocarbamate ligand may reflect the lower ability of the former to transfer electron density to the metal centre.[25] It appears that the electron density on the zinc atom in **1** is just compensated by the lengthening of the axial Zn–S bonds, whereas in $[Zn(S_2CNMe_2)_3]^-$ the addition of the strong $S_2CNMe_2^-$ donor necessitates removal of excess of electron density on the metal atom through stabilization of a four-co-ordinate structure. The oxygen atom of the dithiocarbonate ligand in **1** is oriented towards the Zn atom, and is found in the nearest non-bonding position to the metal at 2.99 Å, somewhat longer than the van der Waals distance (2.90 Å). A similar affinity has been found in $[Cd(S_2COEt)_3]^-$, where the cadmium is co-ordinated by five sulfur atoms and an additional intramolecular Cd···O contact of 2.956(8) Å, which in this case is within the van der Waals distance (3.10 Å).

In complex **3** the larger cadmium atom allows a more regular co-ordination of the three ligands in their bidentate fashion. It is worthwhile to compare the Cd–S distances in **3** with those in the related homoleptic $[Cd(S_2CNEt_2)_3]^-$ and $[Cd(S_2COEt)_3]^-$. The average short and long Cd–S bond lengths of the bidentate dithiocarbamate ligands are 2.618(6) and 2.731(6) Å, whereas in $[Cd(S_2CNEt_2)_3]^-$ the corresponding values are 2.680(3) and 2.742(3) Å, respectively. Thus, there is a shortening of the short bonds of the dithiocarbamate ligands with the long bonds remaining nearly equal. The Cd–S bond lengths for the dithiocarbonate ligand are 2.653(6) and 2.861(6) Å whereas in $[Cd(S_2COEt)_3]^-$ the values for the more asymmetric ligand are 2.647(5) and 2.716(5) Å. respectively. In this case there is a lengthening of the long Cd–S distance with the short bond remaining nearly the same. The only structure previously reported for a mixed-ligand dithiocarbamate/dithiocarbonate complex is that of $[Te(S_2CNEt_2)(S_2COEt)]$, of trapezoidal-planar geometry.[26] The dithiocarbamate ligand was also found more tightly bound to the metal atom than the dithiocarbonate, but with the two Te–S bonds to the dithiocarbamate ligand shorter than in $Te(S_2CNEt_2)_2$ and the two Te–S bonds to the dithiocarbonate ligand longer than in $Te(S_2COEt)_2$. The CdS_6 co-ordination polyhedron shows a large departure from an octahedral configuration[27] and is best described as a trigonal prism with the two triangular faces relatively twisted by approximately 26°. The carbon–sulfur distances of the dithiocarbonate ligand are almost equivalent [1.65(2) and 1.63(2) Å] and similar to those found in other bidentate metal dithio-

Table 4 Selected features (in cm^{-1}) in the vibrational spectra of $[Zn(S_2CNMe_2)_2(S_2COEt)]^-$ and $[Cd(S_2CNEt_2)_2(S_2COEt)]^-$ *

$[Zn(S_2CNMe_2)_2(S_2COEt)]^-$		$[Cd(S_2CNEt_2)_2(S_2COEt)]^-$		
IR	Raman	IR	Raman	Assignment
1490s (br)		1484s (br)	1500vs	ν(CN)
1255s		1270vs		ν(NR)
1180vs		1210s		ν(COR)
		1172m		
1130vs (br)		1142s		ν(COR)
		1132s		
		1114s		
		1077m		
1050vs		1047s		ν(COR)
989s		998s		ν(CS)
975(sh)	968m		973m	ν(CS)
			900m	
	670s		670m	ν(CS)
570m	570vs	560s	556s	ν(CS)
218s	516m			
193(sh)	208m			ν(Zn–S)
		165s (br)		ν(Cd–S)

* s, m, v, w, sh and br refer to strong, medium, very, weak, shoulder and broad, respectively.

carbonates.[16] Angles and other metric parameters of the ligands and cations in **1** and **3** are unexceptional.

Vibrational Spectra.—Selected IR and Raman vibrational frequencies for the mixed-ligand complexes **1** and **2** are given in Table 4. The characteristic infrared features associated with the dithiocarbamate group $S_2CNR_2^-$ occur in the regions[28–30] 1550–1450 and 1050–950 cm^{-1} and those associated with the dithiocarbonate group S_2COEt^- in the regions[31,32] *ca.* 1200, 1100 and 1020 cm^{-1}, respectively. Also, prominent features are seen in the Raman effect at 570 and 670 cm^{-1} for **1** and at 556 and 670 cm^{-1} for **2** and because of their position and intensity are attributed to the ν(C–S) modes of $S_2CNR_2^-$ and S_2COEt^-, respectively. Since these bands are generally coupled modes and in addition obscured by the presence of other vibrations, they do not provide valuable information about the structure and bonding of the ligands.

