Anionic Halide and Isothiocyanate Adducts of Zinc and Cadmium Dithiocarbamates †

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The mixed-ligand complexes $[NEt_4][Zn(S_2CNMe_2)_2X]$ (X = Cl, Br, or NCS) and $[NR_4][Cd(S_2CNEt_2)_2X]$ (R = Et, X = Cl, Br, or NCS; R = Bu^n, X = I) have been prepared by reaction of zinc and cadmium bis(dithiocarbamate) with the tetraalkylammonium salt of the halide or thiocyanate in acetone at room temperature. The single-crystal X-ray structures of $[NEt_4][Zn(S_2CNMe_2)_2(NCS)]$ **1** and $[NEt_4][Cd(S_2CNEt_2)_2(NCS)]$ **2** were determined: **1**, monoclinic, space group $P2_1/n$, a = 9.447(1), b = 16.661(2), c = 15.807(1) Å, β = 97.10(1)° and Z = 4; **2**, orthorhombic, space group $P2_12_12_1$, a = 16.213(1), b = 17.501(2), c = 10.243(1) Å and Z = 4. The central Zn and Cd atoms show distorted trigonal-bipyramidal co-ordination geometry with the thiocyanate N atom occupying an equatorial position and the dithiocarbamate ligands spanning one axial and one equatorial position each. The infrared and Raman spectra (2100–50 cm^{-1}) of the complexes are discussed. The metal–sulfur stretching frequencies are assigned in the ranges 226–205 (Zn–S) and 203–145 cm^{-1} (Cd–S), respectively.

The sulfur-bridged zinc and cadmium bis(dithiocarbamate) dimers $[\{M(S_2CNR_2)_2\}_2]$ (M = Zn or Cd) are known to be cleaved by the potentially chelating dithiocarbamate $(S_2CNR_2^-)$ and benzothiazole-2-thiolate $(C_7H_4NS_2^-)$ anions to give mononuclear adducts,[1,2] whereas acetate anion affords a binuclear zinc adduct.[3] Crystallographic studies of a number of these complexes showed significant distortions from regular four- and five-fold symmetry in the Zn-containing adducts and more regular six-fold symmetry in the cadmium compounds.[4] Only a few zinc and cadmium mixed halide–dithiocarbamate complexes are known. The series $[Zn(S_2CNMe_2)X_2]^-$ (X = Cl, Br, or I) and $[Cd(S_2CNEt_2)I_2]^-$ have been synthesised, while attempts to add a second $S_2CNMe_2^-$ to the former afforded insoluble $[Zn(S_2CNMe_2)_2]$ only.[5] More recently, the preparation and crystal structure of polymeric $[Cd(S_2CNEt_2)I]\infty$, in which the cadmium atom is five-co-ordinated by two sulfur and three iodine atoms, has been described.[6]

In this paper we report the reactions of the zinc and cadmium bis(dithiocarbamate) dimers with monodentate Cl$^-$, Br$^-$, I$^-$ and NCS$^-$ ligands to give 1:1 adducts $[Zn(S_2CNMe_2)_2X]^-$ (X = Cl, Br, or NCS) and $[Cd(S_2CNEt_2)_2X]^-$ (X = Cl, Br, I, or NCS). All these complexes were isolated as their $[NEt_4]^+$ or $[NBu^n_4]^+$ salts and characterized by microanalysis and by spectroscopic techniques. The X-ray crystal structures of $[NEt_4][Zn(S_2CNMe_2)_2(NCS)]$ and of $[NEt_4][Cd(S_2CNEt_2)_2(NCS)]$ were determined in order to examine the effect of the NCS$^-$ co-ordination on the immediate environment of the zinc and cadmium atoms.

Results and Discussion

The synthesis of the 1:1 adducts $[NEt_4][Zn(S_2CNMe_2)_2X]$ (X = Cl, Br, or NCS) and $[NR_4][Cd(S_2CNEt_2)_2X]$ (R = Et, X = Cl, Br, or NCS; R = Bu^n, X = I) is readily achieved from
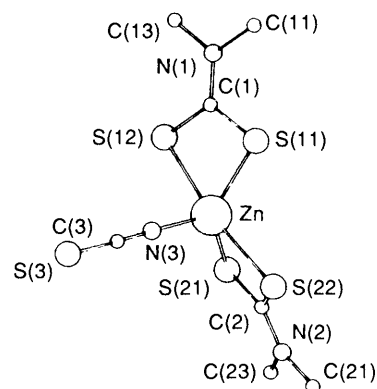

Fig. 1 Structure of the anion $[Zn(S_2CNMe_2)_2(NCS)]^-$ and its numbering scheme
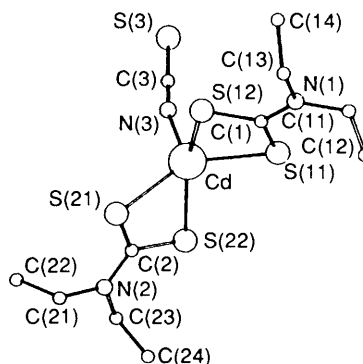

