Aspects of the Inorganic Chemistry of Rubber Vulcanisation. Part 3.[1] Anionic Cadmium Complexes derived from Dialkyldithiocarbamates, 2-Mercaptobenzothiazole and its Derivatives, and Dialkyl Dithiophosphates, and the Crystal and Molecular Structures of $[NBu^n_4][Cd(S_2CNEt_2)_3]$, $[NEt_4][Cd(C_7H_4NS_2)_3]$, and $[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$ †

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The reactions of $[CdI_2\{(S_2CNEt_2)_2\}]$ with certain Lewis bases are described, and the complexes $[NBu^n_4][CdI_2(S_2CNEt_2)]$, $[NR_4][Cd(S_2CNR'_2)_3]$ (R = Me or Bu^n; R' = Me, Et, Bu^n, or NHNMe$_2$), $[NR_4][Cd(OCOMe)(S_2CNEt_2)_2]$, (R = Me or Bu^n), $[\{Cd(S_2CNHNMe_2)_2\}_n]$, $[Cd(py)_2(6\text{-}RC_7H_3NS_2)_2]$ (R = H or EtO, py = pyridine), $[Cd(6\text{-}EtOC_7H_3NS_2)_2]$, $[NBu^n_4][Cd(C_7H_4NS_2)_n(6\text{-}EtOC_7H_3NS_2)_{3-n}]$ (n = 0—3), $[NBu^n_4][Cd(C_7H_4NS_2)_2(S_2CNEt_2)]$, and $[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$ have been prepared. The structures of the title compounds have been determined crystallographically. All three anions have geometries intermediate between trigonal-prismatic and octahedral; in the second, the $C_7H_4NS_2^-$ ligand is bound to the metal *via* the N and the exocyclic S (thiolate) atoms. These structures are compared with those of the corresponding zinc complexes and $[Cd(S_2COEt)_3]^-$.

In previous papers in this series [1-3] we have described the formation and structures of anionic zinc dithiocarbamato-, benzothiazole-2-thiolato- ($C_7H_4NS_2^-$), dithiophosphato-, and dithiophosphinato-complexes. These compounds may be important in the activation of sulphur during zinc-accelerated vulcanisation of 'diene' rubbers, § and could be produced during the complicated reactions between zinc oxide, organosulphur accelerators [*e.g.* $(\text{-}S_2CNR_2)_2$, $C_7H_5NS_2$, or $C_7H_4NS_2\text{-}NR_2$], stearic or other fatty acids, and rubber which constitute the 'sulphurating mixture' in the preliminary stages of the vulcanisation process.

Our work so far has been concerned with the identification, isolation, and characterisation of species which could be present in the 'sulphurating mixture' and which might be catalyst precursors for the activation of S_8 towards attack on rubber hydrocarbons. Clearly, a detailed knowledge of the behaviour of these species in solution, particularly in hydrocarbons, would significantly improve our understanding of this catalytic process. As can be readily appreciated, zinc complexes of dithiocarbamates and $C_7H_4NS_2^-$ have no convenient 'spectroscopic handle' which can be used effectively to study their solution properties. However, dithiophosphate and -phosphinate complexes can be used in ^{31}P n.m.r. studies, and we have briefly described [3] some of our work in this area. In pursuing other model systems of potential spectroscopic use, we have prepared a series of cadmium analogues of the zinc sulphur-ligand complexes described earlier. These species can be employed in ^{111}Cd and/or ^{113}Cd n.m.r. spectral studies and, as a preliminary to these investigations, we describe herein the syntheses, properties, and structures of selected dithiocarbamato-, benzothiazole-2-thiolato-, and dithiophosphato-complexes of cadmium.

Cadmium species can accelerate the vulcanisation of 'diene' rubbers, although they are not commercially important. Cadmium bis(dithiocarbamate) complexes have been described [4] and a brief report of the behaviour of $[Cd(S_2CNMe_2)_3]^-$ in polar solvents, as studied electrochemically, has appeared.[5] The structure of the related *O*-ethyl dithiocarbonate (xanthate) complex, $[Cd(S_2COEt)_3]^-$, has also been reported.[6]

† Tetra-n-butylammonium tris(diethyldithiocarbamato-*SS'*)cadmate, tetraethylammonium tris(benzothiazole-2-thiolato-*NS'*)cadmate, and tetramethylammonium tris(*OO'*-di-isopropyl dithiophosphato-*SS'*)cadmate respectively.

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§ 'Diene' rubbers are those species based on or derived from polyisoprene, polybutadiene, polyacrylonitrile, styrene–butadiene block co-polymers, *etc.*

EXPERIMENTAL

Infrared spectra were recorded using Perkin-Elmer 457 and 180 spectrophotometers. The ^1H n.m.r. spectra were obtained using JEOL PFT-90 and Perkin-Elmer R-34 instruments. Elemental analyses were determined by the Microanalytical Laboratory of this Department.

The compounds $[NR_4][S_2CNR'_2]$ (R = Me, R' = Bu^n; R = Bu^n, R' = Me) and $[NBu^n_4][C_7H_4NS_2]$ were prepared as described previously.[1,7]

Di-iodo(tetraethylthiuram disulphide)cadmium, $[CdI_2\{(S_2CNEt_2)_2\}]$.—To a solution of $[Cd(S_2CNEt_2)_2]$ (4.08 g, 0.01 mol) in chloroform (100 cm^3) was added, dropwise with vigorous stirring, a solution of iodine (2.56 g, 0.01 mol). The resulting solution was evaporated to low bulk and n-pentane was added. After standing, cream needles of the *complex* separated and were collected by filtration, washed with diethyl ether, and dried *in vacuo* (quantitative yield).

Reactions of $[CdI_2\{(S_2CNEt_2)_2\}]$.—*With* 1,2-*diaminoethane*. To a solution of $[CdI_2\{(S_2CNEt_2)_2\}]$ (0.66 g) in chloroform (25 cm^3) was added dropwise a solution of 1,2-diaminoethane (0.06 g) in chloroform (5 cm^3). A white powder precipitated which was collected by filtration, washed with chloroform and diethyl ether, and dried *in vacuo*. The complex, $[Cd(NH_2CH_2CH_2NH_2)_3][CdI_4]$, was characterised by elemental analysis.

With pyridine. To a solution of $[CdI_2\{(S_2CNEt_2)_2\}]$

(0.66 g) in chloroform (25 cm^3) was added dropwise a solution of pyridine (0.08 g) in chloroform (5 cm^3). Diethyl ether (60 cm^3) was then added and the mixture was allowed to stand in a freezer for 24 h. The pale grey powder, $[CdI_2(NC_5H_5)_2]$, was then collected by filtration (yield nearly quantitative).

With PPh_3; *di-iodo(tetraethylthiuram monosulphide)cadmium*, $[CdI_2\{S(SCNEt_2)_2\}]$. To a solution of $[CdI_2\{(S_2CNEt_2)_2\}]$ (0.66 g) in chloroform (25 cm^3) was added a solution of PPh_3 (0.26 g) in chloroform (10 cm^3). A pale yellow solution was formed which was stirred for 30 min. Evaporation of the solvent yielded an oil which was shaken with diethyl ether giving the *complex* as a yellow powder (yield 60%).

With $[NBu^n_4][S_2CNEt_2]$ *or* $[NBu^n_4][C_7H_4NS_2]$; *tetra-n-butylammonium (diethyldithiocarbamato)di-iodocadmate*, $[NBu^n_4][CdI_2(S_2CNEt_2)]$. To a solution of $[CdI_2\{(S_2CNEt_2)_2\}]$ (0.66 g, 1 mmol) in acetone (25 cm^3) was added either $[NBu^n_4][S_2CNEt_2]$ (0.39 g, 1 mmol) or $[NBu^n_4][C_7H_4NS_2]$ (0.41 g, 0.1 mmol) in acetone (25 cm^3). On evaporation of the mixture to low bulk followed by addition of diethyl ether, the *complex* was precipitated as a white powder. It was collected by filtration, washed with diethyl ether, and dried *in vacuo* (yield 40%).

Tetra-n-butylammonium Tris(diethyldithiocarbamato)cadmate, $[NBu^n_4][Cd(S_2CNEt_2)_3]$.—To an acetone solution (20 cm^3) containing $[NBu^n_4][S_2CNEt_2]$ (3.9 g, 0.01 mol) was added, in small amounts and with shaking, $[Cd(S_2CNEt_2)_2]$ (4.08 g, 0.01 mol). After filtration, the solvent was reduced *in vacuo* affording the *complex* as a very pale yellow solid. This was collected by filtration and recrystallised from acetone–light petroleum (b.p. 40—60 °C) (1 : 1 v/v) (yield 60%). The complexes $[NBu^n_4][Cd(S_2CNMe_2)_3]$ and $[NMe_4][Cd(S_2CNBu^n_2)_3]$ were prepared similarly using $[Cd(S_2CNMe_2)_2]$ (3.52 g) and $[NBu^n_4][S_2CNMe_2]$ for the former, and $[Cd(S_2CNBu^n_2)_2]$ (5.20 g, 0.01 mol) and $[NMe_4][S_2CNBu^n_2]$ (2.78 g, 0.01 mol) for the latter.

$[(Et_2NCS)_2S][CdBr_4]$.—To a suspension of $[Cd(S_2CNEt_2)_2]$ (4.08 g, 0.01 mol) in CS_2 (75 cm^3) was added bromine (1.6 g, 0.01 mol) in CS_2 (20 cm^3), and the mixture was shaken for 15 min. The *compound* was formed as a pale yellow solid which was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 45%).

