Aspects of the Inorganic Chemistry of Rubber Vulcanisation. Part 2.[1] Anionic Mixed-ligand Zinc Complexes derived from Dialkyldithiocarbamates, 2-Mercapto-benzothiazole, -benzoxazole, and -benzimidazole, and the Crystal and Molecular Structures of $[NEt_4][Zn(S_2CNMe_2)_3]$, $[NBu^n{}_4][Zn(C_7H_4NS_2)_3(OH_2)]$, $[NBu^n{}_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]\cdot C_2H_5OH$, and $[NBu^n{}_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]$ †

By **Jon A. McCleverty**,*‡ **Norman J. Morrison, Neil Spencer, Christopher C. Ashworth, Neil A. Bailey**,* **Martin R. Johnson, John M. A. Smith, Barbara A. Tabbiner, and Christine R. Taylor**, Department of Chemistry, The University, Sheffield S3 7HF

The complexes $[Zn(S_2CNR_2)_3]^-$ (R = Me or Et), $[Zn(S_2CNR_2)(S_2CNR'_2)_2]^-$ [R = Me, Et, or Bu^n; R′ = Me or Et; $R_2 = (CH_2)_5$, R′ = Me or Et], $[Zn(C_7H_4NS_2)_3(OH_2)]^-$ ($C_7H_4NS_2$ = benzothiazole-2-thiolate), $[Zn(S_2CNR_2)_2(C_7H_4NS_2)]^-$ [R = Me, Et, or Bu^n; $R_2 = (CH_2)_5$], $[Zn(S_2CNR_2)_2(C_7H_4NOS)]^-$ [R = Me, Et, or Bu^n; $R_2 = (CH_2)_5$; C_7H_4NOS = benzoxazole-2-thiolate], $[Zn(S_2CNR_2)(C_7H_4NS_2)_2]^-$ [R = Me, Et, Bu^n, or C_6H_{11}; $R_2 = (CH_2)_5$], $[Zn(S_2CNR_2)(C_7H_4NOS)_2]^-$ [R = Me or Et; $R_2 = (CH_2)_5$], and $[Zn\{S_2C\overline{N(CH_2)_4CH_2}\}(C_7H_5N_2S)_2]^-$ ($C_7H_5N_2S$ = benzimidazole-2-thiolate) have been isolated as their $[NMe_4]^+$ and $[NBu^n{}_4]^+$ salts. The compounds $[NR''_4][S_2CNR_2]$ [R″ = Me or Bu^n; R = Et or C_6H_{11}; $R_2 = (CH_2)_5$], $[NR''_4][C_7H_4NS_2]$, $[NR''_4][C_7H_4NOS]$ (R″ = Me or Bu^n), $[NBu^n{}_4][C_7H_5N_2S]$, and $[NBu^n{}_4][C_3H_4NS_2]$ ($C_3H_4NS_2$ = thiazoline-2-thiolate) have also been prepared. The structures of the four title complexes have been determined crystallographically. The nature of the distortions from regular co-ordination geometries in some of these species are discussed and related to the molecular structures of $[\{Zn(S_2CNR_2)_2\}_2]$ (R = Me or Et).

IN the preceding paper[1] we provided a general description of the acceleration of rubber vulcanisation as catalysed by mixtures of zinc oxide, S_8, stearic acid, and certain organosulphur compounds. In our study of how sulphur is ' activated ' towards attack on rubber hydrocarbons in such systems, we have focused our attention on the interactions between the various components of the vulcanisation mixture (or ' sulphurating system ').

We have observed that the organosulphur additives, or ' accelerators ', typically tetra-alkylthiuram disulphides, $(R_2NCS)_2S_2$, or derivatives of 2-mercaptobenzothiazole, $C_7H_5NS_2$, react with zinc oxide and stearate ion eventually forming anionic zinc complexes. These complexes, $[Zn(S_2CNR_2)_3]^-$ or $[Zn(C_7H_4NS_2)_3(OH_2)]^-$, have been described briefly earlier[2,3] and may be important precursors in the catalysed ring opening of S_8 which must precede addition of sulphur-containing fragments to the rubber hydrocarbon. In this paper we describe the preparation of further examples of $[Zn(S_2CNR_2)_3]^-$, the full synthesis and structural characterisation of $[NBu^n{}_4][Zn(C_7H_4NS_2)_3(OH_2)]^-$, and of $[NEt_4][Zn(S_2CNMe_2)_3]$.

Certain types of vulcanisation accelerator formulations contain mixtures of thiuram disulphides and benzothiazole-2-sulphenamides, $C_7H_4NS_2{-}NR_2$ (R = alkyl). It occurred to us that in such mixed ' sulphurating systems,' anionic mixed-ligand complexes of zinc might be formed. Accordingly, we have complemented our investigations of $[Zn(S_2CNR_2)_3]^-$ and $[Zn(C_7H_4NS_2)_3(OH_2)]^-$ by a study of the mixed-ligand species $[Zn(S_2CNR_2)_{3-n}(C_7H_4NS_2)_n]^-$ (n = 1 or 2). The full structural characterisations of $[NBu^n{}_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]\cdot C_2H_5OH$ and of $[NBu^n{}_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]$ are reported.

Finally, we have investigated the ability of 2-mercaptobenzoxazole (C_7H_5NOS), -benzimidazole ($C_7H_6N_2S$), and -thiazoline ($C_3H_5NS_2$) to form anionic zinc complexes. Neither of the first two compounds significantly accelerates the vulcanisation of rubber when added to ' sulphurating systems '.

EXPERIMENTAL

Infrared spectra were recorded using Perkin-Elmer 457 and 180 spectrophotometers. The ^1H n.m.r. spectra were obtained using JEOL PFT-100 and Perkin-Elmer R-34 instruments. Elemental analyses were determined by the Microanalytical Laboratory of this Department.

The compounds $[NR_4][S_2CNMe_2]$, $[NR_4][Zn(S_2CNMe_2)_3]$ (R = Et or Bu^n), and $[\{Zn(C_7H_4NS_2)_2\}_n]$ were prepared as described previously.[1,3] All yields are quoted relative to the zinc-containing starting material, where appropriate.

Tetra-n-butylammonium Benzothiazole-2-thiolate, $[NBu^n{}_4][C_7H_4NS_2]$.—An aqueous solution of $[NBu^n{}_4][OH]$ (45 cm³, 40%) was added to a hot ethanolic solution (300 cm³) of 2-mercaptobenzothiazole (11.4 g). The solution was filtered, evaporated to dryness, and the yellow *solid* washed with diethyl ether and recrystallised from acetone–light petroleum (b.p. 40—60 °C). The $[NMe_4]^+$ salt was prepared similarly.