Fig. 2 Structure of the anion $[Cd(S_2CNEt_2)_2(NCS)]^-$ and its numbering scheme

the appropriate tetraalkylammonium salt of the ligand X and the neutral zinc(II) or cadmium(II) bis(dithiocarbamate) in acetone at room temperature. Attempts to obtain the iodide adduct from $[NBu^n_4]I$ and $[Zn(S_2CNMe_2)_2]$ under similar

Table 1 Crystal data for $[NEt_4][Zn(S_2CNMe_2)_2(NCS)]$ **1** and $[NEt_4][Cd(S_2CNEt_2)_2(NCS)]$ **2**

	1	2
Formula	$C_{15}H_{32}N_4S_5Zn$	$C_{19}H_{40}CdN_4S_5$
M	436	538
Crystal symmetry	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
$a/\text{Å}$	9.447(1)	16.213(1)
$b/\text{Å}$	16.661(2)	17.501(2)
$c/\text{Å}$	15.807(1)	10.243(1)
$\alpha/°$	90	90
$\beta/°$	97.10(1)	90
$\gamma/°$	90	90
$U/\text{Å}^3$	2468.8(3)	2906.3 (3)
Z	4	4
$D_c/\text{g cm}^{-3}$	1.18	1.24
Crystal size (mm)	$0.15 \times 0.20 \times 0.35$	$0.10 \times 0.30 \times 0.50$
$F(000)$	1032	1232
Data collection range, $2\theta/°$	4–50	4–50
Ranges h, k, l	-1 to 15, 0 to 20, -19 to 19	-1 to 20, -1 to 21, -1 to 13
Unique data	2435 $[I > 3.5\sigma(I)]$	2229 $[I > 2.5\sigma(I)]$
R	0.0678	0.0372
R'	0.0759	0.0356

Table 2 Fractional atomic coordinates for $[NEt_4][Zn(S_2CNMe_2)_2(NCS)]$ **1** and $[NEt_4][Cd(S_2CNEt_2)_2(NCS)]$ **2**

	1			2		
Atom	X/a	Y/b	Z/c	X/a	Y/b	Z/c
M	0.0197(1)	0.2824(1)	0.1503(1)	0.2477(1)	0.2316(1)	0.6700(1)
S(11)	0.0758(2)	0.3560(1)	0.2744(1)	0.2761(1)	0.4782(2)	0.6557(1)
S(12)	$-0.1117(2)$	0.2145(1)	0.2724(2)	0.3711(1)	0.2983(2)	0.7551(1)
S(21)	$-0.1715(3)$	0.3036(2)	0.0452(2)	0.2884(1)	0.0138(2)	0.6029(1)
S(22)	0.1125(3)	0.3734(2)	0.0362(2)	0.1684(1)	0.1833(2)	0.5345(2)
S(3)	0.3141(3)	0.0585(2)	0.1153(2)	0.0519(2)	0.2441(4)	0.8875(2)
N(1)	$-0.0155(7)$	0.2961(4)	0.4131(4)	0.3990(4)	0.5521(6)	0.7385(4)
N(2)	$-0.102(1)$	0.3816(5)	$-0.0898(5)$	0.1970(4)	$-0.0543(7)$	0.4792(4)
N(3)	0.1409(9)	0.1894(5)	0.1367(5)	0.1615(5)	0.207(1)	0.7682(5)
C(1)	$-0.0163(8)$	0.2888(5)	0.3293(5)	0.3534(4)	0.4530(7)	0.7178(4)
C(2)	$-0.056(1)$	0.3556(6)	$-0.0106(6)$	0.2159(4)	0.0375(8)	0.5340(4)
C(3)	0.212(1)	0.1356(6)	0.1270(5)	0.1174(5)	0.2218(9)	0.8170(5)
C(11)	0.067(1)	0.3602(6)	0.4611(6)	0.3861(5)	0.6864(8)	0.7068(6)
C(12)				0.4257(5)	0.709(1)	0.6257(6)
C(13)	$-0.095(1)$	0.2393(7)	0.4622(6)	0.4668(5)	0.533(1)	0.7909(6)
C(14)				0.4489(7)	0.549(1)	0.8805(7)
C(21)	$-0.004(2)$	0.4254(8)	$-0.1390(8)$	0.2373(7)	$-0.181(1)$	0.4736(6)
C(22)				0.192(1)	$-0.283(1)$	0.5187(8)
C(23)	$-0.249(2)$	0.3666(9)	$-0.1309(8)$	0.1326(5)	$-0.040(1)$	0.4213(6)
C(24)				0.1560(7)	0.025(1)	0.3438(7)
N(4)*	0.0787(7)	0.0724(4)	0.7814(4)	0.4043(3)	0.2665(6)	0.3749(3)
C(411)*	0.127(2)	0.1294(8)	0.8532(8)	0.3985(5)	0.247(1)	0.4671(4)
C(412)*	0.014(2)	0.1396(9)	0.9143(8)	0.4456(6)	0.346(1)	0.5174(6)
C(421)*	0.057(1)	$-0.0106(6)$	0.8179(9)	0.3532(7)	0.164(1)	0.3371(7)
C(422)*	0.194(2)	$-0.0462(8)$	0.8683(9)	0.3530(9)	0.171(2)	0.2420(7)
C(431)*	0.198(1)	0.065(1)	0.727(1)	0.4860(4)	0.251(1)	0.3464(6)
C(432)*	0.153(2)	0.014(1)	0.646(1)	0.5210(7)	0.115(1)	0.3641(8)
C(441)*	$-0.056(1)$	0.979(8)	0.7266(8)	0.3765(6)	0.4011(8)	0.3513(8)
C(442)*	$-0.041(2)$	0.1856(8)	0.6963(9)	0.2953(6)	0.436(1)	0.3805(8)

* Atom refined with constraint.

conditions were not successful. All the compounds are stable colourless crystalline solids when kept in a dry atmosphere and are moderately soluble in organic solvents such as acetone, chloroform and dichloromethane.