Tetra-n-butylammonium Acetatobis(diethyldithiocarbamato)cadmate, $[NBu^n_4][Cd(OCOMe)(S_2CNEt_2)_2]$.—To an aqueous solution of $[NBu^n_4][OH]$ (1.3 g) in acetone (25 cm^3) was added acetic acid (0.12 g, 2 mmol), and the mixture was evaporated at 60 °C to afford an oil. This oil was dissolved in acetone (50 cm^3) and $[Cd(S_2CNEt_2)_2]$ (0.81 g, 2 mmol) was added slowly with vigorous stirring until all the cadmium compound had dissolved. On evaporation of the mixture an oil was formed which, on shaking with diethyl ether (30 cm^3) for 30 min, afforded the *complex* as a white powder. This was collected by filtration and dried *in vacuo* (yield 60%). The *complex* $[NBu^n_4][Cd(OCOEt)(S_2CNEt_2)_2]$ was prepared similarly, but could not be separated from traces of $[NBu^n_4][OCOEt]$ and $[Cd(OCOEt)_2]$. Reaction of $[Cd(S_2CNEt_2)_2]$ with $[NBu^n_4][OCOR]$ (R = Pr^n, C_5H_{11}, C_7H_{15}, C_8H_{17}, and $C_{17}H_{35}$) afforded $[NBu^n_4][Cd(S_2CNEt_2)_3]$. The complex $[NMe_4][Cd(OCOMe)(S_2CNEt_2)_2]$ was obtained by reaction of $[NMe_4][OH]$ (1.8 g, 40% aqueous solution), acetic acid (0.3 g, 5 mmol), and $[Cd(S_2CNEt_2)_2]$ (2.04 g, 5 mmol).

Cadmium Bis(3,3-dimethyldithiocarbazate), $[\{Cd(S_2CNHNMe_2)_2\}_n]$.—To a solution of $CdCl_2$ (1.8 g, 0.01 mmol) in water (30 cm^3) was added one drop of dilute acetic acid. This mixture was added dropwise to a solution of dimethylhydrazinium dimethyldithiocarbazate (3.9 g, 0.02 mol) in water (30 cm^3). The *complex* formed as a thick gelatinous white solid which was filtered off, washed with water, and dried *in vacuo* for several days.

Tetra-n-butylammonium Tris(3,3-dimethyldithiocarbazato)cadmate, $[NBu^n_4][Cd(S_2CNHNMe_2)_3]$.—To a solution of dimethylhydrazinium dimethyldithiocarbazate (1.96 g) in in water (40 cm^3) was added, dropwise and with shaking, a solution of $CdCl_2$ (0.018 g, 0.1 mol) in water (10 cm^3). To this mixture was added slowly a warm solution of $[NBu^n_4]I$ in aqueous ethanol. After stirring the mixture for 1 h, the *complex* was filtered off as a white powder, washed with water, ethanol, and diethyl ether, and dried *in vacuo* (yield 55%).

Cadmium Bis(benzothiazole-2-thiolate), $[\{Cd(C_7H_4NS_2)_2\}_n]$. —*Method* 1. To a solution of $Cd(NO_3)_2$ (2.36 g, 0.01 mol) in pyridine and water (1 : 1 v/v, 50 cm^3) was added benzothiazoline-2-thione (3.2 g, 0.02 mol) dissolved in pyridine and ethanol (1 : 1 v/v, 30 cm^3). Addition of water to this mixture caused precipitation of $[Cd(NC_5H_5)_2(C_7H_4NS_2)_2]$ as a yellow powder. This compound was filtered off, and maintained under a high vacuum at 120 °C for at least 48 h. The *complex* was obtained as a white powder (yield 75%).

Method 2. To a solution of $Na[C_7H_4NS_2]$ (0.95 g, 5 mmol) dissolved in warm water (40 cm^3) was added a solution of $CdCl_2$ (0.46 g, 2.5 mmol) in water (5 cm^3). The *complex* was formed as a white precipitate which was filtered off and dried *in vacuo*. It was occasionally contaminated with $[Cd_2(C_7H_4NS_2)_3(OH)]$.

The complex $[Cd(NC_5H_5)_2(6\text{-}EtOC_7H_3NS_2)_2]$ and $[Cd(6\text{-}EtOC_7H_3NS_2)_2]$ were conveniently prepared by Method 1.

Potassium 6-Ethoxybenzothiazole-2-thiolate, $K[6\text{-}EtOC_7H_3NS_2]$.—A mixture of 6-ethoxybenzothiazoline-2-thione (1.06 g, 5 mmol) and KOH (0.28 g, 5 mmol) in hot ethanol (50 cm^3) was evaporated to low bulk (5 cm^3). The *compound* formed as a white solid and was collected by filtration, washed with diethyl ether, and dried *in vacuo*. The *salt* tetramethylammonium 6-ethoxybenzothiazole-2-thiolate, $[NMe_4][6\text{-}EtOC_7H_3NS_2]$, was obtained similarly.

Tetra-n-butylammonium Tris(benzothiazole-2-thiolato)cadmate, $[NBu^n_4][Cd(C_7H_4NS_2)_3]$.—To a solution containing an excess of $[NBu^n_4][C_7H_4NS_2]$ in absolute ethanol was added, slowly and with stirring, $[Cd(C_7H_4NS_2)_2]$ until the mixture became homogeneous. On standing for 12 h at room temperature, the *complex* formed as pale yellow needle-like crystals which were filtered off, washed with diethyl ether, and dried *in vacuo* (yield 65%).

Tetra-n-butylammonium Bis(benzothiazole-2-thiolato)diethyldithiocarbamatocadmate, $[NBu^n_4][Cd(C_7H_4NS_2)_2(S_2CNEt_2)]$.—Cadmium bis(benzothiazole-2-thiolate) (1.1 g, 2.5 mmol) was added in small portions to a solution of $[NBu^n_4][S_2CNEt_2]$ (0.78 g, 2.5 mmol) in acetone (50 cm^3). The mixture was shaken to ensure complete dissolution and then the solvent was removed *in vacuo* yielding an oil. When this oil was shaken with diethyl ether the *complex* was formed as a cream coloured powder. It was collected by filtration and dried *in vacuo*.

Tetramethylammonium Tris(6-ethoxybenzothiazole-2-thiolato)cadmate, $[NMe_4][Cd(6\text{-}EtOC_7H_3NS_2)_3]$.—To a solution of $[NMe_4][6\text{-}EtOC_7H_3NS_2]$ (0.57 g) in acetone (50 cm^3) was added, slowly with shaking, $[Cd(6\text{-}EtOC_7H_3NS_2)_2]$ (1.07 g). The mixture was vigorously shaken for 2 h. It was then filtered and the filtrate evaporated *in vacuo* to low bulk. To this residual filtrate was added light petroleum (b.p. 40—60 °C) and the *complex* precipitated as a pale yellow powder. The compound was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 75%).

Tetra-n-butylammonium Tris(6-*ethoxybenzothiazole*-2-*thiolato*)*cadmate*, $[NBu^n_4][Cd(6\text{-}EtOC_7H_3NS_2)_3]$.—A solution of $[NBu^n_4][OH]$ (40% aqueous solution) in acetone was added to an appropriate amount of acetic, propionic, or butyric acid. The resulting mixture was evaporated at 60 °C to give an oil which was re-dissolved in acetone. To this solution was added $[\{Cd(6\text{-}EtOC_7H_3NS_2)_2\}_n]$ and the resulting mixture was shaken vigorously until all the cadmium complex had dissolved. The solution was then filtered and diethyl ether was added to the filtrate. After overnight storage in a freezer, a white powder was formed which was identified as $[NBu^n_4][Cd(6\text{-}EtOC_7H_3NS_2)_3]$. This was collected by filtration, washed with diethyl ether, and dried *in vacuo* (yield *ca.* 50%).

Tetra-n-butylammonium Bis(*benzothiazole*-2-*thiolato*)(6-*ethoxybenzothiazole*-2-*thiolato*)*cadmate*, $[NBu^n_4][Cd(C_7H_4NS_2)_2(6\text{-}EtOC_7H_3NS_2)]$.—To a solution of $[NBu^n_4][OH]$ (0.65 g, 40% aqueous solution) in acetone (20 cm^3) was added 6-ethoxybenzothiazoline-2-thione (0.21 g). The mixture was stirred and then filtered, and to the filtrate was added $[\{Cd(C_7H_4NS_2)_2\}_n]$ (0.44 g). After shaking the solution which had formed for 15 min, light petroleum (b.p. 40—60 °C) was added, and the complex precipitated as a pale yellow powder. It was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 65%).

Tetra-n-butylammonium Benzothiazole-2-*thiolatobis*(6-*ethoxybenzothiazole*-2-*thiolato*)*cadmate*, $[NBu^n_4][Cd(C_7H_4NS_2)(6\text{-}EtOC_7H_3NS_2)_2]$.—To a solution of $[NBu^n_4][C_7H_4NS_2]$ (0.82 g) in acetone (50 cm^3) was added $[\{Cd(6\text{-}EtOC_7H_3NS_2)_2\}_n]$ (1.07 g). The mixture was shaken for 2 h during which time a homogeneous solution had been formed. This was filtered and the filtrate was evaporated to low bulk. To the residual solution light petroleum (b.p. 40—60 °C) was added and, after a short period of shaking, the *complex* formed as a white solid which was filtered off, washed with diethyl ether, and dried *in vacuo*.

Cadmium Bis(OO′-*di-isopropyl dithiophosphate*), $[Cd\{S_2P(OPr^i)_2\}_2]_2$.—To a solution of $HS_2P(OPr^i)_2$ (0.05 mol) in propan-2-ol was added $Cd(NO_3)_2\cdot 6H_2O$ (0.025 mol) with stirring and heating. The solution was concentrated *in vacuo* and white crystals of the *complex* formed and were collected by filtration, washed with propan-2-ol, and dried *in vacuo* (yield quantitative).