Tetramethylammonium Benzoxazole-2-thiolate, $[NMe_4][C_7H_4NOS]$.—To a solution of 2-mercaptobenzoxazole (15.1 g) in hot ethanol (250 cm³) was added $[NMe_4][OH]$ (36.4 cm³, 25% aqueous solution) and the mixture was evaporated to dryness. The beige *crystals* which formed were recrystallised from acetone–light petroleum (b.p. 40—60 °C) (yield

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† Tetraethylammonium (dimethyldithiocarbamato-*S*,s′)bis(dimethyldithiocarbamato-*S*)zincate, tetra-n-butylammonium aqua(benzothiazole-2-thiolato-*N*)bis(benzothiazole-2-thiolato-*S*″)zincate, tetra-n-butylammonium (benzothiazole-2-thiolato-*N*)bis(dimethyldithiocarbamato-*S*,*S*′)zincate–ethanol(1/1), and tetra-n-butylammonium bis(benzothiazole-2-thiolato-*N*)(dimethyldithiocarbamato-*S*,*S*′)zincate respectively.

‡ *Present address:* Department of Chemistry, University of Birmingham, Birmingham B15 2TT.

quantitative). The $[\mathrm{NBu^n_4}]^+$ salt was obtained similarly using $[\mathrm{NBu^n_4}][\mathrm{OH}]$ (25.9 g, 64.8 cm^3, 40% aqueous solution).

Tetramethylammonium Benzimidazole-2-thiolate, $[\mathrm{NMe_4}][\mathrm{C_7H_5N_2S}]$.—This compound was obtained in the same way as its benzoxazole analogue, using 2-mercaptobenzimidazole (15.0 g) and $[\mathrm{NMe_4}][\mathrm{OH}]$ (36.4 cm^3, 25% aqueous solution) (yield quantitative). The $[\mathrm{NBu^n_4}]^+$ salt was obtained similarly.

Tetramethylammonium Δ^2-*1,3-Thiazoline-2-thiolate*, $[\mathrm{NMe_4}][\mathrm{C_3H_4NS_2}]\cdot\mathrm{EtOH}$.—This compound was obtained in the same way as its benzoxazole analogue, using 2-mercaptothiazoline (11.9 g) and $[\mathrm{NMe_4}][\mathrm{OH}]$. The $[\mathrm{NBu^n_4}]^+$ salt was obtained in the same way.

Zinc Bis(benzoxazole-2-thiolate), $[\{\mathrm{Zn(C_7H_4NOS)_2}\}_n]$.—To an ethanol solution (250 cm^3) of 2-mercaptobenzoxazole (15.1 g) was added $\mathrm{K[OH]}$ (5.6 g) in aqueous ethanol. The mixture was heated until it became homogeneous and to it was added an ethanolic solution (100 cm^3) of $[\mathrm{Zn(OCOMe)_2}]\cdot\mathrm{2H_2O}$ (10.9 g). The mixture was allowed to cool, and the pale yellow precipitate of the *compound* was filtered off, washed with ethanol, and dried *in vacuo* (84%).

Zinc bis(benzimidazole-2-thiolate), $[\{\mathrm{Zn(C_7H_5N_2S)}\}_n]$, *and zinc bis(thiazoline-2-thiolate)*, $[\{\mathrm{Zn(C_3H_4NS_2)_2}\}_n]$, were prepared in the same way as the benzoxazole analogue, using 2-mercaptobenzimidazole (15.0 g) and 2-mercaptothiazoline (11.9 g) respectively (yields nearly quantitative).

Tetra-n-butylammonium Aquatris(benzothiazole-2-thiolato)zincate, $[\mathrm{NBu^n_4}][\mathrm{Zn(C_7H_4NS_2)_3(OH_2)}]$.—A mixture of $[\{\mathrm{Zn(C_7H_4NS_2)_2}\}_n]$ (2.0 g) and $[\mathrm{NBu^n_4}][\mathrm{C_7H_4NS_2}]$ (2.0 g) was shaken in acetone (80 cm^3) for 1 h. The yellow solution which formed was filtered, and, on addition of light petroleum (b.p. 40—60 °C) followed by partial evaporation *in vacuo*, pale yellow crystals of the *complex* formed. These were filtered off and recrystallised from acetone–light petroleum (yield quantitative).

Tetra-n-butylammonium (Benzothiazole-2-thiolato)bis(dimethyldithiocarbamato)zincate, $[\mathrm{NBu^n_4}][\mathrm{Zn(S_2CNMe_2)_2(C_7H_4NS_2)}]$.—A mixture of $[\mathrm{Zn(S_2CNMe_2)_2}]$ (1.8 g) and $[\mathrm{NBu^n_4}][\mathrm{C_7H_4NS_2}]$ (2.0 g) was refluxed in acetone (80 cm^3) for 1 h. The yellow solution was filtered and on partial evaporation of the filtrate, yellow crystals of the complex formed. These were filtered off and recrystallised from ethanol–light petroleum (b.p. 60—80 °C) (yield quantitative).

The related complexes $[\mathrm{NR_4}][\mathrm{Zn(S_2CNR'_2)_2(C_7H_4NS_2)}]$ [R = Me or Bu^n; R$'$ = Et or Bu^n; $\mathrm{R'_2 = (CH_2)_5}$] were prepared similarly from $[\mathrm{Zn(S_2CNR'_2)_2}]$ and $[\mathrm{NR_4}][\mathrm{C_7H_4N_2S}]$.

Tetra-n-butylammonium Bis(benzothiazole-2-thiolato)(dimethyldithiocarbamato)zincate, $[\mathrm{NBu^n_4}][\mathrm{Zn(S_2CNMe_2)(C_7H_4NS_2)_2}]$.—A mixture of $[\{\mathrm{Zn(C_7H_4NS_2)_2}\}_n]$ (1.7 g) and $[\mathrm{NBu^n_4}][\mathrm{S_2CNMe_2}]$ (1.5 g) was refluxed in acetone (80 cm^3) for 1 h. The yellow solution was filtered and partial evaporation of the filtrate afforded yellow crystals of the *complex*. These were filtered off and recrystallised from acetone–light petroleum (b.p. 40—60 °C) (yield quantitative). The related complexes $[\mathrm{NR_4}][\mathrm{Zn(S_2CNR'_2)(C_7H_4NS_2)_2}]$ [R = Me or Bu^n; R$'$ = Et, Bu^n, or $\mathrm{C_6H_{11}}$; $\mathrm{R'_2 = (CH_2)_5}$] were obtained similarly from the appropriate $[\mathrm{NR_4}][\mathrm{S_2CNR'_2}]$.

Tetra-n-butylammonium (Benzoxazole-2-thiolato)bis(dimethyldithiocarbamato)zincate, $[\mathrm{NBu^n_4}][\mathrm{Zn(S_2CNMe_2)_2(C_7H_4NOS)}]$.—To an acetone solution (100 cm^3) of $[\mathrm{NBu^n_4}][\mathrm{C_7H_4NOS}]$ (4.1 g) was added $[\mathrm{Zn(S_2CNMe_2)_2}]$ (3.1 g) and the mixture was stirred and refluxed for 2 h. The solution was cooled and filtered, and on addition of light petroleum (b.p. 40—60 °C) the *complex* precipitated. The compound was filtered off, washed with light petroleum, and air-dried (yield quantitative).