Description of the Structures.—Crystal data for the complexes $[NEt_4][Zn(S_2CNMe_2)_2(NCS)]$ **1** and $[NEt_4][Cd(S_2-CNEt_2)_2(NCS)]$ **2** are given in Table 1 and final atomic coordinates in Table 2. Figs. 1 and 2 show the anions and the atomic numbering schemes. Selected bond distances and angles are given in Table 3. Both molecules are monomeric with five-

coordinate MS_4N (M = Zn or Cd) units in which the metal atom is co-ordinated to the four S atoms of the dithiocarbamate ligands and to the N atom of the thiocyanate ligand. The overall geometry of the ligand donor atoms around the metal is that of a distorted trigonal bipyramid. The metal atom lies in a trigonal plane determined by the two sulfur atoms S(11) and S(21), one from each dithiocarbamate ligand, and by the N atom from the thiocyanate ligand. The co-ordination sphere around the zinc in complex **1** is analogous to that found in the neutral pyridine adduct[7] $[Zn(S_2CNMe_2)_2(py)]$, but different to the square-based pyramid in the binuclear $[\{Zn(S_2CNMe_2)_2\}_2$-

Table 3 Interatomic bond distances (Å) and angles (°) for [NEt$_4$]-[Zn(S$_2$CNMe$_2$)$_2$(NCS)] **1** and [NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$(NCS)] **2**

	1	**2**
M–S(11)	2.319(2)	2.585(2)
M–S(12)	2.672(3)	2.650(2)
M–S(21)	2.325(4)	2.582(2)
M–S(22)	2.591(1)	2.647(3)
M–N(3)	1.954(9)	2.208(8)
C(1)–N(1)	1.33(1)	1.33(1)
C(2)–N(2)	1.35(1)	1.34(2)
C(3)–N(3)	1.14(1)	1.12(1)
C(1)–S(11)	1.718(8)	1.707(8)
C(1)–S(12)	1.718(8)	1.724(7)
C(2)–S(21)	1.72(2)	1.708(8)
C(2)–S(22)	1.70(1)	1.709(8)
C(3)–S(3)	1.64(2)	1.635(9)
N(1)–C(11)	1.48(1)	1.49(2)
N(1)–C(13)	1.49(1)	1.47(1)
N(2)–C(21)	1.47(1)	1.48(1)
N(2)–C(23)	1.48(2)	1.47(1)
C(11)–C(12)		1.50(1)
C(13)–C(14)		1.50(1)
C(21)–C(22)		1.50(2)
C(23)–C(24)		1.48(2)
N(4)–C(411)	1.51(1)	1.512(8)
N(4)–C(421)	1.52(1)	1.51(1)
N(4)–C(431)	1.50(2)	1.51(1)
N(4)–C(441)	1.51(1)	1.51(2)
C(411)–C(412)	1.53(2)	1.55(1)
C(421)–C(422)	1.55(2)	1.54(2)
C(431)–C(432)	1.55(2)	1.55(1)
C(441)–C(442)	1.55(2)	1.54(2)
S(11)–M–S(12)	71.99(9)	68.84(7)
S(11)–M–S(21)	126.9(1)	138.89(5)
S(11)–M–S(22)	102.6(1)	102.02(6)
S(12)–M–S(21)	101.0(2)	102.60(6)
S(12)–M–S(22)	168.0(2)	155.15(6)
S(21)–M–S(22)	73.4(2)	68.45(6)
N(3)–M–S(11)	115.9(2)	107.9(3)
N(3)–M–S(12)	94.3(3)	102.2(2)
N(3)–M–S(21)	117.1(2)	113.2(2)
N(3)–M–S(22)	97.7(3)	102.6(2)
S(11)–C(1)–S(12)	118.1(5)	119.2(4)
S(21)–C(2)–S(22)	119.0(6)	118.8(4)
C(11)–N(1)–C(1)	121.1(8)	121.8(7)
C(13)–N(1)–C(1)	121.4(7)	121.7(7)
C(21)–N(2)–C(2)	120(1)	122.8(7)
C(23)–N(2)–C(2)	122(1)	122.9(7)
S(11)–C(1)–N(1)	120.2(7)	120.6(6)
S(12)–C(1)–N(1)	121.7(6)	120.2(5)
S(21)–C(2)–N(2)	119.2(7)	121.3(7)
S(22)–C(2)–N(2)	121.8(9)	119.9(6)
C(11)–N(1)–C(13)	117.5(8)	116.4(7)
C(21)–N(2)–C(23)	118(1)	114.4(7)
S(3)–C(3)–N(3)	178.9(8)	179.2(9)

(μ-OCOMe)]$^-$ and to the rectangular-based pyramid [Zn-(S$_2$CNMe$_2$)$_2$(C$_7$H$_4$NS$_2$)]$^-$, where the O and the N ligand donor atoms are apically bonded.