Reaction of CdI_2 *with* $[NBu^n_4][S_2P(OPr^i)_2]$.—To a solution of $[NBu^n_4][S_2P(OPr^i)_2]$ (5 mmol) in propan-2-ol was slowly added a solution of CdI_2 in propan-2-ol. White needle-shaped crystals of $[NBu^n_4]_2[CdI_4]$ formed which were collected by filtration.

Tetramethylammonium Tris(OO′-*di-isopropyl dithiophosphato*)*cadmate*, $[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$.—To a solution of $[NMe_4][S_2P(OPr^i)_2]$ (0.01 mol) in propan-2-ol was slowly added a solution of $[Cd\{S_2P(OPr^i)_2\}_2]_2$ in propan-2-ol. The homogeneous solution was then slowly evaporated *in vacuo* ultimately affording the *complex* as white crystals. The compound was collected by filtration, washed with propan-2-ol, and dried *in vacuo*.

$HS_2P(OPr^i)_2$.—To P_4S_{10} (11.1 g) was added an excess of propan-2-ol (50 cm^3). Hydrogen sulphide was evolved at room temperature, and the mixture which formed was stirred and gently heated on a water-bath until a homogeneous solution had been formed. The solvent was then evaporated *in vacuo* affording the compound as a colourless oil.

Tetramethylammonium OO′-*Di-isopropyl Dithiophosphate*, $[NMe_4][S_2P(OPr^i)_2]$.—To a solution of $HS_2P(OPr^i)_2$ (0.1 mol) in toluene (50 cm^3) was added an aqueous solution of $[NMe_4][OH]$ (0.1 mol). The mixture was stirred overnight, the aqueous layer was then separated, washed with diethyl ether (2 × 20 cm^3), and then evaporated *in vacuo*. The residue was washed with toluene and light petroleum (b.p. 30—40 °C), and then recrystallised from acetone affording the *compound* as white crystals (yield 70%).

Crystal Data.—$[NBu^n_4][Cd(S_2CNEt_2)_3]$, $C_{31}H_{66}CdN_4S_6$, $M = 799.66$, obtained from acetone–petroleum ether (b.p. 40—60 °C) (1 : 1 v/v) as elongated, colourless bricks (crystal dimensions 0.46 × 0.24 × 0.14 mm); Monoclinic, $a = 11.199(7)$, $b = 10.294(7)$, and $c = 36.595(24)$ Å, $\beta = 94.510(7)°$, $U = 4\,206(5)$ Å^3, $D_m = 1.25$, $Z = 4$, $D_c = 1.263$ g cm^{-3}, space group $P2_1/c$ (from systematic absences), Mo-K_α X-radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 8.27 cm^{-1}, and $F(000) = 1\,696$.

Three-dimensional, X-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 two-circle diffractometer using the moving-crystal, stationary-counter method. The 3 234 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz, polarisation, and absorption effects and the structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares methods. In the later stages of refinement, geometric constraints (C–C 1.537 Å, C–C–C 110°) were imposed on the terminal three carbon atoms of each of two n-butyl groups which showed signs of some slight disorder. Hydrogen atoms were detected and positioned (C–H 0.95 Å) on all methylene carbon atoms and in localised sites (C–C–H 109.5°) on five of the six methyl-group carbon atoms of the anion and on the two ordered methyl-group carbon atoms of the cation. The remaining methyl group of the anion [C(10)] showed no localised sites and six half-population hydrogen atoms were inserted around the annulus. No evidence was found for hydrogen atoms on the disordered methyl-group carbon atoms of the cation and none was inserted. The contributions of all hydrogen atoms to structure-factor calculations ($B = 10.0$ Å^2) were included in the later stages of refinement but positional parameters were not varied. Refinement converged at R 0.0466 after allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of cadmium and sulphur. Atomic scattering factors were taken from ref. 8; unit weights were used throughout least-squares refinement. Computer programs formed part of the Sheffield X-ray system.

$[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$, $C_{22}H_{54}CdNO_6P_3S_6$, $M = 826.35$, obtained from chloroform as colourless plates (crystal dimensions 0.45 × 0.20 × 0.40 mm); Rhombohedral, $a = 15.414(5)$ Å, $\alpha = 50.68(2)°$, $U = 2\,021(1)$ Å^3, $D_m = 1.31$, $Z = 2$, $D_c = 1.358$ g cm^{-3}, space group $R\bar{3}$ (confirmed by successful structural analysis), Mo-K_α X-radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 9.83 cm^{-1}, and $F(000) = 860$.

The data were collected (1 971 independent reflections) and the structure solved and refined (R 0.0287) as for $[NBu^n_4][Cd(S_2CNEt_2)_3]$ above but, in this case, no cation disorder was detected and all hydrogen atoms were located.

$[NEt_4][Cd(C_7H_4NS_2)_3]$, $C_{29}H_{32}CdN_4S_6$, $M = 741.36$, obtained from ethanol as colourless, plate-shaped crystals (crystal dimensions 0.20 × 0.18 × 0.10 mm); Cubic, $a =$

18.59(1) Å, U = 6 428(6) $Å^3$, D_m = 1.50, Z = 8, D_c = 1.532 g cm^{-3}, space group $Pa3$ (from systematic absences), Mo-K_α X-radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 10.77 cm^{-1}, and $F(000)$ = 3 024.

Three dimensional X-ray data were collected on a Nicolet(Syntex) $P3$ X-ray diffractometer using the θ—2θ scanning method. The 729 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects; no corrections were made for absorption. The structure was solved and refined (R 0.0615) as for $[NBu^n_4][Cd(S_2CNEt_2)_3]$ above. Extensive disorder of the cation was found to occur about the crystallographic threefold axis, the approximate C_3 symmetry of this species not being utilised. A satisfactory disorder model for the nitrogen and carbon atoms was finally achieved but no attempt was made to locate the hydrogen atoms of the cation and only isotropic thermal vibration was permitted for the atoms of the cation.

Tables 1, 2, and 3 list atomic positional parameters and estimated standard deviations for the non-hydrogen atoms of $[NBu^n_4][Cd(S_2CNEt_2)_3]$, $[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$, and $[NEt_4][Cd(C_7H_4NS_2)_3]$ respectively (the latter also including the positions of the four hydrogen atoms). Tables of hydrogen-atom positions {except for $[NEt_4][Cd(C_7H_4NS_2)_3]$}, anisotropic thermal vibrational parameters, and their estimated standard deviations, of observed structure amplitudes, and calculated structure factors for all three structures are deposited in Supplementary Publication No. SUP 23195 (64 pp).*

TABLE 1

Atomic positional parameters and estimated standard deviations for $[NBu^n_4][Cd(S_2CNEt_2)_3]$

Atom	X/a	Y/b	Z/c
Cd(1)	0.005 60(6)	0.011 68(6)	−0.126 50(2)
S(1)	−0.165 4(2)	−0.043 3(3)	−0.182 6(1)
S(2)	0.083 5(2)	−0.131 2(3)	−0.180 2(1)
S(3)	−0.099 7(2)	−0.110 6(3)	−0.072 7(1)
S(4)	0.160 1(2)	−0.090 9(3)	−0.072 5(1)
S(5)	0.153 4(3)	0.216 1(3)	−0.138 6(1)
S(6)	−0.083 8(3)	0.246 7(3)	−0.110 6(1)
N(1)	−0.077 1(6)	−0.187 9(8)	−0.234 6(2)
N(2)	0.048 9(6)	−0.167 8(7)	−0.015 2(2)
N(3)	0.054 7(7)	0.444 0(7)	−0.125 2(2)
N(4)	0.508 4(6)	−0.009 9(7)	−0.124 5(2)
C(1)	−0.056 1(8)	−0.127 8(8)	−0.202 3(2)
C(2)	−0.197 3(10)	−0.186 5(11)	−0.254 9(3)
C(3)	−0.265 8(12)	−0.302 1(16)	−0.247 6(4)
C(4)	0.014 4(9)	−0.264 4(11)	−0.252 4(3)
C(5)	0.077 9(11)	−0.180 9(14)	−0.277 2(3)
C(6)	0.037 4(7)	−0.128 9(8)	−0.049 8(2)
C(7)	−0.054 3(9)	−0.193 4(10)	0.006 3(3)
C(8)	−0.087 3(11)	−0.332 8(12)	0.006 2(4)
C(9)	0.168 5(10)	−0.179 0(11)	0.005 6(3)
C(10)	0.219 8(11)	−0.306 8(13)	0.000 5(4)
C(11)	0.044 0(8)	0.314 9(8)	−0.124 4(2)
C(12)	0.162 5(10)	0.506 4(11)	−0.138 9(3)
C(13)	0.248 0(14)	0.536 2(15)	−0.109 6(5)
C(14)	−0.036 2(11)	0.535 6(10)	−0.113 9(3)
C(15)	−0.116 8(11)	0.576 0(12)	−0.147 1(4)
C(16)	0.586 9(8)	0.097 1(10)	−0.138 7(3)
C(17)	0.520 9(9)	0.218 1(12)	−0.152 8(3)
C(18)	0.605 0(12)	0.313 7(13)	−0.165 7(4)
C(19)	0.546 9(14)	0.437 1(14)	−0.178 1(4)
C(20)	0.594 1(8)	−0.116 3(11)	−0.110 9(3)
C(21)	0.535 6(10)	−0.235 6(11)	−0.094 9(4)
C(22)	0.624 9(12)	−0.331 0(14)	−0.082 5(5)
C(23)	0.578 5(15)	−0.448 7(17)	−0.066 4(6)
C(24)	0.418 3(8)	−0.059 6(11)	−0.154 5(3)
C(25)	0.474 9(20)	−0.113 1(22)	−0.187 2(6)
C(26)	0.382 0(10)	−0.158 5(14)	−0.217 7(3)
C(27)	0.381 5(22)	−0.307 6(15)	−0.220 1(7)
C(28)	0.435 0(8)	0.042 1(11)	−0.094 6(3)
C(29)	0.507 5(22)	0.105 5(29)	−0.061 9(7)
C(30)	0.423 2(13)	0.136 7(16)	−0.031 9(4)
C(31)	0.404 4(26)	0.284 2(19)	−0.029 3(9)

Atoms C(16)—C(19), C(20)—C(23), C(24)—C(27), C(28)—C(31) are those of the four n-butyl groups of the cation; the lowest numbered atom of each group is bonded to the central nitrogen atom N(4). The estimated standard deviations of atoms C(25)—C(27) and C(29)—C(31) were derived from the e.s.d.s of the refined group translational and rotational parameters which were used to locate them.