The complexes $[\mathrm{NR_4}][\mathrm{Zn(S_2CNR'_2)_2(C_7H_4NOS)}]$ [R = Me, R$'$ = Me, Et, or Bu^n (as a dihydrate); $\mathrm{R'_2 = (CH_2)_5}$ (as a 1 : 1 acetone solvate)] were similarly prepared. Attempts to synthesise $[\mathrm{NBu^n_4}][\mathrm{Zn(S_2CNEt_2)_2(C_7H_4NOS)}]$ afforded only $[\mathrm{NBu^n_4}][\mathrm{Zn(S_2CNEt_2)(C_7H_4NOS)_2}]$.

Tetra-n-butylammonium (Benzimidazole-2-thiolato)bis(piperidinedithiocarbamato)zincate, $[\mathrm{NBu^n_4}][\mathrm{Zn\{S_2C\overline{N(CH_2)_4CH_2}\}_2(C_7H_5N_2S)}]$.—This compound was prepared in the same way as $[\mathrm{NBu^n_4}][\mathrm{Zn(S_2CNMe_2)_2(C_7H_4NOS)}]$, using $[\mathrm{Zn\{S_2C\overline{N(CH_2)_4CH_2}\}_2}]$ (3.9 g) and $[\mathrm{NBu^n_4}][\mathrm{C_7H_5N_2S}]$ (4.1 g). The yield was quantitative.

Tetra-n-butylammonium Bis(benzoxazole-2-thiolato)(dimethyldithiocarbamato)zincate, $[\mathrm{NBu^n_4}][\mathrm{Zn(S_2CNMe_2)(C_7H_4NOS)_2}]$.—This complex was prepared in the same way as $[\mathrm{NBu^n_4}][\mathrm{Zn(S_2CNMe_2)(C_7H_5N_2S)_2}]$ using $[\{\mathrm{Zn(C_7H_4NOS)_2}\}_n]$ (3.7 g) and $[\mathrm{NBu^n_4}][\mathrm{S_2CNMe_2}]$ (3.8 g). The complexes $[\mathrm{NBu^n_4}][\mathrm{Zn(S_2CNR_2)(C_7H_4NOS)_2}]$ [R = Et or $\mathrm{R_2 = (CH_2)_5}$] were obtained similarly. Attempts to make $[\mathrm{NMe_4}][\mathrm{Zn(S_2CNR_2)(C_7H_4NOS)_2}]$ (R = Me or Et) afforded the rearranged products $[\mathrm{NMe_4}][\mathrm{Zn(S_2CNR_2)_2(C_7H_4NOS)}]$.

Tetra-alkylammonium Dialkyldithiocarbamates, $[\mathrm{NR_4}][\mathrm{S_2CNR'_2}]$ [R = Me *or* Bu^n; R$'$ = Et *or* $\mathrm{C_6H_{11}}$; $\mathrm{R'_2 = (CH_2)_5}$].—These compounds were obtained in a way similar to that described for $[\mathrm{NBu^n_4}][\mathrm{S_2CNMe_2}]$.[3] To an aqueous solution of $[\mathrm{NR_4}][\mathrm{OH}]$ (*ca.* 1 mol) was added $\mathrm{CS_2}$ (1 mol) and the mixture was homogenised with the appropriate dialkylamine (*ca.* 1 mol). The water was then evaporated *in vacuo* keeping the temperature below 40 °C, and the solid residue was recrystallised from acetone–light petroleum (b.p. 40—60 °C).

Tetra-alkylammonium Tris(dithiocarbamato)zincate, $[\mathrm{NR_4}][\mathrm{Zn(S_2CNR'_2)(S_2CNR''_2)_2}]$ (R = Me, R$'$ = R$''$ = Me; R = R$'$ = Me, R$''$ = Et; R = R$''$ = Me, R$'$ = Et; R = Bu^n, R$'$ = Me, R$''$ = Et *or* R$'$ = Et, R$''$ = Me).—These complexes were prepared in a way similar to that described for $[\mathrm{NBu^n_4}][\mathrm{Zn(S_2CNMe_2)_3}]$.[3] To an acetone solution of $[\mathrm{NR_4}][\mathrm{S_2CNR'_2}]$ (*ca.* 1 mol) was added $[\mathrm{Zn(S_2CNR''_2)_2}]$ (*ca.* 1 mol) and the mixture stirred for 2 h. After filtration, the filtrate was treated with light petroleum (b.p. 40—60 °C) and on partial evaporation the *complex* precipitated. The solid was filtered off and recrystallised from acetone–light petroleum. On occasions it proved necessary to reflux the reaction mixture, or to use refluxing toluene as the reaction medium. Despite careful control of the reaction stoicheiometry, it was often impossible to prevent ligand redistribution.

Crystal Data.—$[\mathrm{NEt_4}][\mathrm{Zn(S_2CNMe_2)_3}]$, $\mathrm{C_{17}H_{38}N_4S_6Zn}$, M = 556.27, crystallises from acetone–light petroleum (b.p. 40—60 °C) as colourless needles, crystal dimensions 0.108 × 0.538 × 0.262 mm, Orthorhombic, a = 14.709(14), b = 18.780(13), c = 20.130(19) Å, U = 5 561(8) Å^3, D_m = 1.30, Z = 8, D_c = 1.328 g cm^{-3}, space group *Pbca* from systematic absences, Mo-K_α radiation, (λ = 0.710 69 Å), μ(Mo-K_α) = 13.49 cm^{-1}, $F(000)$ = 2 352.

Three-dimensional X-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 two-circle diffractometer by the moving-crystal–stationary-counter method. 2 065 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions (C–H 0.95 Å) and those of the methyl groups were satisfactorily located on the annulus (X–C–H 109.5°, X = C or N); the contributions of all hydrogen atoms were included in structure-factor calculations (B = 7.0 Å^2) but no least-squares refinement of positional parameters was permitted. Refinement converged at R 0.042 5 with allowance being made for the anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of zinc and sulphur atoms. Table 4 lists the atomic positions and estimated standard deviations.

$[NBu^n_4][Zn(C_7H_4NS_2)_3(OH_2)]$, $C_{37}H_{50}N_4OS_6Zn$, M = 824.59, crystallises from aqueous acetone as pale yellow needles (mean crystal dimensions 0.43 × 0.08 × 0.07 mm), Monoclinic, a = 9.854(5), b = 16.027(13), c = 27.008(22) Å, β = 94.325(6)°, U = 4 253(5) Å^3, D_m = 1.28, Z = 4, D_c = 1.288 g cm^{-3}, space group $P2_1/c$ from systematic absences, Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 9.05 cm^{-1}, F(000) = 1 736.

The data were collected and processed (3 407 independent reflections) and the structure solved and refined (R = 0.040 3) as for $[NEt_4][Zn(S_2CNMe_2)_3]$ but refinement of positional parameters for the hydrogen atoms of the co-ordinated water molecule was permitted. Table 5 lists the atomic positions and estimated standard deviations.