The dithiocarbamate ligands in each molecule are nearly planar and normal to the equatorial plane, being asymmetrically attached to the metal ion through one short equatorial and one long axial M–S bond. Ligand bond distances and angles are regarded as normal. For comparison, Table 4 lists the main metal–sulfur bond distances in **1** and **2** and in a few other selected compounds of various co-ordination geometries. The average Zn–S and Cd–S bond distances are clearly correlated with the metal co-ordination number. The difference between the longest and the shortest Zn–S bonds in **1** is 0.353 Å, whereas the corresponding value for the Cd–S bonds in **2** is only 0.068 Å. The wide range of Zn–S bond lengths is similar to that found in [Zn(S$_2$CNMe$_2$)$_2$(py)] and shows that addition

of NCS$^-$ or py to the parent [Zn(S$_2$CNMe$_2$)$_2$] brings about a strong increase in the asymmetry of the bidentate co-ordination of the S$_2$CNMe$_2$ ligands. The shortest Zn–S bonds approach the values given for tetrahedral units, suggesting that the zinc ion prefers stronger bonds to a lower number of sulfur sites at the expense of the dithiocarbamate ligands becoming more monodentate. The small distortion of the Cd–S bonds in **2** shows a tendency for the larger Cd atom to form longer and weaker bonds to all co-ordinated ligands.

The thiocyanate-N group is essentially linear in complexes **1** and **2**. The Zn–N [1.954(9) Å] and the Cd–N [2.208(8) Å] bonds are at the lower end of the ranges 2.083–1.923 and 2.259–2.212 Å reported for relevant zinc and cadmium complexes with terminal Zn–NCS and Cd–NCS bonds.[11] The former is significantly shorter than the sum of the covalent radii (2.06 Å) and than the values for [Zn(S$_2$CNMe$_2$)$_2$(py)] (2.097 Å) and [NBu$^n_4$][Zn(S$_2$CNMe$_2$)$_2$(C$_7$H$_4$NS$_2$)] (2.06 Å). The main departures from trigonal symmetry in complex **1** are the S(11)–Zn–S(21) angle of 126.9(1)° instead of 120°, and the deviation of the axial Zn–S bonds by 18° from the normal to the equatorial plane. The corresponding values in complex **2** are 138.89(5) and 22.0°, respectively. These deviations may be largely attributed to the acute bite angles of the spanning dithiocarbamate ligands, mean 72.7° in **1** and 68.6° in **2**.

The MS$_4$N structural units in complexes **1** and **2** are very similar in spite of the different affinities of the zinc(II) and cadmium(II) ions towards the 'hard' and 'soft' ends of the NCS$^-$ ligand,[12,13] and the known propensity of cadmium to form oligomeric species with sulfur ligands. Actually, all the Zn ⋯ S and Cd ⋯ S intermolecular distances in complexes **1** and **2** are well above the van der Waals distances. It would seem that the thiocyanate addition compensates the co-ordinative unsaturation of the zinc and cadmium atoms and there is no need for additional long metal–sulfur interactions similar to those found in a number of related adducts. It is to be noted that in the six-co-ordinate MS$_4$N$_2$ units of complexes with bidentate nitrogen ligands [Zn(S$_2$CNBu$_2$)$_2$(phen)],[14] [Cd(S$_2$CNEt$_2$)$_2$(phen)] (phen = 1,10-phenanthroline) and [Cd(S$_2$CNEt$_2$)$_2$(bipy)] (bipy = 2,2′-bipyridine)[15] the average bond lengths are systematically longer than the values here reported for the MS$_4$N units and that the dithiocarbamate ligands in [Zn(S$_2$CNBu$_2$)$_2$(phen)] are symmetrically bonded.

Vibrational Analysis.—The IR and Raman spectra of the co-ordination compounds clearly show the presence of dithiocarbamate and isothiocyanate or halide (Cl$^-$, Br$^-$, I$^-$) ligands. Selected vibrational frequencies are listed in Table 5. Complexes **1** and **2** show the ν(C–N), ν(C–S) and δ(NCS) modes of the thiocyanate anion at *ca.* 2100, 785 and 475 cm^{-1} respectively, consistent with the presence of thiocyanate-N groups in both complexes.[17] The distinct vibrational features in the region of *ca.* 1500 and 1000 cm^{-1} may be associated with the prevailing contribution of the S$_2$C–NR$_2$ and C–S modes of the dithiocarbamate ligands, regardless of the nature of the ligand bonding.[18–20] The low-frequency absorption bands at 250 and 248 cm^{-1} shown in Fig. 3 are easy to assign to the Zn–N and Cd–N modes, since no vibrations appear in this range for the reactants. The value of ν(Zn–N) is about the same as that reported[12] for the tetrahedral solids Zn(NCS)$_2$ and [Zn-(NCS)$_4$]$^{2-}$. This suggests a strong Zn–N bond in complex **1** which is in accordance with the rather short bond distance found [1.954(9) Å]. The ν(Cd–N) value is 50 cm^{-1} higher than in polymeric Cd(SCN)$_2$ where the Cd^{II} is octahedrally co-ordinated to four S and two *trans* N atoms.[12,16] The difference is consistent with the lower co-ordination number in complex **2**. The next vibrational features below 250 cm^{-1} are assigned to the Zn–S and Cd–S modes. They occur as a strong IR band at 226 cm^{-1} (Zn–S) and as a medium Raman line at 203 cm^{-1} (Cd–S), nearly at the same positions as those found for the bis(dithiocarbamates) of Zn and Cd.[21]