The vibrations below 400 cm^{-1} include a strong IR doublet with maxima at 218 and 193 cm^{-1} for complex **1** and at 165 cm^{-1} for **2**. These bands are straightforwardly assigned to Zn–S and Cd–S modes since they are not found in the spectra of the reactants. The Raman counterparts are very weak lines, particularly in complex **2** probably due to a high degree of ionic character of the metal–ligand bonds. The present assignments are consistent with those recently reported by us[33] for five-coordinate $[Zn(S_2CNMe_2)_2X]^-$ (X = Cl, Br or NCS) and $[Cd(S_2CNEt_2)_2X]^-$ (X = Cl, Br, I or NCS). For these complexes the metal–sulfur modes were assigned in the ranges 226–205 (Zn–S) and 203–145 (Cd–S) cm^{-1}, respectively. The assignments of Zn–S and Cd–S modes may be of considerable practical interest for the characterization of zinc– and cadmium–sulfur structural units by vibrational spectroscopy, particularly due to the inertness of these d^{10} ions to other accessible spectroscopies.

Thermolysis.—Thermogravimetric analyses have been made for complexes **1** and **2**. The complexes are not volatile and they decompose in air to give the corresponding metal sulfides as shown by elemental analysis of metal and sulfur. Decomposition commences at 115 and 140 °C and mass is lost smoothly up to 250 and 310 °C, respectively. Complex **2** is only slightly more stable than **1** as evidenced by the temperature at which decomposition starts. The mass of solid residue from **1** and **2** after heating for 3 h at 400 °C corresponded within 3–4% to that required for ZnS (14.5%) and CdS (18.7%). The X-ray diffraction pattern of the ZnS showed broad peaks. The presence of the α-ZnS form is shown by the peak at d = 1.76 Å. However, the presence of the β-ZnS form cannot be excluded because of the broadness of the bands and the proximity of the α- and β-ZnS lines. The X-ray diffraction pattern of CdS shows sharp peaks characteristic of the α form with small sharp peaks of the β form. The preparation of ZnS and CdS by thermolysis at 260 °C of the polymeric methanethiolate complexes $[\{M(SMe)_2\}_n]$ (M = Zn or Cd) has recently been reported.[34] The rather mild conditions found here for the thermal degradation of **1** and **2**, together with their solubility in organic solvents, suggest that they may be promising materials for ZnS and CdS thin-film preparations.

Experimental

Starting Materials.—The complexes $[Zn(S_2CNMe_2)_2]$ and $[Cd(S_2CNEt_2)_2]$ were prepared by the reaction between the sodium salt of the *N,N*-dialkyldithiocarbamate ligand and the corresponding metal(II) chloride in water. The solid complexes $[M(S_2CNR_2)_2]$ precipitated immediately and were filtered while hot to remove the NaCl and any excess of unreacted $Na(S_2CNR_2)$. The solids were dried *in vacuo* at 80 °C. Recrystallization was from boiling benzene. The $[NBu^n_4]Cl$, $[PPh_4]Br$ and $K(S_2COEt)$ were purchased from Aldrich and used without further purification. The salt $[NBu^n_4][S_2COEt]$ in acetone solution was prepared by addition of $[NBu^n_4]Cl$ (5.56 g, 0.02 mol) in acetone (100 cm^3) to $K(S_2COEt)$ (3.20 g, 0.02 mol) in acetone (100 cm^3). The mixture was cooled to 0 °C and the KCl was filtered off. The filtrate was condensed to about 100 cm^3 in a rotary evaporator and used in this form in the following preparations. The salts $[NBu^n_4][S_2COEt]$ and $[PPh_4][S_2COEt]$ were similarly prepared.

Preparations.—$[NBu^n_4][Zn(S_2CNMe_2)_2(S_2COEt)]$ **1**. To a solution of $[NBu^n_4][S_2COEt]$ (3.64 g, 0.01 mol) in acetone (100 cm^3) at room temperature was added solid $[Zn(S_2CNMe_2)_2]$ (3.06 g, 0.01 mol) in small portions. The mixture was well stirred for 2 h and then filtered to remove any unreacted $[Zn(S_2CNMe_2)_2]$. Light petroleum (b.p. 60–80 °C) (50 cm^3) was added, and the mixture refrigerated at 0 °C for 2 d. A colourless crystalline product was collected by suction filtration in air, and dried. Recrystallization was from light petroleum–acetone (1:1) at room temperature. Yield: 5.4 g (80%) (Found: C, 44.75; H, 7.75; N, 6.00; S, 26.60; Zn, 9.75. Calc. for $C_{25}H_{53}N_3OS_6Zn$: C, 44.80; H, 8.00; N, 6.30; S, 28.70; Zn, 9.80%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.33 (t, 3 H, $\mathrm{S_2COCH_2C}H_3$), 3.48 [s, 6 H, $\mathrm{S_2CN(C}H_3)_2$] and 4.46 (q, 2 H, $\mathrm{S_2COC}H_2\mathrm{CH_3}$).