TABLE 2

Atomic positional parameters and estimated standard deviations for $[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$

Atom	X/a	Y/b	Z/c
Cd(1)	0.073 24(4)	0.073 24(4)	0.073 24(4)
S(1)	−0.023 17(9)	0.310 00(9)	0.047 12(9)
S(2)	0.049 99(9)	0.213 23(8)	−0.139 26(8)
P(1)	−0.014 66(8)	0.355 08(7)	−0.109 73(8)
O(1)	0.056 3(2)	0.443 6(2)	−0.219 1(2)
O(2)	−0.140 8(2)	0.452 0(2)	−0.124 8(2)
N(1)	0.208 2(4)	0.208 2(4)	0.208 2(4)
C(1)	0.183 5(3)	0.398 8(4)	−0.243 6(4)
C(2)	0.259 0(5)	0.395 4(6)	−0.367 6(5)
C(3)	0.192 6(5)	0.482 6(5)	−0.232 4(6)
C(4)	−0.240 2(4)	0.414 5(3)	−0.060 7(4)
C(5)	−0.284 1(5)	0.466 0(5)	−0.152 9(6)
C(6)	−0.336 0(5)	0.461 7(6)	0.039 0(6)
C(7)	0.245 3(5)	0.245 3(5)	0.245 3(5)
C(8)	0.293 5(5)	0.083 1(4)	0.212 8(5)

Atoms N(1), C(7), and C(8) are the unique atoms of the tetramethylammonium cation.

TABLE 3

Atomic positional parameters and estimated standard deviations for $[NEt_4][Cd(C_7H_4NS_2)_3]$

Atom	X/a	Y/b	Z/c
Cd(1)	0.153 9(2)	0.153 9(2)	0.153 9(2)
S(1)	0.182 5(2)	0.284 9(3)	0.102 8(3)
S(2)	0.065 5(2)	0.326 9(2)	−0.001 2(3)
N(1)	0.067 9(6)	0.207 5(5)	0.067 6(6)
N(2)	0.329 2(13)	0.317 0(15)	0.324 7(17)
C(1)	0.104 0(7)	0.267 1(7)	0.060 2(8)
C(2)	0.004 1(7)	0.206 0(7)	0.027 3(7)
C(3)	−0.006 5(8)	0.267 2(7)	−0.014 1(8)
C(4)	−0.067 7(8)	0.274 4(8)	−0.055 9(8)
C(5)	−0.118 5(8)	0.222 2(9)	−0.053 5(7)
C(6)	−0.106 6(8)	0.160 6(8)	−0.011 9(8)
C(7)	−0.045 4(7)	0.151 9(8)	0.027 8(7)
C(8)	0.332 3(19)	0.377 6(17)	0.377 8(21)
C(9)	0.409 0(23)	0.394 8(25)	0.400 3(27)
C(10)	0.294 5(18)	0.252 8(17)	0.359 1(22)
C(11)	0.229 3(21)	0.273 5(27)	0.403 9(26)
C(12)	0.286 0(18)	0.339 7(20)	0.260 5(20)
C(13)	0.314 5(28)	0.408 8(23)	0.227 3(24)
C(14)	0.404 1(14)	0.297 8(21)	0.301 4(22)
C(15)	0.410 7(23)	0.218 8(22)	0.281 5(29)
H(4)	−0.0758	0.3173	−0.0858
H(5)	−0.1621	0.2284	−0.0828
H(6)	−0.1423	0.1226	−0.0109
H(7)	−0.0380	0.1090	0.0575

Atoms N(2) and C(8)—C(15) constitute the tetraethylammonium cation. Hydrogen atoms (of the anion only) are numbered according to the carbon atoms to which they are attached.

RESULTS AND DISCUSSION

Synthetic Studies.—Reaction of $[Cd(S_2CNEt_2)_2]$ with iodine afforded the thiuram disulphide complex $[CdI_2\{(S_2CNEt_2)_2\}]$. The disulphide ligand was readily

* For details see Notices to Authors No. 7, *J. Chem. Soc. Dalton Trans.*, 1981, Index issue.

TABLE 4

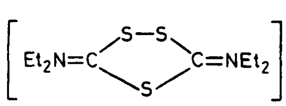
Analytical data (%) obtained from cadmium complexes

Complex	Found				Calc.			
	C	H	N	S	C	H	N	S
$[CdI_2\{(S_2CNEt_2)_2\}]$	18.6	3.1	3.9	19.3	18.1	3.0	4.2	19.3
$[CdI_2\{Et_2NC(S)SC(S)NEt_2)\}]$	19.1	3.4	4.2	14.2	19.0	3.2	4.4	15.2
$[Cd(NH_2CH_2CH_2NH_2)_3][CdI_4]$	7.9	1.9	8.7	56.2 [a]	8.0	1.8	9.2	56.1 [a]
$[(Et_2NCS)_2S][CdBr_4]$	17.2	2.2	4.0		17.2	3.8	4.0	
$[(Bu^n{}_2NCS)_2S][CdBr_4]$	26.2	4.2	3.4	11.5	26.2	4.4	3.4	11.8
$[NBu^n{}_4][CdI_2(S_2CNEt_2)]$	33.9	6.4	3.5	8.3	33.3	6.1	3.7	8.5
$[NBu^n{}_4][Cd(S_2CNMe_2)_3]$	42.8	7.6	7.6	24.7	42.0	7.6	7.8	26.4
$[NBu^n{}_4][Cd(S_2CNEt_2)_3]$	46.8	8.5	6.9	23.1	46.6	8.3	7.0	24.1
$[NMe_4][Cd(S_2CNBu^n{}_2)_3]$	46.6	8.2	7.2	23.9	46.6	8.3	7.0	24.1
$[NMe_4][Cd(OCOMe)(S_2CNEt_2)_2]$	35.0	6.1	7.5	23.7	35.4	6.5	7.7	23.7
$[NBu^n{}_4][Cd(OCOMe)(S_2CNEt_2)_2]$	48.8	8.4	5.8		48.5	8.5	6.1	
$[\{Cd(S_2CNHNMe_2)_2\}_n]$	18.3	3.3	13.8		18.8	3.7	14.6	
$[NBu^n{}_4][Cd(S_2CNHNMe_2)_3]$	39.4	7.7	13.1	25.1	39.5	7.5	12.9	25.2
$[\{Cd(C_7H_4NS_2)_2\}_n]$	37.5	1.5	6.0	28.6	37.8	1.8	6.3	28.8
$[Cd_2(C_7H_4NS_2)_3(OH)]$	33.8	1.9	6.4		33.9	1.9	5.7	
$[Cd(C_5H_5N)_2(C_7H_4NS_2)_2]$	48.9	3.3	9.0	21.3	48.0	3.0	9.4	21.5
$[\{Cd(6\text{-}EtOC_7H_3NS_2)_2\}_n]$	40.8	3.1	5.4	23.7	40.9	3.0	5.2	23.9
$[NBu^n{}_4][Cd(C_7H_4NS_2)_3]$	51.7	5.2	6.4	22.3	52.1	5.6	6.6	22.5
$[NBu^n{}_4][Cd(C_7H_4NS_2)_2(S_2CNEt_2)]$	50.9	6.4	6.7	22.5	50.3	6.5	6.7	23.0
$[NMe_4][Cd(6\text{-}EtOC_7H_3NS_2)_3]$	46.5	4.5	7.0	23.0	45.9	4.4	6.9	23.4
$[NBu^n{}_4][Cd(C_7H_4NS_2)_2(6\text{-}EtOC_7H_3NS_2)]$	52.6	6.5	5.8	19.6	52.1	5.8	6.2	21.3
$[NBu^n{}_4][Cd(C_7H_4NS_2)(6\text{-}EtOC_7H_3NS_2)_2]$	52.4	6.2	6.2	20.5	52.3	6.0	6.0	20.4
$[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$	32.3	6.7	1.9	24.7	32.0	6.6	1.7	23.3
$[Cd\{S_2P(OPr^i)_2\}_2]_2$	26.9	5.4		24.0	26.7	5.2		23.8
$[NBu^n{}_4]_2[CdI_4]$	34.8	6.2	2.4		34.8	6.6	2.5	

[a] % Iodine.

displaced from the metal by ethylenediamine (en) or pyridine, giving $[Cd(en)_3][CdI_4]$ and an impure sample of $[CdI_2(py)_2]$, respectively (analytical data, Table 4). With triphenylphosphine, a sulphur atom could be extracted, affording the thiuram monosulphide complex $[CdI_2\{S(SCNEt_2)_2\}]$. These reactions are very similar to those of the analogous species $[ZnI_2\{(S_2CNMe_2)_2\}]$,[7] but unlike its zinc counterpart, $[CdI_2\{S(SCNEt_2)_2\}]$ does not react further with PPh_3 giving $[Ph_3P\{C(NMe_2)\}]$-$[CdI_2(S_2CNEt_2)]$. However, the ion $[CdI_2(S_2CNEt_2)]^-$ could be synthesised by reaction of $[CdI_2\{(S_2CNEt_2)_2\}]$ with $[NBu^n{}_4][S_2CNEt_2]$.