$[NBu^n_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]\cdot C_2H_5OH$, $C_{31}H_{58}N_4OS_6Zn$, M = 760.58, crystallises from ethanol–light petroleum (b.p. 60—80 °C) as regular bricks, crystal dimensions 0.142 × 0.146 × 0.330 mm, Monoclinic, a = 16.797(19), b = 15.349(17), c = 16.677(10) Å, β = 111.74(4)°, U = 3 994(7) Å^3, D_m = 1.28 Z = 4, D_c = 1.265 g cm^{-3} (for the ethanol solvate as formulated above), space group $P2_1/n$ from systematic absences, Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 9.58 cm^{-1}, F(000) = 1 520.

The data were collected and processed (1 756 independent reflections) and the structure solved and refined (R = 0.038 9) as for $[NEt_4][Zn(S_2CNMe_2)_3]$; the data were corrected for absorption. The contributions from all hydrogen atoms were included in structure-factor calculations but positional parameters were not varied. The non-methyl-group hydrogen atoms were located on difference-Fourier syntheses and were assigned B = 10.0 Å^2; little evidence was found for methyl-group hydrogen atoms but account was taken of their necessary presence by positioning six half-population hydrogen atoms distributed around each annulus (X–C–H 109.5°, X = C or N; B = 12.0 Å^2). Table 6 lists atomic positional parameters and estimated standard deviations.

$[NBu^n_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]$, $C_{33}H_{50}N_4S_6Zn$, M = 760.54, crystallises from acetone–light petroleum (b.p. 60—80 °C) as elongated bricks (chosen crystal 0.108 × 0.127 × 0.608 mm), Orthorhombic, a = 20.292(26), b = 9.947(13), c = 19.278(24) Å, U = 3 891(9) Å^3, D_m = 1.29, Z = 4, D_c = 1.298 g cm^{-3}, space group $Pca2_1$ from systematic absences (centrosymmetric alternative exluded as a result of a successful analysis), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 9.82 cm^{-1}, F(000) = 1 608.

The data were collected and processed (1 999 independent reflections) and the structure solved and refined (R = 0.032 5) as for $[NEt_4][Zn(S_2CNMe_2)_3]$ above; the data were corrected for absorption. The last two carbon atoms of one butyl group were found to be disordered and a second butyl group showed an unacceptable geometry: the final refinement constrained the geometry of these fragments (C–C 1.537 Å, C–C–C 110°) and, for the disordered group, the two components were given occupancy factors of 0.6 and 0.4. Hydrogen atoms were not positioned on the lower-population conformer of the disordered butyl group; one methyl group of the S_2CNMe_2 ligand showed no evidence for localised sites for hydrogen atoms which were accommodated by the positioning of six half-population hydrogen atoms around the annulus. The contributions of hydrogen atoms so defined were included (but not varied) in structure-factor calculations (B = 10.0 Å^2). Table 7 lists atomic positions and estimated standard deviations.

Scattering factors were taken from ref. 4; unit weights were used throughout all refinements. Computer programs used formed part of the Sheffield X-ray system. For all structural analyses, Tables of anisotropic thermal vibrational parameters with estimated standard deviations, predicted hydrogen-atom positional parameters, and observed structure amplitudes and calculated structure factors are deposited in Supplementary Publication No. SUP 22784 (110 pp.).*

RESULTS AND DISCUSSION

Tris(dithiocarbamato)-complexes.—In an earlier paper [3] we showed that tris(dithiocarbamato)zincate species could be prepared by adding $[NR_4][S_2CNR'_2]$ to $[Zn(S_2CNR''_2)_2]$ in solution. In this way we obtained $[NEt_4]^+$ and $[NBu^n_4]^+$ salts of $[Zn(S_2CNMe_2)_3]^-$ (R′ = R″ = Me) and $[Zn(S_2CNMe_2)(S_2CNEt_2)_2]^-$ (R′ = Me, R″ = Et). However, we were surprisingly unable to obtain $[NMe_4]^+$ salts of these species, and also, on attempting to prepare $[NBu^n_4][Zn(S_2CNMe_2)(S_2CNBu^n_2)_2]$ (R′ = Me, R″ = Bu) by the route outlined above, we could isolate only the ligand-redistributed product $[NBu^n_4][Zn(S_2CNMe_2)_2(S_2CNBu^n_2)]$.

In further studies of these tris(dithiocarbamato)-species, we have now been able to obtain $[NMe_4][Zn(S_2CNMe_2)_3]$ (R′ = R″ = Me), isolated as a monohydrate, as well as $[NMe_4][Zn(S_2CNEt_2)_3]$ (R′ = R″ = Et) (analytical data are summarised in Table 1). We have also made several other mixed-ligand species $[Zn(S_2CNR'_2)(S_2CNR''_2)_2]^-$ [R″ = Et, R′ = Me and R″ = Me or Et, R′ = $(CH_2)_5$]. However, on attempting to isolate $[Zn(S_2CNEt_2)(S_2CNBu^n_2)_2]^-$ from the reaction between $[NMe_4][S_2CNEt_2]$ and $[Zn(S_2CNBu^n_2)_2]$, we obtained instead $[NMe_4][Zn(S_2CNEt_2)_2(S_2CNBu^n_2)]$. Furthermore, in reactions between $[Zn(S_2CNMe_2)_2]$ and $[NMe_4][S_2CNBu^n_2]$ and its cyclohexyl analogue (R′ = C_6H_{11}), we could isolate only $[NMe_4][S_2CNMe_2]$ and $[Zn\{S_2CN(C_6H_{11})_2\}_2]$, respectively, and no anionic tris(ligand) species. These redistribution reactions indicate very strongly that in solutions containing, initially, $[Zn(S_2CNR''_2)_2]$ and $[S_2CNR'_2]^-$, a series of equilibria must be established [equations (1)—(5), *etc.*]. As yet, we have

$$[Zn(S_2CNR''_2)_2] + [S_2CNR'_2]^- \rightleftharpoons [Zn(S_2CNR''_2)_2(S_2CNR'_2)]^- \quad (1)$$

$$[Zn(S_2CNR''_2)_2(S_2CNR'_2)]^- \rightleftharpoons [Zn(S_2CNR''_2)(S_2CNR'_2)] + [S_2CNR''_2]^- \quad (2)$$

$$[Zn(S_2CNR''_2)(S_2CNR'_2)] + [S_2CNR'_2]^- \rightleftharpoons [Zn(S_2CNR''_2)(S_2CNR'_2)_2]^- \quad (3)$$

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

$$[Zn(S_2CNR''_2)(S_2CNR'_2)_2]^- \rightleftharpoons [Zn(S_2CNR'_2)_2] + [S_2CNR''_2]^- \quad (4)$$

$$[Zn(S_2CNR'_2)_2] + [S_2CNR'_2]^- \rightleftharpoons [Zn(S_2CNR'_2)_3]^- \quad (5)$$

not isolated the symmetrical species $[Zn(S_2CNR'_2)_3]^-$ or $[Zn(S_2CNR''_2)_3]^-$ from reactions involving $[S_2CNR'_2]^-$ and $[Zn(S_2CNR''_2)_2]$. This presumably reflects the relative concentrations of such species in solution, the relative values of the equilibrium constants, and the relative solubilities of the various components of the system.