The vibrational spectra of the mixed halide–dithiocarbamate

Table 4 Bond distances (Å) Zn–S and Cd–S for distinct co-ordination units in selected compounds

Compound	Unit	M–S av.	M–S Maximum	M–S Minimum	Range	Ref.
[NPr$^n_4$][Zn(SC$_6$HMe$_4$-2,3,5,6)$_3$]	ZnS$_3$	2.23	2.243	2.217	0.026	8
[NMe$_4$]$_2$[Zn(SPh)$_4$]	ZnS$_4$	2.357	2.378	2.344	0.034	9
[NPr$^n_4$][Zn(SC$_6$HMe$_4$-2,3,5,6)$_3$(mim)]^a	ZnS$_3$N	2.36	2.351	2.298	0.053	10
[Zn(S$_2$CNMe$_2$)$_2$]	ZnS$_4$	2.362	2.429	2.312	0.117	4, b
[Zn(S$_2$CNMe$_2$)$_2$(py)]	ZnS$_4$N	2.466	2.612	2.330	0.282	7
[NEt$_4$][Zn(S$_2$CNMe$_2$)$_2$(NCS)]	ZnS$_4$N	2.477	2.672	2.319	0.353	This work
[NBu$^n_4$][Cd(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_3$]	CdS$_3$	2.420	2.428	2.419	0.009	8
[NMe$_4$]$_2$[Cd(SPh)$_4$]	CdS$_4$	2.541	2.556	2.531	0.025	9
[NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$(NCS)]	CdS$_4$N	2.616	2.650	2.582	0.068	This work

^{a} mim = 1-Methylimidazole. ^{b} The additional M–S in the dimer is excluded.

Table 5 Selected infrared and Raman bands (cm^{-1}) of [Zn(S$_2$CNMe$_2$)$_2$X]$^-$ (X = NCS, Cl, or Br) and [Cd(S$_2$CNEt$_2$)$_2$X]$^-$ (X = NCS, Cl, Br, or I)^a

Complex	NCS$^-$ ligand v(C–N)	v(C–S)	δ(NCS)	S$_2$CNR$_2$$^-$ ligand v(C–N)	v(C–S)	v(M–X)	v(M–S)
[NEt$_4$][Zn(S$_2$CNMe$_2$)$_2$(NCS)]	2092vs 2060m	788m	478m	1512s 1488s	982s 975m	250s	226s
[NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$(NCS)]	2078vs	785m	475w 465w	1492vs	994vs	248s	200w [203m] [191(sh)]
[NEt$_4$][Zn(S$_2$CNMe$_2$)$_2$Cl]				1485s	997s	280s	215m
[NEt$_4$][Zn(S$_2$CNMe$_2$)$_2$Br]				1510s	998s	205s	205s^b
[NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$Cl]				1489s	996s	250s	163mw
[NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$Br]				1489s	1008m 996s	170s	152(sh)
[NBu$_4$][Cd(S$_2$CNEt$_2$)$_2$I]				1487s	997m	145(vbr)^c	
[Zn(S$_2$CNMe$_2$)$_2$]^d				1530s 1520m	978s		228s
[Cd(S$_2$CNEt$_2$)$_2$]^d				1505s	994s		193ms

^{a} All Raman lines coincide with infrared bands within ± 10 cm^{-1}, and are not included. Only relevant lines are given in square brackets. s, m, v, w, sh and br refer to strong, medium, very weak, shoulder and broad, respectively. ^{b} Assumed overlapped. ^{c} Unresolved broad band, centred at about 145 cm^{-1}. ^{d} Ref. 21.
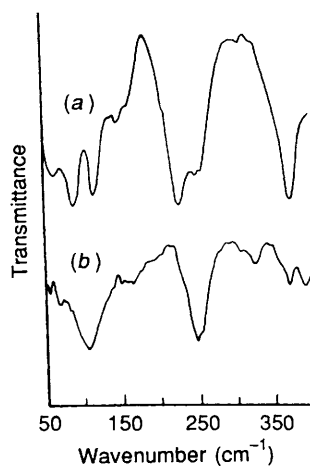
Fig. 3 Far IR spectra of (a) [NEt$_4$][Zn(S$_2$CNMe$_2$)$_2$(NCS)] and (b) [NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$(NCS)]