Treatment of $[Cd(S_2CNEt_2)_2]$ with bromine in chloroform afforded the salt $[(Et_2NCS)_2S][CdBr_4]$, which probably contains the cation (1), as reported previously.[9]



(1)

This cation was also formed when $CdCl_2$ or $CdBr_2$ reacts with tetra-alkylthiuram disulphides.

In a reaction entirely parallel to its zinc analogues $[Cd(S_2CNEt_2)_2]$ reacted with $[NBu^n{}_4][S_2CNEt_2]$ giving the tris(dithiocarbamato)-species $[NBu^n{}_4][Cd(S_2CNEt_2)_3]$. Reaction of the bis(dithiocarbamate) with $[NBu^n{}_4]$-$[OCOMe]$ similarly afforded $[NBu^n{}_4][Cd(OCOMe)(S_2CNEt_2)_2]$, and the tris(3,3-dimethyldithiocarbazate) complex $[NBu^n{}_4][Cd(S_2CNHNMe_2)_3]$ was prepared using the appropriate dimethyldithiocarbazates.

Cadmium complexes containing benzothiazole-2-thiolato-ligands (Figure 1) have not been extensively investigated. However, $[\{Cd(C_7H_4NS_2)_2\}_n]$ has been described,[10] and is thought to be polymeric. The pyridine adducts $[Cd(py)_2(6\text{-}RC_7H_3NS_2)_2]$ (R = H or EtO) were obtained by reaction of cadmium salts with the appropriate benzothiazoline-2-thione in pyridine–ethanol mixtures. The pyridine could be driven off by heating the

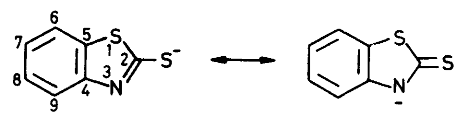


FIGURE 1 Structure and numbering of $C_7H_4NS_2^-$ ligand

adducts *in vacuo* at 120 °C, and $[\{Cd(6\text{-}RC_7H_3NS_2)_2\}_n]$ could also be obtained by treating Cd^{2+} with sodium or potassium salts of the appropriate thiolate anion. However, reaction of cadmium acetate with KOH and benzothiazoline-2-thione afforded the basic cadmium species $[Cd_2(C_7H_4NS_2)_3(OH)]$.

Following procedures established earlier,[1] the $[NBu^n{}_4]^+$ salts of $[Cd(C_7H_4NS_2)_n(6\text{-}EtOC_7H_3NS_2)_{3-n}]^-$ (n = 0—3) and $[Cd(C_7H_4NS_2)_2(S_2CNEt_2)]^-$ were obtained by addition of the $[NBu^n{}_4]^+$ salt of a thiolate anion to the appropriate cadmium bis(thiolate) species. However, $[NBu^n{}_4][Cd(6\text{-}EtOC_7H_3NS_2)_3]$ was isolated from the reaction of $[\{Cd(6\text{-}EtOC_7H_3NS_2)_2\}_n]$ with $[NBu^n{}_4][OCOR]$ (R = Me, Et, or Pr^i). It may be noted that none of these anionic benzothiazole species contains water of co-ordination or crystallisation, in direct contrast to $[NBu^n{}_4][Zn(C_7H_4NS_2)_3(OH_2)]$, where the water molecule plays a critical role in stabilisation of the structure of this anion, and cannot be readily removed.

Reaction of cadmium salts with $P(=S)(SH)(OPr^i)_2$ gave $[Cd\{S_2P(OPr^i)_2\}_2]_2$ which reacted further with $[NMe_4]$-$[S_2P(OPr^i)_2]$ giving the tris(dithiophosphato)-species $[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$. However, attempts to prepare $[NBu^n_4][CdI_2\{S_2P(OPr^i)_2\}]$ by treatment of CdI_2 with $[NBu^n_4][S_2P(OPr^i)_2]$ failed, the product being $[NBu^n_4]_2[CdI_4]$.

Thus, it is clear that the general chemistry of cadmium dithiocarbamates, benzothiazole-2-thiolate, and dialkyldithiophosphates parallels that of the zinc analogues. However, there are a few species we have been unable to isolate, in particular, salts of $[Cd(C_7H_4NS_2)(S_2CNR_2)_2]^-$ The anionic species $[Cd(S_2CNEt_2)_3]^-$ reacts with sulphur in refluxing xylene giving, like its zinc analogue,[11] a red oil. However, this reaction is qualitatively much slower than that involving $[Zn(S_2CNR_2)_3]^-$. This may be a reflection of the greater kinetic stability of $[Cd(S_2CNEt_2)_3]^-$ in solution relative to the zinc analogue, or, in other words, that the equilibrium lies more to the left

$$[M(S_2CNR_2)_3]^- \rightleftharpoons [M(S_2CNR_2)_2] + [S_2CNR_2]^-$$

when M = Cd. There is electrochemical evidence to support this view[5,12] although it must be stated that these data were obtained in polar solvents, whereas the reaction with S_8 is occurring in a hydrocarbon.

Spectroscopic Studies.—The i.r. and ^1H n.m.r. spectral results are contained in Table 5. For the most part, they are entirely consistent with the formulations of the

TABLE 5

Selected spectroscopic data obtained from some cadmium complexes

Complex	I.r. data[a]	^1H N.m.r. data: δ[b]	r.a.[c]	Multiplicity	Remarks
$[CdI_2\{S_2CNEt_2)_2\}]$	1 520 [ν(CN)]	4.29	1	q	} $N(CH_2Me)_2$
		4.02	1	q	
		1.63 }	3	t	} $N(CH_2CH_3)_2$
		1.39		t	
$[CdI_2\{Et_2NC(S)SC(S)NEt_2\}]$	1 425 [ν(CN)]				
$[Cd(en)_3][CdI_4]$	3 350 [ν(NH)]				
	3 260				
$[\{Bu^n_2N{=}C(S)\}_2S][CdBr_4]$	1 555 [ν(CN)]				
$[Cd(S_2CNMe_2)_2]_2$	1 510 [ν(CN)]				
	955 [ν(SCS)]				
$[Cd(S_2CNEt_2)_2]_2$	1 490 [ν(CN)]				
	985 [ν(SCS)]				
$[Cd(S_2CNBu^n_2)_2]_2$	1 490 [ν(CN)]	3.94[d]	2	t	$N(CH_2Pr^n)_2$
	950 [ν(SCS)]	1.83	2	m	$N(CH_2CH_2Et)_2$
		1.35	2	sxt	$N(CH_2CH_2CH_2Me)_2$
		0.94	3	t	$N(CH_2CH_2CH_2CH_3)_2$
$[NBu^n_4][CdI_2(S_2CNEt_2)]$	1 495 [ν(CN)]	3.88	2	q	$N(CH_2Pr^n)_2$
	985 [ν(SCS)]	3.45	4	t	$N(CH_2Pr^n)_4$
		1.81	4	m	$N(CH_2CH_2Et)_4$
		1.44	4	m	$N(CH_2CH_2CH_2Me)_4$
		1.25	3	t	$N(CH_2CH_3)_2$
		0.97	6	t	$N[(CH_2)_3CH_3]_4$
$[NBu^n_4][Cd(S_2CNEt_2)_3]$	1 475 [ν(CN)]	3.86[d]	6	q	$N(CH_2Me)_2$
	990 [ν(SCS)]	3.35	4	t	$N(CH_2Pr^n)_4$
		1.71	4	m	$N(CH_2CH_2Et)_4$
		1.38	4	m	$N(CH_2CH_2CH_2Me)_4$
		1.15	9	t	$N(CH_2CH_3)_2$
		0.89	6	t	$N[(CH_2)_3CH_3]_4$
$[NMe_4][Cd(S_2CNBu^n_2)_3]$	1 475 [ν(CN)]	3.86	2	t	$N(CH_2Pr^n)_2$
	990 [ν(SCS)]	3.47	2	s	$N(CH_3)_4$
		1.75	2	sxt	$N(CH_2CH_2Et)_2$
		1.30	2	sxt	$N(CH_2CH_2CH_2Me)_2$
		0.91	3	t	$N[(CH_2)_3CH_3]_2$
$[NMe_4][Cd(OCOMe)(S_2CNEt_2)_2]$	1 560 [ν(OCO)]				
	1 490 [ν(CN)]				
	1 485				
	985 [ν(SCS)]				
$[NBu^n_4][Cd(OCOMe)(S_2CNEt_2)_2]$	1 565 [ν(OCO)]	3.87[d]	8	q	$N(CH_2Me)_2$
	1 480 [ν(CN)]	3.42	8	m	$N(CH_2Pr^n)_4$
	990 [ν(SCS)]	1.79	11	s	$OCOCH_3$
		1.75	11	m	$N(CH_2CH_2Et)_4$
		1.42	8	sxt	$N(CH_2CH_2CH_2Me)_4$
		1.21	12	t	$N(CH_2CH_3)_2$
		0.89	12	t	$N[(CH_2)_3CH_3]_4$
$[\{Cd(S_2CNHNMe_2)_2\}_n]$	3 130 [ν(NH)]	10.75[e]	1	br s	N*H*
	1 490 [ν(CN)]	3.42	6	s	$N(CH_3)_2$
$[NBu^n_4][Cd(S_2CNHNMe_2)_3]$	3 080 [ν(NH)]	9.31[d]	3	br s	N*H*
	1 470 [ν(CN)]	3.45	8	m	$N(CH_2Pr^n)_4$
		2.78	18	d	$NHN(CH_3)_2$, ^3J(HH) 16 Hz
		1.81	8	m	$N(CH_2CH_2Et)_4$
		1.45	8	m	$N(CH_2CH_2CH_2Me)_4$
		0.97	12	t	$N[(CH_2)_3CH_3]_4$
$[\{Cd(C_7H_4NS_2)_2\}_n]$	1 385[f]	7.69[e]	1	d	} $C_7H_4NS_2$
		7.45	1	d	
		7.24	1	t	
		7.13	1	t	