Tris(benzothiazolethiolato)-species.—Reaction of ZnO with $C_7H_5NS_2$ or of Zn^{2+} salts with $K[C_7H_4NS_2]$ afforded the insoluble and presumably polymeric $[\{Zn(C_7H_4NS_2)_2\}_n]$. Treatment of this species with $[NBu^n_4][C_7H_4NS_2]$, or with $[NBu^n_4][OCOR]$ (R = Me or $C_{17}H_{35}$)[1] in damp acetone, gave $[NBu^n_4][Zn(C_7H_4NS_2)_3(OH_2)]$ which is reasonably soluble in common organic solvents. Attempts to prepare alkali-metal salts of $[Zn(C_7H_4$-

TABLE 1

Microanalytical data (%)

Compound	Found C	Found H	Found N	Found S	Calc. C	Calc. H	Calc. N	Calc. S
$[NMe_4][S_2CNEt_2]$	48.3	9.7	12.8		48.6	10.0	12.6	
$[NBu^n_4][S_2CNEt_2]$	64.6	11.9	7.2		64.3	12.1	7.1	
$[NMe_4][S_2CN(CH_2)_4CH_2]$	50.9	9.2	12.1		51.2	9.5	12.0	
$[NBu^n_4][S_2CN(CH_2)_4CH_2]$	65.6	11.5	7.0		65.7	11.5	6.9	
$[NMe_4][S_2CN(C_6H_{11})_2]$	61.9	10.2	8.3		61.8	10.4	8.5	
$[NBu^n_4][S_2CN(C_6H_{11})_2]$	69.3	12.2	5.8		69.8	11.7	5.6	
$[NMe_4][C_7H_4NS_2]$	54.7	6.7	11.5		55.0	6.7	11.7	
$[NBu^n_4][C_7H_4NS_2]$	67.5	10.0	6.9	15.9	67.6	9.9	6.9	15.7
$[NMe_4][C_7H_4NOS]$	58.5	7.4	12.4	14.5	58.9	7.2	12.5	14.3
$[NBu^n_4][C_7H_4NOS]$	70.4	10.0	7.2	8.2	70.4	10.3	7.1	8.2
$[NBu^n_4][C_7H_5N_2S]$	67.9	10.3	10.1		67.4	10.6	10.3	
$[NBu^n_4][C_3H_4NS_2]\cdot EtOH$	61.9	11.4	7.6		62.0	11.4	6.9	
$[NMe_4][Zn(S_2CNMe_2)_3]\cdot H_2O$	30.0	6.0	10.7	38.5	30.1	6.2	10.8	37.1
$[NMe_4][Zn(S_2CNEt_2)_3]$	38.7	7.1	9.5	32.7	39.1	7.2	9.6	32.9
$[NBu^n_4][Zn(S_2CNMe_2)_3]$	44.7	7.8	8.2		44.9	8.1	8.4	28.8
$[NMe_4][Zn(S_2CNMe_2)_2(S_2CNEt_2)]$	34.8	6.4	10.5	37.2	34.1	6.5	10.6	36.4
$[NBu^n_4][Zn(S_2CNMe_2)_2(S_2CNEt_2)]$	46.0	8.7	8.1	29.2	46.6	8.4	8.0	27.6
$[NMe_4][Zn(S_2CNMe_2)(S_2CNEt_2)_2]$	37.1	7.2	10.1	36.0	36.7	6.9	10.1	34.6
$[NBu^n_4][Zn(S_2CNMe_2)(S_2CNEt_2)_2]$	48.1	8.6	7.7	27.1	48.2	8.7	8.0	26.4
$[NMe_4][Zn(S_2CNEt_2)_2(S_2CNBu^n_2)]$	43.2	8.0	8.4	30.4	43.1	7.5	8.8	30.0
$[NMe_4][Zn(S_2CNMe_2)_2\{S_2CN(CH_2)_4CH_2\}]$	35.5	6.5	10.1	33.8	35.6	6.3	10.4	35.6
$[NMe_4][Zn(S_2CNEt_2)_2\{S_2CN(CH_2)_4CH_2\}]$	40.1	7.3	9.3	32.2	40.3	7.1	9.4	32.3
$[NBu^n_4][Zn(C_7H_4NS_2)_3(OH_2)]$	54.2	6.3	6.8	23.3	53.9	6.1	6.8	23.3
$[NMe_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]$	37.9	4.7	10.0	37.4	37.4	5.2	10.3	35.2
$[NBu^n_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]$	48.8	7.3	7.8	26.9	48.8	7.5	7.6	26.5
$[NMe_4][Zn(S_2CNEt_2)_2(C_7H_4NS_2)]$	41.7	6.0	9.4	31.9	41.9	6.0	9.3	31.9
$[NMe_4][Zn(S_2CNBu^n_2)_2(C_7H_4NS_2)]$	48.4	7.3	7.9	27.7	48.8	7.3	7.8	26.9
$[NMe_4][Zn\{S_2CN(CH_2)_4CH_2\}_2(C_7H_4NS_2)]$	43.9	5.5	8.9	30.5	44.1	5.8	9.0	30.7
$[NBu^n_4][Zn\{S_2CN(CH_2)_4CH_2\}_2(C_7H_4NS_2)]$	53.2	7.4	7.2	24.0	52.9	7.6	7.1	24.2
$[NMe_4][Zn(S_2CNMe_2)_2(C_7H_4NOS)]$	38.3	5.3	10.5	30.0	38.5	5.3	10.6	30.2
$[NBu^n_4][Zn(S_2CNMe_2)_2(C_7H_4NOS)]$	50.3	7.6	7.6	20.8	49.9	7.5	8.0	23.0
$[NMe_4][Zn(S_2CNEt_2)_2(C_7H_4NOS)]$	43.0	6.1	9.6	27.2	43.0	6.2	9.6	27.3
$[NMe_4][Zn\{S_2CN(CH_2)_4CH_2\}_2(C_7H_4NOS)]$	45.7	5.6	9.0	26.9	45.3	6.0	9.2	26.9
$[NBu^n_4][Zn\{S_2CN(CH_2)_4CH_2\}_2(C_7H_4NOS)]\cdot(CH_3)_2CO$	54.9	8.1	7.1	19.8	54.6	8.0	6.7	19.2
$[NBu^n_4][Zn(S_2CNBu^n_2)_2(C_7H_4NOS)]\cdot 2H_2O$	54.3	8.8	6.7	17.6	56.6	8.9	6.2	17.8
$[NBu^n_4][Zn\{S_2CN(CH_2)_4CH_2\}_2(C_7H_5N_2S)]$	54.3	7.6	9.1	19.9	54.1	7.9	9.1	20.6
$[NMe_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]\cdot H_2O\cdot(CH_3)_2CO$	43.1	5.1	8.4	28.8	43.7	5.0	8.6	28.8
$[NBu^n_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]$	52.5	6.3	7.0	24.7	52.1	6.6	7.4	25.3
$[NMe_4][Zn(S_2CNEt_2)(C_7H_4NS_2)_2]$	44.7	4.5	8.9	31.4	44.5	4.9	9.0	31.0
$[NBu^n_4][Zn(S_2CNEt_2)(C_7H_4NS_2)_2]$	52.8	6.9	6.9	24.5	53.3	6.9	7.1	24.4
$[NMe_4][Zn(S_2CNBu^n_2)(C_7H_4NS_2)_2]$	48.5	5.8	8.0	27.5	48.0	5.7	8.3	28.4
$[NMe_4][Zn\{S_2CN(CH_2)_4CH_2\}(C_7H_4NS_2)_2]$	45.4	5.0	8.8	30.8	45.6	4.8	8.9	30.4
$[NBu^n_4][Zn\{S_2CN(CH_2)_4CH_2\}(C_7H_4NS_2)_2]$	53.9	6.8	6.8	23.8	54.4	6.8	7.0	24.0
$[NBu^n_4][Zn\{S_2CN(C_6H_{11})_2\}(C_7H_4NS_2)_2]$	57.4	7.5	6.5	21.6	57.6	7.4	6.3	21.5
$[NMe_4][Zn\{S_2CN(C_6H_{11})_2\}(C_7H_4NS_2)_2]$	49.9	5.4	7.9	24.5	49.9	5.9	7.5	25.8
$[NBu^n_4][Zn(S_2CNMe_2)(C_7H_4NOS)_2]$	54.3	7.0	7.3	17.5	54.5	7.3	7.7	17.6
$[NBu^n_4][Zn(S_2CNEt_2)(C_7H_4NOS)_2]$	55.8	7.4	7.2	16.8	55.6	7.2	7.4	17.0
$[NBu^n_4][Zn\{S_2CN(CH_2)_4CH_2\}(C_7H_4NOS)_2]$	56.5	7.1	7.0	16.7	56.3	7.1	7.3	16.7