$[\mathrm{NBu^n}_4][\mathrm{Cd(S_2CNEt_2)_2(S_2COEt)}]$ **2**. To a solution of $[\mathrm{NBu^n}_4][\mathrm{S_2COEt}]$ (3.64 g, 0.01 mol) in acetone (100 cm^3) at room temperature was added powdered solid $[\mathrm{Cd(S_2CNEt_2)_2}]$ (4.09 g, 0.01 mol) in small portions. The mixture was well stirred for 1 h and then filtered to remove unreacted $[\mathrm{Cd(S_2CNEt_2)_2}]$. By slow evaporation of the reaction mixture at room temperature followed by drying over $\mathrm{P_4O_{10}}$ in a desiccator, $[\mathrm{NBu^n}_4][\mathrm{Cd(S_2CNEt_2)_2(S_2COEt)}]$ was obtained as a light cream solid. Recrystallization was from light petroleum–acetone (1 : 1) at room temperature. Yield: 5.40 g (70%) (Found: C, 45.10; H, 7.90; Cd, 14.60; N, 5.40; S, 24.90. Calc. for $\mathrm{C_{29}H_{61}CdN_3OS_6}$: C, 45.00; H, 8.00; Cd, 14.55; N, 5.40; S, 24.90%). ^{1}H NMR (25 °C, $\mathrm{CDCl_3}$): 1.22 [t, 6 H, $\mathrm{S_2CN(CH_2C}H_3)_2$], 1.43 (t, 3 H. $\mathrm{S_2COCH_2C}H_3$), 3.94 [q, 4 H, $\mathrm{S_2CN(C}H_2\mathrm{CH_3})_2$] and 4.45 (q, 2 H, $\mathrm{S_2COC}H_2\mathrm{CH_3}$).

$[\mathrm{PPh_4}][\mathrm{Cd(S_2CNEt_2)_2(S_2COEt)}]$ **3**. This complex was synthesized in an analogous manner from $[\mathrm{PPh_4}]\mathrm{Br}$ (2.10 g, 0.005 mol) and $[\mathrm{Cd(S_2CNEt_2)_2}]$ (2.05 g, 0.005 mol). Slow evaporation of the acetone reaction mixture afforded well shaped light cream crystals. Yield: 3.90 g (90%) (Found: C, 51.15; H, 5.30; Cd, 13.00; N, 3.25; S, 22.00. Calc. for $\mathrm{C_{37}H_{45}CdN_2OPS_6}$: C, 51.10; H, 5.20; Cd, 12.90; N, 3.20; S, 22.10%).

Physical Measurements.—Microanalyses and ^{1}H NMR spectra in $\mathrm{CDCl_3}$ at 100 MHz on a Varian HA100 spectrometer were performed at UMYMFOR (Unidad de Microanalisis y Metodos Fisicos Organicos). Analyses of zinc and cadmium were carried out by atomic absorption spectroscopy at the Analytical Division of the Department of Inorganic Chemistry. Infrared spectra were recorded on a Beckman 4260 grating spectrophotometer and in the 530–50 cm^{-1} range with a Fourier Digilab FTS-18C. Readings were calibrated with polystyrene film and water vapour. The samples were studied as Nujol and halogeno carbon mulls supported between CsI and polyethylene disks; KBr pellets were also run and no significant differences were observed. Raman spectra of pressed powdered solids were obtained from a Jarrel Ash 25-300 spectrophotometer equipped with a Coherent Radiation 52G argon-ion laser. The laser power of the 5145 Å excitation line measured at the solid samples was *ca.* 100 mW. Scattered radiation was observed at 90° to the incident beam and the spectral slit width was conveniently adjusted at different frequency ranges. The estimated accuracy in the positions of the IR and Raman wavenumbers is ± 2 cm^{-1}. Thermogravimetry (TG) diagrams were recorded on a Mettler TG-50 thermal analyser in a dynamic atmosphere of pure air at a heating rate of 5° min^{-1}.

Crystal Structure Determinations.—Crystals of complexes **1** and **3** were grown by slow evaporation of acetone–light petroleum (b.p. 40–60 °C) (1:1) solutions of the compounds. Intensity data were collected at 293 °C on a Nonius CAD4 diffractometer, by the ω–2θ scan technique in the range $4 < 2\theta < 50°$, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å). The data sets were empirically corrected for absorption, after convergence of the isotropic refinement had been achieved.[35] The structures were solved by conventional direct and Fourier methods using SHELX 86[36] and refined with SHELX 76[37] by full-matrix least squares with anisotropic thermal parameters for Zn, Cd and S and isotropic thermal parameters for all other atoms, until parameter shifts were less than 0.1 times their estimated standard deviations (e.s.d.s). The scattering factors and anomalous scattering coefficients used were those provided by the programs for the lighter atoms, and those from ref. 38 for zinc and cadmium. The $[\mathrm{NBu^n}_4]^+$ and $[\mathrm{PPh_4}]^+$ cations could only be solved by imposing constraints on the C–N, C–P and C–C bond lengths. All hydrogen atoms were included in their idealized positions in the final stages of refinement.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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