TABLE 5 (*continued*)

Complex	I.r. data [a]	δ [b]	r.a. [c]	Multiplicity	Remarks
				¹H N.m.r. data	
$[\{Cd(6\text{-}EtOC_7H_3NS_2)_2\}_n]$	1 385	7.40	2	d	} $C_7H_3NS_2$
		6.88	1	m	
		3.99	2	q	OCH_2Me
		1.29	3	t	OCH_2CH_3
$[Cd(C_5H_5N)(6\text{-}EtOC_7H_3NS_2)_2]$		8.61	2	d	} C_5H_5N
		7.85	1	t	
		7.45	4	t	} $C_7H_3NS_2$
		7.36		d	
		7.25	2	s	C_5H_5N
		6.85	2	m	$C_7H_3NS_2$
		3.96	4	q	OCH_2Me
		1.29	6	t	OCH_2CH_3
$[NBu^n_4][Cd(C_7H_4NS_2)_3]$	1 380	7.51	3	d	} $C_7H_4NS_2$
		7.43		d	
		7.10	3	m	
		2.85	4	m	$N(CH_2Pr^n)_4$
		1.27	4	m	$N(CH_2CH_2Et)_4$
		1.01	4	m	$N(CH_2CH_2CH_2Me)_4$
		0.72	6	t	$N[(CH_2)_3CH_3]_4$
$[NBu^n_4][Cd(C_7H_4NS_2)_2(S_2CNEt_2)]$	1 490 [ν(CN)]	7.55	2	m	} $C_7H_4NS_2$
	1 380	7.19	1	t	
		7.05	1	t	
		3.88	2	q	$N(CH_2Me)_2$
		3.30	4	t	$N(CH_2Pr^n)_4$
		1.69	4	m	$N(CH_2CH_2Et)_4$
		1.28	7	m	$N(CH_2CH_2CH_2Me)_4$ and $N(CH_2CH_3)_2$
		0.88	6	t	$N[(CH_2)_3CH_3]_4$
$[NMe_4][Cd(6\text{-}EtOC_7H_3NS_2)_3]$	1 390	7.30		d	} $C_7H_3NS_2$
		7.05	3	d	
		6.67		d	
		3.92	2	q	OCH_2Me
		3.30	4	s	$N(CH_3)_4$
		1.26	3	t	OCH_2CH_3
$[NBu^n_4][Cd(C_7H_4NS_2)(6\text{-}EtOC_7H_3NS_2)_2]$	1 380	7.56		t	} $C_7H_4NS_2$ and
		7.45	5	d	
		7.10		m	} $C_7H_3NS_2$
		6.78		m	
		3.97	2	q	OCH_2Me
		3.25	4	t	$N(CH_2Pr^n)_4$
		1.65	4	m	$N(CH_2CH_2Et)_4$
		1.30	7	m	$N(CH_2CH_2CH_2Me)_4$ and OCH_2CH_3
		0.85		t	$N[(CH_2)_3CH_3]_4$
$[NMe_4][Cd(S_2CNEt_2)_2(6\text{-}EtOC_7H_3NS_2)]$	1 480 [ν(CH)]	7.40	3	d	} $C_7H_3NS_2$
	1 385	7.05		d	
		6.70		d	
		3.95	10	q	} OCH_2Me and $N(CH_2Me)_2$
		3.83		q	
		3.35	12	s	$N(CH_3)_4$
		1.27	15	q	} OCH_2CH_3 and $N(CH_2CH_3)_2$
		1.14		t	
$[Cd\{S_2P(OPr^i)_2\}_2]$		4.93	1	spt	$OCHMe_2$
		1.38	6	d	$OCH(CH_3)_2$
$[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$		4.92	1	spt	$OCHMe_2$
		3.40	2	s	$N(CH_3)_4$
		1.33	6	d	$OCH(CH_3)_2$

[a] KBr discs (cm^{-1}). [b] $CDCl_3$ solution unless otherwise stated (p.p.m.). [c] Relative area. [d] In $(CD_3)_2CO$. [e] In $(CD_3)_2SO$. [f] Unassigned band associated with thiazole ring.

complexes. The i.r. spectral data obtained from salts of $[Cd(OCOMe)(S_2CNEt_2)_2]^-$ are consistent with a unidentate acetate group, as in the zinc analogues,[2] presumably in a species which is five-co-ordinate. The ¹H n.m.r. spectral information obtained from these acetato-species is consistent with a mononuclear species, and we could find no evidence for binuclear species of the type $[\{Cd(S_2CNEt_2)_2\}_2(\mu\text{-}OCOMe)]^-$, analogous to the previously reported zinc complex.

Structural Studies.—The structures of the three anions with atomic labelling are shown in Figures 2, 3, and 4; Tables 6—11 list bond lengths and angles with estimated standard deviations and details of planar fragments for the three structures.

$[NBu^n_4][Cd(S_2CNEt_2)_3]$. The cadmium atom is six-co-ordinate with a geometry which is intermediate between trigonal prismatic and octahedral; the two almost equilateral triangular faces of the prism are defined by atoms S(1), S(3), S(6), and S(2), S(4), S(5), and are relatively twisted by approximately 17°. The chelation of each diethyldithiocarbamato-ligand is slightly asymmetric with one cadmium–sulphur bond

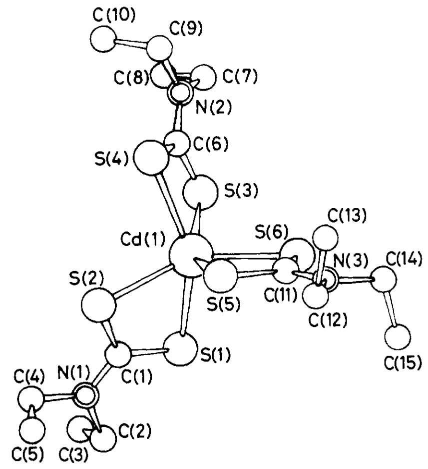


FIGURE 2 The structure and atom labelling for the anion $[Cd(S_2CNEt_2)_3]^-$

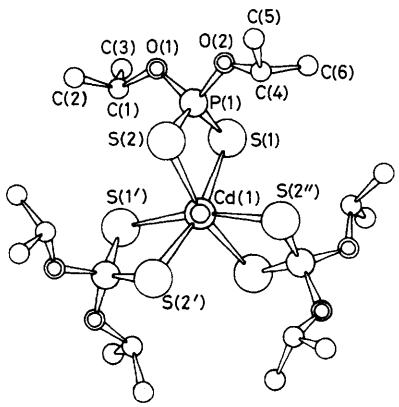


FIGURE 3 The structure and atom labelling for the anion $[Cd\{S_2P(OPr^i)_2\}_3]^-$

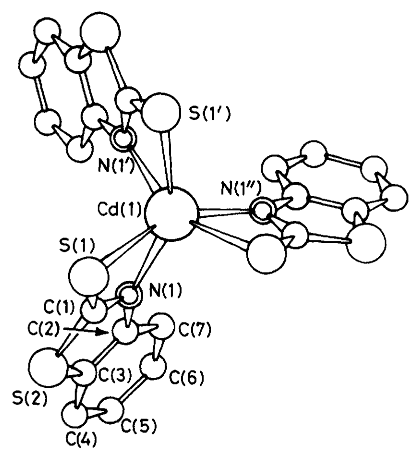


FIGURE 4 The structure and atom labelling for the anion $[Cd(C_7H_4NS_2)_3]^-$

significantly longer (up to 30σ) than the other; the more distant sulphur atoms are distributed between the two triangular faces of the trigonal prism. This asymmetry does not give rise, within estimated standard deviations, to any variation in otherwise chemically equivalent bonds within the ligands which have unexceptionable

TABLE 6

Bond lengths (Å) and angles (°) with estimated standard deviations for $[NBu^n_4][Cd(S_2CNEt_2)_3]$

Cd(1)–S(1)	2.755(3)	S(1)–C(1)	1.706(9)
Cd(1)–S(2)	2.655(3)	S(2)–C(1)	1.704(9)
Cd(1)–S(3)	2.686(3)	N(1)–C(1)	1.339(11)
Cd(1)–S(4)	2.735(3)	N(1)–C(2)	1.484(13)
Cd(1)–S(5)	2.736(3)	N(1)–C(4)	1.482(13)
Cd(1)–S(6)	2.699(3)	C(2)–C(3)	1.451(19)
		C(4)–C(5)	1.474(17)
N(4)–C(16)	1.526(12)		
N(4)–C(20)	1.515(12)	S(3)–C(6)	1.701(8)
N(4)–C(24)	1.520(12)	S(4)–C(6)	1.704(9)
N(4)–C(28)	1.518(12)	N(2)–C(6)	1.328(11)
C(16)–C(17)	1.517(15)	N(2)–C(7)	1.470(12)
C(17)–C(18)	1.465(18)	N(2)–C(9)	1.492(13)
C(18)–C(19)	1.482(21)	C(7)–C(8)	1.482(16)
C(20)–C(21)	1.531(15)	C(9)–C(10)	1.455(17)
C(21)–C(22)	1.450(19)		
C(22)–C(23)	1.459(24)	S(5)–C(11)	1.706(9)
C(24)–C(25)	1.503(24)	S(6)–C(11)	1.705(9)
C(25)–C(26) *	1.537(—)	N(3)–C(11)	1.335(11)
C(26)–C(27) *	1.537(—)	N(3)–C(12)	1.490(14)
C(28)–C(29)	1.537(28)	N(3)–C(14)	1.471(14)
C(29)–C(30) *	1.537(—)	C(12)–C(13)	1.413(20)
C(30)–C(31) *	1.537(—)	C(14)–C(15)	1.515(18)