TABLE 2

Proton n.m.r. spectral data obtained from selected zinc and related sulphur-containing compounds

Compound	δ [a]	Relative area	Multiplicity	Assignment
$[NMe_4][S_2CNMe_2]$	3.58 [b]	1	s	$S_2CN(CH_3)_2$
	3.51	2	s	$[N(CH_3)_4]^+$
$[NMe_4][S_2CNEt_2]$	4.11 [b]	2	q	$S_2CN(C\mathit{H}_2CH_3)_2$
	3.52	6	s	$[N(CH_3)_4]^+$
	1.20	3	t	$S_2CN(CH_2C\mathit{H}_3)_2$
$[NMe_4][C_7H_4NS_2]$	7.14 [b]	1	m	C_7H_4NS
	3.32	3	s	$[N(CH_3)_4]^+$
$[NBu^n_4][C_7H_4NS_2]$	7.13 [c]	1	m	$C_7H_4NS_2$
	3.16	2	t	$[N(C\mathit{H}_2Pr^n)_4]^+$
	1.38	4	m	$[N\{CH_2(C\mathit{H}_2)_2CH_3\}_4]^+$
	0.88	3	t	$[N\{(CH_2)_3C\mathit{H}_3\}_4]^+$
$[NMe_4][C_7H_4NOS]\cdot H_2O$ [d]	6.92	4	m	C_7H_4NOS
	3.49	12	s	$[N(CH_3)_4]^+$
	2.88	1	s	H_2O
$[NBu^n_4][C_7H_5N_2S]$ [d]	6.98 [b,e]	1	m	$C_7H_4N_2S$
	2.99	2	m	$[N(C\mathit{H}_2Pr^n)_4]^+$
	1.34	4	m	$[N\{CH_2(C\mathit{H}_2)_2Me\}_4]^+$
	0.89	3	t	$[N\{(CH_2)_3C\mathit{H}_3\}_4]^+$
$[NBu^n_4][C_3H_4NS_2]\cdot EtOH$	3.79 [c]	2	t	$SCH_2CH_2N{=}C(S)$
	3.41	8	t	$[N(C\mathit{H}_2Pr^n)_4]^+$
	2.90	2	t	$SCH_2CH_2N{=}C(S)$
	1.69—1.30	16	m	$[N\{CH_2(C\mathit{H}_2)_2Me\}_4]^+$
	0.83	12	t	$[N\{(CH_2)_3C\mathit{H}_3\}_4]^+$
	1.90	2	q	$MeC\mathit{H}_2OH$
	0.80	3	t	$C\mathit{H}_3CH_2OH$
$[NMe_4][Zn(S_2CNMe_2)_3]$	3.43 [b]	3	s	$S_2CN(CH_3)_2$
	3.22	2	s	$[N(CH_3)_4]^+$
$[NMe_4][Zn(S_2CNEt_2)_3]$	3.99 [c]	2	t	$S_2CN(C\mathit{H}_2Me)_2$
	3.49	2	s	$[N(CH_3)_4]^+$
	1.24	3	t	$S_2CN(CH_2C\mathit{H}_3)_2$
$[NMe_4][Zn(S_2CNMe_2)_2(S_2CNEt_2)]$	3.92 [b]	2	q	$S_2CN(C\mathit{H}_2Me)_2$
	3.46	12	s	$[N(CH_3)_4]^+$ and $S_2CN(CH_3)_2$
	1.26	3	t	$S_2CN(CH_2C\mathit{H}_3)_2$
$[NMe_4][Zn(S_2CNMe_2)(S_2CNEt_2)_2]$	3.93 [c]	4	q	$S_2CN(C\mathit{H}_2CH_3)_2$
	3.47	6	s	$[N(CH_3)_4]^+$
	3.43	3	s	$S_2CN(CH_3)_2$
	1.22	6	t	$S_2CN(CH_2C\mathit{H}_3)_2$
$[NBu^n_4][Zn(C_7H_4NS_2)_3(OH_2)]$	7.44 [c]	3	m	$C_7H_4NS_2$
	3.08	2	m	$[N(C\mathit{H}_2Pr^n)_4]^+$
	1.22	4	m	$[N\{CH_2(C\mathit{H}_2)_2Me\}_4]^+$
	0.78	3	t	$[N\{(CH_2)_3C\mathit{H}_3\}_4]^+$
$[NMe_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]$	7.50 [c]	1	m	$C_7H_4NS_2$
	3.34	3	s	$S_2CN(CH_3)_2$
	3.38	3	s	$[N(CH_3)_4]^+$
$[NMe_4][Zn(S_2CNMe_2)_2(C_7H_4NOS)]$ [d]	7.12 [c]	1	m	C_7H_4NOS
	3.41	3	s	$[N(CH_3)_4]^+$
	3.38	3	s	$S_2CN(CH_3)_2$
$[NMe_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]\cdot H_2O\cdot(CH_3)_2CO$	7.96	4	m	$C_7H_4NS_2$
	3.34	3	s	$S_2CN(CH_3)_2$
	3.27	6	s	$[N(CH_3)_4]^+$
	2.74	1	s	H_2O
	2.05	3	s	$(CH_3)_2CO$
$[NMe_4][Zn(S_2CNEt_2)(C_7H_4NS_2)_2]$ [d]	7.53 [b]	4	m	$C_7H_4NS_2$
	3.85	2	q	$S_2CN(C\mathit{H}_2CH_3)_2$
	3.31	6	5	$[N(CH_3)_4]^+$
	1.21	3	t	$S_2CN(CH_2C\mathit{H}_3)_2$
$[NBu^n_4][Zn(S_2CNMe_2)(C_7H_4NOS)_2]$ [d]	7.38 [c]	2	m	C_7H_4NOS
	3.40	3	s	$S_2CN(CH_3)_2$
	3.36	4	t	$[N(C\mathit{H}_2Pr^n)_4]^+$
	1.78	4	qnt	$[N(CH_2C\mathit{H}_2Et)_4]^+$
	1.36	4	sxt	$[N(CH_2CH_2C\mathit{H}_2CH_3)_4]^+$
	0.92	6	t	$[N\{(CH_2)_3C\mathit{H}_3\}_4]^+$