complexes reveal only minor differences in the range 4000–300 cm^{-1}. The M–X vibrations are readily attributed to terminal bonds through the steady shift to lower frequency with the change to heavier halogen, Cl ⟶ Br ⟶ I, Fig. 4 and 5. The Zn–Cl and Zn–Br modes are assigned at 280 and 205 cm^{-1} respectively, showing the usual v(Zn–Br)/v(Zn–Cl) ratio of 0.74:1 given in ref. 17 for terminal bonds. The Cd–Cl, Cd–Br and Cd–I modes are assigned here at 250, 170 and 145 cm^{-1}

respectively, with the last two strongly overlapped by Cd–S modes. Systematic studies of Cd–X (X = Cl, Br, or I) modes in complexes of known structures are very limited. Terminal Cd–Cl modes in octahedral complexes have been assigned[22] below 200 cm^{-1} and in the trigonal-bipyramidal complex [CdCl$_5$]$^{3-}$ at 251 and at 236 cm^{-1}.[17] For tetrahedral complexes terminal Cd–I modes have been found in the 170–140 cm^{-1} range.[23] These assignments are consistent with those given in Table 5 for the chloride and iodide adducts. The bands assignable to the Zn–S and Cd–S stretching modes are found at 210 ± 5 cm^{-1} for the zinc complexes and at 155 ± 10 cm^{-1} for the cadmium complexes. The v(M–S) are well resolved only for the chloride adducts; for the bromide and iodide adducts strong overlapping with v(M–X) occurs and the assignments are more uncertain. It is clear, however, that the v(Zn–S) and the v(Cd–S) values are lower than the corresponding modes in the NCS$^-$ adducts, and decrease on going from Cl$^-$ to I$^-$. Although on the basis of the above spectroscopic data alone we cannot exclude the presence of sulfur- or halide-bridged dimers, they appear to support the presence of mononuclear units.

In conclusion, the vibrational features assigned here to the Zn–S and Cd–S bonds in the MS$_4$X units lie in the ranges 226–205 and 203–145 cm^{-1}, just below the 267–225 and 237–203 cm^{-1} reported for the tetrahedral MS$_4$ units in the thiourea[24] and dithiocarbamate complexes. We recently assigned the Zn–S and the Cd–S vibrations of the largely distorted tetrahedral [Zn(S$_2$CNMe$_2$)$_3$]$^-$ and the nearly octahedral [Cd(S$_2$CNEt$_2$)$_3$]$^-$ to the low-frequency bands at 206 and at 150 cm^{-1}, respectively.[21] For the thiolate complexes [M(SPh)$_4$]$^{2-}$ (M = Zn or Cd) with distorted-tetrahedral
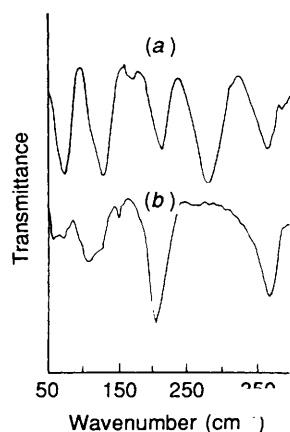
Fig. 4 Far IR spectra of (a) [NEt$_4$][Zn(S$_2$CNMe$_2$)$_2$Cl] and (b) [NEt$_4$][Zn(S$_2$CNMe$_2$)$_2$Br]
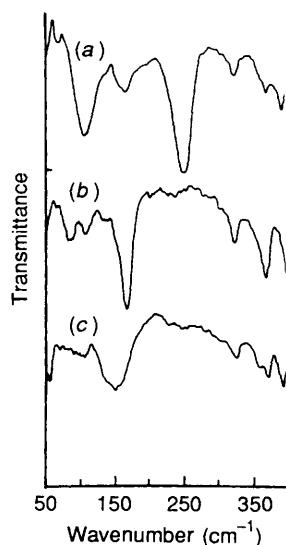
Fig. 5 Far IR spectra of (a) [NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$Cl], (b) [NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$Br] and (c) [NBu$_4$][Cd(S$_2$CNEt$_2$)$_2$I]

structures the Zn–S and the Cd–S modes were assigned at 200 and at 180 cm^{-1} respectively,[9,25] while for [Cd$_{10}$(SCH$_2$CH$_2$-OH)$_{16}$]$^{4+}$ where four-, five-, and six-co-ordinate cadium atoms are present the Cd–S modes have been reported[26] at 197 and 160 cm^{-1}. These correlations of ν(M–S) with stereochemistry and co-ordination number might be used to determine the nature of the Zn–S and Cd–S bonds in related compounds.

Experimental

Preparation of Compounds.—The complexes [Zn(S$_2$-CNMe$_2$)$_2$] and [Cd(S$_2$CNEt$_2$)$_2$] were prepared according to reported methods[4] and recrystallized twice from boiling benzene. Acetone solutions of [NEt$_4$][NCS] were prepared by addition of [NEt$_4$]Cl (3.00 g, 0.01 mol) in acetone (100 cm^3) to KNCS (1.00 g, 0.001 mol) in acetone (100 cm^3). The KCl formed was removed by filtration and the filtrate evaporated *in vacuo* to a volume of *ca.* 100 cm^3.