S(1)–Cd(1)–S(2)	65.44(8)	Cd(1)–S(1)–C(1)	86.5(3)
S(1)–Cd(1)–S(3)	97.52(8)	Cd(1)–S(2)–C(1)	89.9(3)
S(1)–Cd(1)–S(4)	145.39(9)	S(1)–C(1)–S(2)	118.2(5)
S(1)–Cd(1)–S(5)	115.53(8)	S(1)–C(1)–N(1)	121.7(6)
S(1)–Cd(1)–S(6)	95.57(8)	S(2)–C(1)–N(1)	120.1(6)
S(2)–Cd(1)–S(3)	118.12(8)	C(1)–N(1)–C(2)	121.7(7)
S(2)–Cd(1)–S(4)	95.45(8)	C(1)–N(1)–C(4)	123.6(8)
S(2)–Cd(1)–S(5)	93.89(8)	C(2)–N(1)–C(4)	114.7(8)
S(2)–Cd(1)–S(6)	143.60(9)	N(1)–C(2)–C(3)	111.9(10)
S(3)–Cd(1)–S(4)	65.06(8)	N(1)–C(4)–C(5)	110.2(9)
S(3)–Cd(1)–S(5)	141.77(8)		
S(3)–Cd(1)–S(6)	94.03(8)	Cd(1)–S(3)–C(6)	88.9(3)
S(4)–Cd(1)–S(5)	93.32(9)	Cd(1)–S(4)–C(6)	87.2(3)
S(4)–Cd(1)–S(6)	114.48(9)	S(3)–C(6)–S(4)	117.9(5)
S(5)–Cd(1)–S(6)	65.47(9)	S(3)–C(6)–N(2)	121.3(6)
		S(4)–C(6)–N(2)	120.8(6)
C(16)–N(4)–C(20)	105.5(7)	C(6)–N(2)–C(7)	122.9(7)
C(16)–N(4)–C(24)	111.4(7)	C(6)–N(2)–C(9)	121.7(7)
C(16)–N(4)–C(28)	110.5(7)	C(7)–N(2)–C(9)	115.2(7)
C(20)–N(4)–C(24)	111.2(7)	N(2)–C(7)–C(8)	112.2(9)
C(20)–N(4)–C(28)	112.5(7)	N(2)–C(9)–C(10)	110.6(9)
C(24)–N(4)–C(28)	105.9(7)		
N(4)–C(16)–C(17)	115.5(8)	Cd(1)–S(5)–C(11)	87.1(3)
C(16)–C(17)–C(18)	110.6(10)	Cd(1)–S(6)–C(11)	88.3(3)
C(17)–C(18)–C(19)	113.3(12)	S(5)–C(11)–S(6)	119.0(5)
N(4)–C(20)–C(21)	115.2(8)	S(5)–C(11)–N(3)	121.2(7)
C(20)–C(21)–C(22)	111.0(10)	S(6)–C(11)–N(3)	119.7(7)
C(21)–C(22)–C(23)	115.5(13)	C(11)–N(3)–C(12)	120.9(8)
N(4)–C(24)–C(25)	113.6(11)	C(11)–N(3)–C(14)	124.5(8)
C(24)–C(25)–C(26)	112.7(15)	C(12)–N(3)–C(14)	114.6(8)
C(25)–C(26)–C(27) *	110.1(—)	N(3)–C(12)–C(13)	110.9(10)
N(4)–C(28)–C(29)	115.4(12)	N(3)–C(14)–C(15)	109.4(9)
C(28)–C(29)–C(30)	109.2(18)		
C(29)–C(30)–C(31) *	110.1(—)		

* Constrained during refinement.

geometries. In one ligand the ethyl groups both lie on the same side of the mean plane; this slightly less preferable conformation is, presumably, a consequence of improved crystal packing. The cation comprises two n-butyl groups in the preferred antiperiplanar conformation and two in a less favourable anticlinal conformation; the bond lengths and angles in the cation are acceptable.

The small asymmetry in the metal co-ordination polyhedron may be compared with the gross asymmetry observed in the closely related zinc species $[NEt_4]$-$[Zn(S_2CNMe_2)_3]$ where two of the dithiocarbamato-

TABLE 7

Mean planes of planar fragments for $[NBu^n_4][Cd(S_2CNEt_2)_3]$. The mean planes of the fragments are expressed as $pX + qY + rZ = d$ where p, q, and r are the direction cosines of the normal to the plane referred to orthogonal crystal axes a, b, and c.* Deviations (Å) of atoms from the mean planes are shown in square brackets

	p	q	r	d
Plane A: S(1), S(2), N(1), C(1), C(2), C(4)	0.2903	0.8257	−0.4837	2.4772
[S(1) −0.007, S(2) 0.009, N(1) 0.012, C(1) −0.007, C(2) 0.006, C(4) −0.013, Cd(1) −0.022, C(3) −1.333, C(5) 1.363]				
Plane B: S(3), S(4), N(2), C(6), C(7), C(9)	−0.0617	0.9534	0.2954	−1.8159
[S(3) 0.003, S(4) 0.020, N(2) −0.031, C(6) −0.021, C(7) 0.024, C(9) 0.005, Cd(1) 0.541, C(8) −1.322, C(10) −1.342]				
Plane C: S(5), S(6), N(3), C(11), C(12), C(14)	−0.3562	0.0177	−0.9342	4.0139
[S(5) −0.004, S(6) 0.022, N(3) −0.013, C(11) −0.020, C(12) 0.023, C(14) −0.007, Cd(1) 0.148, C(13) −1.281, C(15) 1.421]				
Plane D: C(16)—C(19)	−0.0562	−0.3834	−0.9219	3.9082
[C(16) −0.017, C(17) 0.016, C(18) 0.019, C(19) −0.018, N(4) −0.022]				
Plane E: C(20)—C(23)	−0.0089	−0.4279	−0.9038	4.1091
[C(20) −0.002, C(21) 0.002, C(22) 0.003, C(23) −0.002, N(4) −0.014]				
Plane F: C(24)—C(26)	0.0252	0.9135	−0.4060	1.8571
[N(4) 0.047, C(27) −1.366]				
Plane G: C(25)—C(27)	−0.7503	−0.0389	0.6599	−8.8564
[C(24) 1.313]				
Plane H: C(28)—C(30)	0.1487	−0.9023	0.4046	−1.0220
[N(4) 0.176, C(31) −1.365]				
Plane I: C(29)—C(31)	−0.7364	−0.0651	−0.6734	−2.8666
[C(28) 1.374]				
Plane J: S(2), S(4), S(5)	−0.9838	0.1303	0.1233	−2.4167
[Cd(1) 1.444]				
Plane K: S(1), S(3), S(6)	−0.9845	0.1237	0.1243	0.4232
[Cd(1) −1.402]				

Angles (°) between planes F—G 108.8; H—I 108.9; J—K 0.4.

ligands are formally unidentate.[1] In the present compound, the larger covalent radius of cadmium is almost enough to allow the symmetrically bidentate accommodation of three S_2CNR_2 units.

That the structure observed is intermediate between idealised D_{3d} and D_{3h} symmetry for the CdS_6 core is not especially surprising in view of the discussion by Kepert [13] about the relation between ligand bite angle, M–S bond lengths, and the relative disposition of three bidentate ligands in a six-co-ordinate complex.

However, an interesting comparison can be made between the structure of $[Cd(S_2CNEt_2)_3]^-$ and the closely related xanthate, $[Cd(S_2COEt)_3]^-$. The latter has a five-co-ordinate geometry,[6] being a distorted tetragonal pyramid, with Cd–S (basal) 2.67 Å, Cd–S (apical) 2.51 Å, and the S–Cd–S intraligand bond angle 66°. It would seem that, rather than adopt a slightly overcrowded $Cd(S_2CR)_3$ geometry (see later), the xanthate structure completes full co-ordination by the inclusion of a smaller (oxygen) atom in or near to the co-ordination sphere, at a Cd · · · O distance of 2.96 Å. Thus the formally unidentate axial S_2COEt group could be viewed as a very distorted (chelating) η^2-*S*,*O*-xanthate ligand. Such an option is not available to the diethyldithiocarbamato-ligand.