[a] In p.p.m. *vs.* $SiMe_4$ at 100 MHz, unless otherwise stated. [b] In $CDCl_3$ solution. [c] In $(CD_3)_2CO$ solution. [d] At 220 MHz. [e] In presence of D_2O.

$NS_2)_3]^-$ were unsuccessful, as were efforts to dehydrate $[NBu^n_4][Zn(C_7H_4NS_2)_3(OH_2)]$. Indeed, attempts to produce the anhydrous complex under scrupulously dry conditions failed since, as soon as $[\{Zn(C_7H_4NS_2)_2\}_n]$ was dissolved in solutions containing $[NBu^n_4][C_7H_4NS_2]$ and this mixture was exposed even to minute traces of moisture, $[NBu^n_4][Zn(C_7H_4NS_2)_3(OH_2)]$ crystallised out. The importance of water in this sytem will be discussed in more detail in the section dealing with the structure of this zincate ion.

Mixed Dithiocarbamato–Benzothiazole-2-thiolato-species.—Following the general synthetic technique used to prepare $[Zn(S_2CNR'_2)(S_2CNR''_2)_2]^-$, we were able to make the mixed-ligand species $[Zn(S_2CNR''_2)_2(C_7H_4NS_2)]^-$ and $[Zn(S_2CNR'_2)(C_7H_4NS_2)_2]^-$, by adding $[NR_4][C_7H_4NS_2]$ to $[Zn(S_2CNR''_2)_2]$, and $[NR_4][S_2CNR'_2]$ to

TABLE 3

Values of ν(C$\overset{...}{=}$N) obtained from selected dithiocarbamato-compounds in KBr discs

Compound	ν(C$\overset{...}{=}$N)/cm^{-1}		
	Neutral	$[NMe_4]^+$	$[NBu^n_4]^+$
$[Zn(S_2CNMe_2)_2]$	1 520		
$[Zn(S_2CNEt_2)_2]$	1 499		
$[Zn(S_2CNBu^n_2)_2]$	1 490		
$[Zn\{S_2CN(CH_2)_4CH_2\}_2]$	1 490		
$[Zn\{S_2CN(C_6H_{11})_2\}_2]$	1 490		
$[Zn(S_2CNMe_2)_3]^-$		1 505, 1 490	1 505
$[Zn(S_2CNEt_2)_3]^-$		1 480	
$[Zn(S_2CNMe_2)_2(C_7H_4NS_2)]^-$		1 510	1 485
$[Zn(S_2CNEt_2)_2(C_7H_4NS_2)]^-$		1 500	
$[Zn(S_2CNBu^n_2)_2(C_7H_4NS_2)]^-$		1 490	1 490
$[Zn\{S_2CN(CH_2)_4CH_2\}_2(C_7H_4NS_2)]^-$		1 490	1 485
$[Zn(S_2CNMe_2)_2(C_7H_4NOS)]^-$		1 505	1 500
$[Zn(S_2CNEt_2)_2(C_7H_4NOS)]^-$		1 490	
$[Zn(S_2CNBu_2)_2(C_7H_4NOS)]^-$			1 485
$[Zn\{S_2CN(CH_2)_4CH_2\}_2(C_7H_4NOS)]^-$		1 470	1 485

$[\{Zn(C_7H_4NS_2)_2\}_n]$, respectively. None of these species apparently contains water bound to the complex anion as in $[Zn(C_7H_4NS_2)_3(OH_2)]^-$, although some species were isolated as hydrates and/or acetone solvates. Again, ligand redistribution was observed, as in attempts to prepare $[NBu^n_4][Zn(S_2CNEt_2)_2(C_7H_4NS_2)]$, when only $[NBu^n_4][Zn(S_2CNEt_2)(C_7H_4NS_2)_2]$ could be isolated.

Compounds derived from Benzoxazole-, Benzimidazole-, and Thiazoline-2-thiolates.—Treatment of zinc acetate with $K[C_7H_4NOS]$, $K[C_7H_5N_2S]$, and $K[C_3H_4NS_2]$ afforded the insoluble $[\{Zn(C_7H_4NOS)_2\}_n]$, $[\{Zn(C_7H_5N_2S)_2\}_n]$, and $[\{Zn(C_3H_4NS_2)_2\}_n]$, respectively. While our attempts to isolate salts of $[Zn(C_7H_4NOS)_3]^-$ were unsuccessful, we noted that $[\{Zn(C_7H_4NOS)_2\}_n]$ dissolved in acetone solutions containing $[NR_4][C_7H_4NOS]$ (R = Me, Et, or Bu^n), or with $[PPh_3(CH_2Ph)]^+$ as counter cation, and, on work-up, oils which steadfastly resisted crystallisation were produced. We presume that this oil contained $[NR_4][Zn(C_7H_4NOS)_3]$.