[NEt$_4$][Zn(S$_2$CNMe$_2$)$_2$(NCS)]. To a solution of [NEt$_4$][NCS] (1.00 g, 0.01 mol) in acetone (100 cm^3) at room temperature was added powdered solid [Zn(S$_2$CNMe$_2$)$_2$] (3.00 g, 0.01 mol) in small portions with stirring (*ca.* 1 h). The solution was filtered to remove traces of a yellow solid, and allowed to stand overnight at 0 °C. The product separated as colourless crystals. Recyrstallization was from acetone at room temperature. Yield: 2.80 g, 70% (Found: C, 36.3; H, 6.2; N, 11.2;

S, 32.1; Zn, 14.1. C$_{15}$H$_{32}$N$_4$S$_5$Zn requires C, 36.4; H, 6.5; N, 11.3; S, 32.45; Zn, 13.2%).

[NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$(NCS)]. This was prepared by the same procedure from [NEt$_4$][NCS] (1.00 g, 0.01 mol) and [Cd(S$_2$CNEt$_2$)$_2$] (4.00 g, 0.01 mol). Reaction mixtures containing a ten-fold excess of [NEt$_4$][NCS] under similar conditions afforded the same adduct. Yield: 3.90 g, 78% (Found: C, 38.3; H, 6.5; Cd, 19.8; N, 9.2; S, 27.25. C$_{19}$H$_{40}$CdN$_4$S$_5$ requires C, 38.2; H, 6.75; Cd, 18.8; N, 9.4; S, 26.8%).

[NEt$_4$][Zn(S$_2$CNMe$_2$)$_2$Cl]. To a solution of [NEt$_4$][Cl] (1.70 g, 0.01 mol) in acetone (100 cm^3) was slowly added solid [Zn(S$_2$CNMe$_2$)$_2$] (3.00 g, 0.01 mol) at room temperature with constant stirring. The resulting mixture was filtered after 4 h, and the filtrate was left at 0 °C for 48 h. Colourless crystals of the product were isolated by filtration and washed with light petroleum. Yield: 4.60 g, 98% (Found: C, 35.4; H, 6.65; Cl, 7.6; N, 8.65; S, 27.0; Zn, 14.0. C$_{14}$H$_{32}$ClN$_3$S$_4$Zn requires C, 35.65; H, 6.8; Cl, 7.5; N, 8.9; S, 27.2; Zn, 13.9%).

[NEt$_4$][Zn(S$_2$CNMe$_2$)$_2$Br]. This was made similarly from [NEt$_4$][Br] (2.10 g, 0.01 mol) and [Zn(S$_2$CNMe$_2$)$_2$] (3.00 g, 0.01 mol). Yield: 2.04 g, 40% (Found: C, 32.8; H, 6.15; Br, 15.0; N, 8.0; S, 25.0; Zn, 12.9. C$_{14}$H$_{32}$BrN$_3$S$_4$Zn requires C, 32.6; H, 6.3; Br, 15.5; N, 8.1; S, 24.9; Zn, 12.7%).

[NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$Cl]. This complex was prepared in an identical manner to its zinc analogue using [NEt$_4$][Cl] (1.70 g, 0.01 mol) and [Cd(S$_2$CNEt$_2$)$_2$] (4.00 g, 0.01 mol). Yield: 5.23 g, 93% (Found: C, 37.20; H, 7.00; Cd, 20.20; Cl, 6.35; N, 7.20; S, 22.55. C$_{18}$H$_{40}$CdClN$_3$S$_4$ requires C, 37.60; H, 7.00; Cd, 19.55; Cl, 6.20; N, 7.30; S, 22.35%).

[NEt$_4$][Cd(S$_2$CNEt$_2$)$_2$Br]. This complex was also obtained in an identical manner to its zinc analogue from [NEt$_4$][Br] (2.10 g, 0.01 mol) and [Cd(S$_2$CNEt$_2$)$_2$] (4.00 g, 0.01 mol). Yield: 2.62 g, 43% (Found: C, 34.65; H, 6.25; Br, 13.15; Cd, 19.05; N, 6.55; S, 21.00. C$_{18}$H$_{40}$BrCdN$_3$S$_4$ requires C, 34.90; H, 6.50; Br, 12.90; Cd, 18.15; N, 6.80; S, 20.70%).

[NBu$_4$][Cd(S$_2$CNEt$_2$)$_2$I]. To a solution of [NBu$_4$][I] (3.70 g, 0.01 mol) in acetone (100 cm^3) kept in an ice-bath was added powdered [Cd(S$_2$CNEt$_2$)$_2$] (4.00 g, 0.01 mol) with stirring. The solution was evaporated *in vacuo* to *ca.* 50 cm^3 and left overnight at 0 °C. The product separated as white flakes. Yield: 3.08 g, 40% (Found: C, 40.25; H, 7.65; Cd, 15.25; I, 16.50; N, 5.20; S, 16.85. C$_{26}$H$_{56}$CdIN$_3$S$_4$ requires C, 40.10; H, 7.25; Cd, 14.45; I, 16.30; N, 5.40; S, 16.50%).