TABLE 8

Bond lengths (Å) and angles (°) with estimated standard deviations for $[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$

Cd(1)–S(1)	2.777(2)	O(2)–C(4)	1.461(7)
Cd(1)–S(2)	2.658(1)	C(1)–C(2)	1.497(10)
S(1)–P(1)	1.982(2)	C(1)–C(3)	1.503(9)
S(2)–P(1)	1.976(2)	C(4)–C(5)	1.488(10)
P(1)–O(1)	1.593(3)	C(4)–C(6)	1.500(10)
P(1)–O(2)	1.587(3)	N(1)–C(7)	1.490(9)
O(1)–C(1)	1.463(5)	N(1)–C(8)	1.479(9)
S(1)–Cd(1)–S(2)	74.95(4)	O(1)–P(1)–O(2)	95.07(17)
S(1)–Cd(1)–S(1′)	92.54(4)	P(1)–O(1)–C(1)	118.5(3)
S(1)–Cd(1)–S(2′)	165.57(5)	P(1)–O(2)–C(4)	120.5(3)
S(1)–Cd(1)–S(2″)	95.14(4)	O(1)–C(1)–C(2)	107.6(4)
S(2)–Cd(1)–S(2′)	98.65(4)	O(1)–C(1)–C(3)	107.5(4)
Cd(1)–S(1)–P(1)	84.14(6)	C(2)–C(1)–C(3)	113.6(5)
Cd(1)–S(2)–P(1)	87.54(6)	O(2)–C(4)–C(5)	106.7(5)
S(1)–P(1)–S(2)	113.36(8)	O(2)–C(4)–C(6)	107.8(5)
S(1)–P(1)–O(1)	110.69(14)	C(5)–C(4)–C(6)	113.0(6)
S(1)–P(1)–O(2)	112.07(14)	C(7)–N(1)–C(8)	108.7(5)
S(2)–P(1)–O(1)	112.72(14)	C(8)–N(1)–C(8′)	110.2(5)
S(2)–P(1)–O(2)	111.60(14)		

Atoms carrying a single prime superscript are related to the corresponding un-superscripted atoms by the symmetry operation [*y*, *z*, *x*]; those carrying a double prime superscript are related by the operation [*z*, *x*, *y*].

TABLE 9

Mean planes of planar fragments for $[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$. The mean planes are expressed as $pX + qY + rZ = d$ where p, q, and r are the direction cosines of the normal to the plane referred to orthogonal crystal axes a, b^*, c'. Deviations (Å) of atoms from the mean planes are shown in square brackets

	p	q	r	d
Plane A: S(1), S(2), P(1)	−0.8593	0.0437	0.5097	−1.5241
[Cd(1) −0.022]				
Plane B: O(1), O(2), P(1)	0.4822	0.3126	0.8184	2.5396
[C(1) 0.057, C(4) −0.258]				

Angle between planes: A—B 89.1°.

With the exception of the ethyl substituents, the anion has approximate D_3 symmetry.

$[NEt_4][Cd(C_7H_4NS_2)_3]$. The anion is constrained to possess strict C_3 symmetry; the cadmium atom is six-co-ordinate, with each $C_7H_4NS_2^-$ ligand bonded to the cadmium through the exocyclic sulphur atom (2.667 Å) and through the nitrogen atom (2.474 Å). The rather

TABLE 10

Bond lengths (Å) and angles (°) with estimated standard deviations for $[NEt_4][Cd(C_7H_4NS_2)_3]$

Cd(1)–S(1)	2.667(6)	C(3)–C(4)	1.384(20)
Cd(1)–N(1)	2.474(11)	C(4)–C(5)	1.356(21)
S(1)–C(1)	1.693(14)	C(5)–C(6)	1.399(21)
S(2)–C(1)	1.746(14)	C(6)–C(7)	1.365(20)
S(2)–C(3)	1.755(14)	C(2)–C(7)	1.364(19)
N(1)–C(1)	1.303(17)		
N(1)–C(2)	1.404(17)	N(2)–C(8) *etc.*	1.500(—) [b]
C(2)–C(3)	1.386(19)	C(8)–C(9) *etc.*	1.520(—) [b]
S(1)–Cd(1)–N(1)	62.0(3)	N(1)–C(2)–C(7)	125.5(12)
S(1)–Cd(1)–S(1′) [a]	102.4(2)	C(3)–C(2)–C(7)	120.8(12)
S(1)–Cd(1)–N(1′) [a]	106.4(3)	S(2)–C(3)–C(2)	109.6(10)
S(1)–Cd(1)–N(1″) [a]	149.6(3)	S(2)–C(3)–C(4)	129.9(11)
N(1)–Cd(1)–N(1′) [a]	95.8(4)	C(2)–C(3)–C(4)	120.6(13)
		C(3)–C(4)–C(5)	119.0(14)
Cd(1)–S(1)–C(1)	79.5(5)	C(4)–C(5)–C(6)	119.6(14)
Cd(1)–N(1)–C(1)	94.5(8)	C(5)–C(6)–C(7)	121.9(14)
Cd(1)–N(1)–C(2)	152.2(8)	C(6)–C(7)–C(2)	118.1(13)
C(1)–N(1)–C(2)	113.2(11)		
S(1)–C(1)–S(2)	122.4(8)		
S(1)–C(1)–N(1)	124.0(11)	C(8)–N(2)–C(10) *etc.*	109.5(—) [b]
S(2)–C(1)–N(1)	113.6(10)		
C(1)–S(2)–C(3)	90.0(7)	N(2)–C(8)–C(9) *etc.*	112.0(—) [b]
N(1)–C(2)–C(3)	113.6(11)		

[a] See footnote to Table 8. [b] Constrained during refinement to the stated values which are representative of a number of chemically equivalent values.

TABLE 11

Mean planes of planar fragments for $[NEt_4][Cd(C_7H_4NS_2)_3]$. The mean planes are expressed as $pX + qY + rZ = d$ where p, q, and r are the direction cosines of the normal to the plane referred to orthogonal crystal axes a, b, c. Deviations (Å) of atoms from the mean planes are shown in square brackets

	p	q	r	d
Plane A: C(2)—C(7)	−0.4531	0.4437	0.7732	2.0486
Plane B: S(2), N(1), C(1)—C(3)	−0.5009	0.4255	0.7537	1.9707
Plane C: Cd(1), S(1), N(1)	−0.5081	0.4073	0.7589	1.8831

Plane A: [Cd(1) 0.137, S(1) 0.241, S(2) 0.079, N(1) 0.062, C(1) 0.144, C(2) 0.008, C(3) 0.008, C(4) −0.018, C(5) 0.013, C(6) 0.004, C(7) −0.014]

Plane B: [Cd(1) −0.030, S(1) 0.023, S(2) −0.012, N(1) −0.015, C(1) 0.017, C(2) 0.003, C(3) 0.006, C(4) 0.047, C(5) 0.140, C(6) 0.126, C(7) 0.043]

Plane C: [S(2) −0.043, C(1) 0.006, C(2) 0.023, C(3) 0.003]

Angles (°) between planes: A—B 3.1; B—C 1.2.

small ' bite ' angle of this N–C–S linkage leads to a smaller distortion from trigonal prismatic towards octahedral (25.8°) than observed in the dithiophosphate complex below but a larger angle than in the less symmetric dithiocarbamato-complex. This results in very unusual bond angles at the donor nitrogen atom which are only justified by the need for the cadmium atom to achieve co-ordinative saturation. This mode of bonding can be compared to the two distinct types found in the related, but structurally dissimilar zinc-containing complex anion $[Zn(C_7H_4NS_2)_3(OH_2)]^-$ [1] In this latter structure, one $C_7H_4NS_2^-$ ligand is bonded *via* the nitrogen atom but exhibits a short (3.1 Å) zinc–sulphur contact whereas the other two ligands bond *via* their exocyclic sulphur atoms and the nitrogen atoms are hydrogen bonded to a co-ordinated water molecule. Clearly, steric factors would, in that case, preclude a bonding mode as found in the $[Cd(C_7H_4NS_2)_3]^-$ anion.

The carbon–sulphur exocyclic bond is longer than that found in the free molecule 2-mercaptobenzothiazole.[14] This is consistent with the reduction in bond order resulting from the co-ordination of the exocyclic sulphur to the cadmium: similar values were found in the related zinc anion $[Zn(C_7H_4NS_2)_3(OH_2)]^-$ [1]

The geometry of the cation was constrained during refinement in order to take account of disorder about the crystallographic C_3 axis; the nitrogen atom and the terminal methyl-group carbon atoms comply *approximately* with the C_3 symmetry but the methylene carbon atoms are extensively disordered.

$[NMe_4][Cd\{S_2P(OPr^i)_2\}_3]$. The geometries of both anion and cation are constrained to possess strict, crystallographically imposed C_3 symmetry. The cadmium atom is again six-co-ordinate with a geometry which is intermediate between trigonal prismatic and octahedral, the two exactly equilateral triangles of sulphur atoms being relatively twisted by 44.0°. This larger angle, as compared to that in the anion $[Cd(S_2CNEt_2)_3]^-$ described above, is directly attributable to the larger ' bite ' of an S_2PR_2 unit as compared to that of the S_2CNR_2 unit, thus allowing the more favourable octahedral geometry to be more closely approached. Each chelate linkage is again asymmetric with the two unique Cd–S distances differing by 0.12 Å (80σ), but here the two sets of three equivalently distanced sulphur atoms are constrained by symmetry to each constitute an equilateral triangular face of the cadmium co-ordination polyhedron. The geometry of the di-isopropyl dithiophosphate ligand is unexceptionable and shows no features which reflect this slight asymmetry in chelation. The geometry of the cation is similarly unexceptionable.

The co-ordination geometry of the cadmium atom may be compared to that of the zinc atom in the related anions $[Zn\{S_2P(OC_6H_4Me)_2\}_3]^-$ and $[Zn(S_2PPh_2)_3]^-$ [3] In both these latter cases, two of the S_2PR_2 units are monohapto in their bonding whilst the remaining ligand is symmetrically bidentate. This again illustrates the difficulty in increasing the co-ordination number of zinc beyond four when using sulphur donor ligands, unless using bidentate ligands with small ' bite ' angles (*e.g.* $S_2CNR_2^-$). On moving to comparable cadmium-containing complex anions, this steric problem is *almost* completely relieved and the extent of the distortion from trigonal prismatic towards octahedral geometry is determined only by the ' bite ' angle of the chelate.

In conclusion, we would note that in comparing the structures of related zinc and cadmium complexes, it is obvious that an increase in the size of the central metal atom allows the adoption of more regular structures, especially in the species containing S_2CNR_2 and $C_7H_4NS_2$. We anticipate that this trend will be continued in the parallel series of mercury(II) complexes, and work towards this end is in progress.

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