Crystal Structure Determinations.—Crystals of complexes **1** and **2** suitable for X-ray analysis were grown by the slow evaporation of acetone–hexane solutions of the compounds. Intensity data were collected at 298 K on a Nicolet P3 automatic diffractometer, by the ω–2θ scan technique, using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å).

The usual Lorentz polarization corrections were applied. The data sets were also empirically corrected for absorption, after convergence of the isotropic refinement had been achieved.[27] The structures were solved by conventional direct and Fourier methods using SHELXS 86 [28] and refined with SHELX 76 [29] by full-matrix least squares with anisotropic thermal parameters, until parameter shifts were less than 0.1 times their estimated standard deviations (e.s.d.s). Weights were assigned according to the formula $w = 1/[\sigma^2(F) + kF^2]$, where $k = 6 \times 10^{-4}$ for Zn and 6×10^{-5} for Cd. The scattering factors and anomalous scattering coefficients used were those provided by the programs for the lighter atoms, and those from ref. 30 for zinc and cadmium. The terminal alkyl groups in the ligand molecules, as well as the NEt_4^+ cations, were found to be rather mobile, with very large mean-square amplitudes. The latter posed some problems in refinement, which could only be solved by imposing constraints on the C–N and C–C bond lengths. Methyl and ethyl hydrogen atoms were included in their idealized positions in the final stages of refinement.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

References

1 J. A. McCleverty, N. J. Morrison, N. Spencer, C. C. Ashworth, N. A. Bailey, M. R. Johnson, J. M. A. Smith, B. A. Tabbiner and C. R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1980, 1945.

2 J. A. McCleverty, S. Gill, R. S. Z. Kowalski, N. A. Bailey, H. Adams, K. W. Lumbard and M. A. Murphy, *J. Chem. Soc., Dalton Trans.*, 1982, 493.

3 J. A. McCleverty, N. Spencer, N. A. Bailey and S. L. Shackelton, *J. Chem. Soc., Dalton Trans.*, 1980, 1939.

4 D. Coucouvanis, *Prog. Inorg. Chem.*, 1970, 11, 234; 1979, 22, 301.

5 J. A. McCleverty and N. J. Morrison, *J. Chem. Soc., Dalton Trans.*, 1976, 2169.

6 A. K. Duhme, S. Pohl and H. Strasdeit, *Inorg. Chim. Acta*, 1990, 175, 5.

7 K. A. Fraser and M. M. Harding, *Acta Crystallogr.*, 1967, 22, 75.

8 R. A. Santos, E. S. Gruff, S. A. Koch and G. S. Harbison, *J. Am. Chem. Soc.*, 1991, 113, 469.

9 N. Ueyama, T. Sugawara, K. Sasaki, A. Nakamura, S. Yamashita, Y. Wakatsuki, H. Yamazaki and N. Yasuoka, *Inorg. Chem.*, 1988, 27, 741.

10 E. S. Gruff and S. A. Koch, *J. Am. Chem. Soc.*, 1989, 111, 8762.

11 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, SI.

12 I. Persson, A. Iverfeldt and S. Ahrland, *Acta Chem. Scand., Ser. A*, 1981, 35, 295.

13 W. G. Haanstra, W. L. Driessen, J. Reedijk, U. Turpeinen and R. Hamalainen, *J. Chem. Soc., Dalton Trans.*, 1989, 2309.

14 N. A. Bell, E. Johnson, L. A. March, S. D. Mardsen, I. W. Nowell and Y. Walker, *Inorg. Chim. Acta*, 1989, 156, 205.

15 C. Airoldi, S. F. De Oliveira, S. G. Ruggiero and J. R. Lechat, *Inorg. Chim. Acta*, 1990, 176, 103.

16 R. G. Goel, W. P. Henry and R. Srivastava, *Inorg. Chem.*, 1981, 20, 1727; R. G. Goel, *Spectrochim. Acta, Part A*, 1981, 37, 557.

17 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley-Interscience, New York, 1986, Part III-15.A.

18 F. Bonati and R. Ugo, *J. Organomet. Chem.*, 1967, 10, 257.

19 D. Brown, W. K. Glass and M. A. Burke, *Spectrochim. Acta, Part A.*, 1976, 32, 137.

20 R. Kellner, G. St. Nikolov and N. Trendafilova, *Inorg. Chim. Acta*, 1984, 84, 233.

21 A. Frigerio, B. Halac and M. Perec, *Inorg. Chim. Acta*, 1989, 164, 149.

22 G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.

23 M. Goldstein and W. D. Unsworth, *J. Mol. Struct.*, 1972, 14, 451.

24 D. M. Adams and J. B. Cornell, *J. Chem. Soc. A*, 1967, 428; D. M. Adams and M. A. Hooper, *J. Chem. Soc., Dalton Trans.*, 1972, 631.

25 G. I. Dance, A. Choy and M. L. Scudder, *J. Am. Chem. Soc.*, 1984, 106, 62.

26 R. A. Haberkorn, L. Que, jun., W. O. Gillum, R. H. Holm, C. S. Liu and R. C. Lord, *Inorg. Chem.*, 1976, 15, 2048.

27 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, 39, 158.

28 G. M. Sheldrick, SHELXS 86, in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985, p. 175.

29 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

30 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.