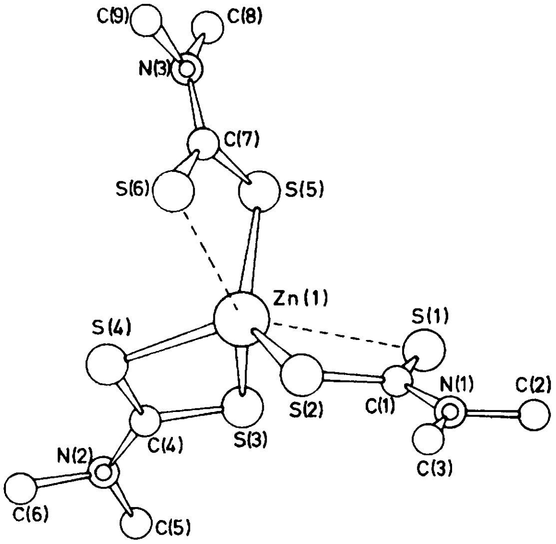


FIGURE 1 Structure and atom labelling for the anion $[Zn(S_2CNMe_2)_3]^-$

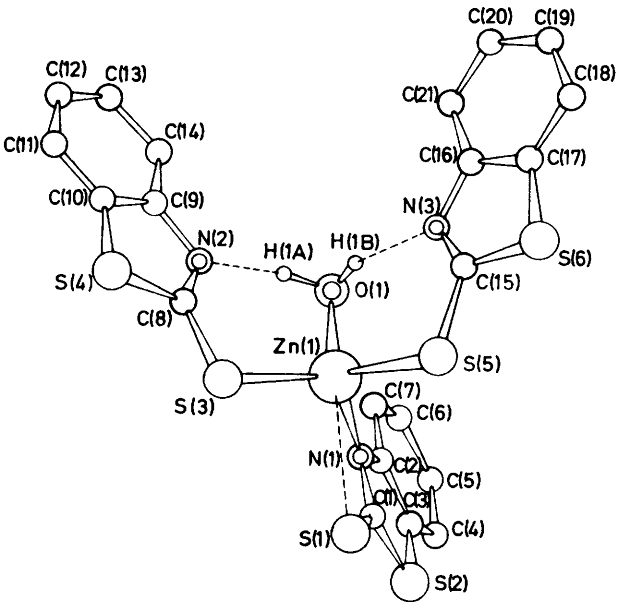


FIGURE 2 Structure and atom labelling for the anion $[Zn(C_7H_4NS_2)_3(OH_2)]^-$

We were unable to isolate tris complexes of $C_7H_5N_2S$ or $C_3H_4NS_2$, but the mixed-ligand complexes $[NBu^n_4][Zn(S_2CNMe_2)_2(C_7H_4NOS)]$, $[NBu^n_4][Zn(S_2CNMe_2)(C_7H_4NOS)_2]$, and $[NBu^n_4][Zn\{S_2CN(CH_2)_4CH_2\}_2(C_7H_5N_2S)]$ were obtained by addition of $[NBu^n_4][C_7H_4NOS]$

TABLE 4

Atomic positional parameters and estimated standard deviations for $[NEt_4][Zn(S_2CNMe_2)_3]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zn(1)	0.175 47(6)	0.136 37(5)	0.095 75(5)
S(1)	0.159 15(14)	0.164 80(12)	0.249 55(10)
S(2)	0.300 93(14)	0.187 57(11)	0.145 76(9)
S(3)	0.043 32(14)	0.218 31(11)	0.096 51(10)
S(4)	0.158 99(14)	0.179 66(11)	−0.018 79(9)
S(5)	0.129 26(15)	0.020 39(11)	0.109 87(12)
S(6)	0.303 81(17)	0.020 52(14)	0.036 90(12)
N(1)	0.321 5(4)	0.220 9(4)	0.272 0(3)
N(2)	0.029 4(4)	0.278 6(4)	−0.021 8(3)
N(3)	0.195 6(5)	−0.091 6(3)	0.048 4(3)
N(4)	0.341 1(4)	−0.035 7(3)	0.285 1(3)
C(1)	0.262 6(5)	0.193 4(4)	0.227 0(3)
C(2)	0.297 8(6)	0.223 6(5)	0.342 8(4)
C(3)	0.410 1(6)	0.246 7(5)	0.253 7(5)
C(4)	0.073 5(5)	0.230 6(4)	0.013 4(3)
C(5)	−0.041 6(7)	0.324 6(6)	0.006 4(5)
C(6)	0.051 2(6)	0.292 4(6)	−0.091 3(4)
C(7)	0.209 7(5)	−0.022 3(4)	0.062 3(3)
C(8)	0.112 0(8)	−0.128 8(5)	0.065 4(5)
C(9)	0.262 2(8)	−0.135 1(6)	0.013 9(5)
C(10)	0.241 1(6)	−0.024 1(5)	0.295 2(4)
C(11)	0.195 6(7)	−0.074 9(7)	0.341 9(6)
C(12)	0.360 3(7)	−0.109 0(4)	0.257 8(5)
C(13)	0.315 9(9)	−0.124 6(6)	0.191 3(5)
C(14)	0.370 6(7)	0.022 3(5)	0.237 8(4)
C(15)	0.470 2(9)	0.020 7(7)	0.219 5(6)
C(16)	0.392 7(6)	−0.031 5(5)	0.350 9(4)
C(17)	0.382 2(8)	0.037 3(7)	0.389 0(6)

Atoms C(10)—C(11), C(12)—C(13), C(14)—C(15), and C(16)—C(17) comprise the atoms of the four ethyl groups with the lower numbered atom in each group bonded to the central nitrogen atom N(4).

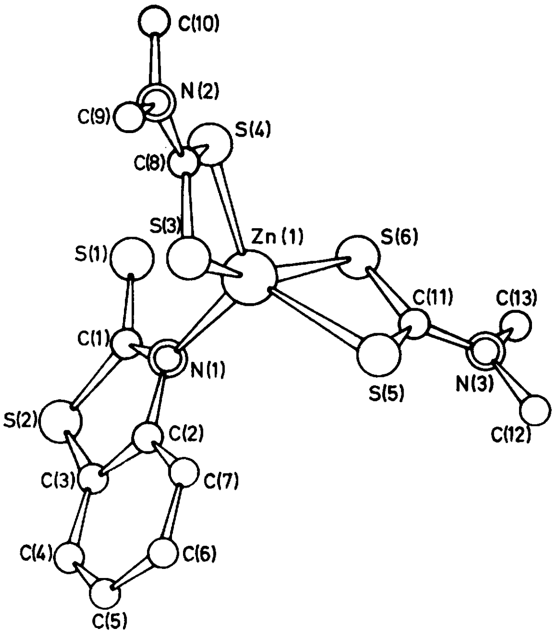


FIGURE 3 Structure and atom labelling for the anion $[Zn(S_2CNMe_2)_2(C_7H_4NS_2)]^-$

or its $[C_7H_5N_2S]^-$ analogue to the respective zinc bis(dithiocarbamates), and by treatment of $[\{Zn(C_7H_4NOS)_2\}_n]$ with $[NBu^n{}_4][S_2CNMe_2]$.

Spectroscopic Studies.—The ^1H n.m.r. spectra of the complexes (Table 2 and also SUP 22784) were unexceptional, but conformed to the formulation of the complexes. The i.r. spectra (Table 3) of the compounds were also consistent with their formulations. In those complexes containing the group $Zn(S_2CNR_2)_2$, $\nu(C\cdots N)$ was generally clearly visible in the range 1 490—1 520 cm^{-1}. For the species containing only one S_2CNR_2 ligand, $\nu(C\cdots N)$ could not be assigned with certainty since it occurs at or below 1 490 cm^{-1}, close to ligand- and cation-group vibrations or deformations.

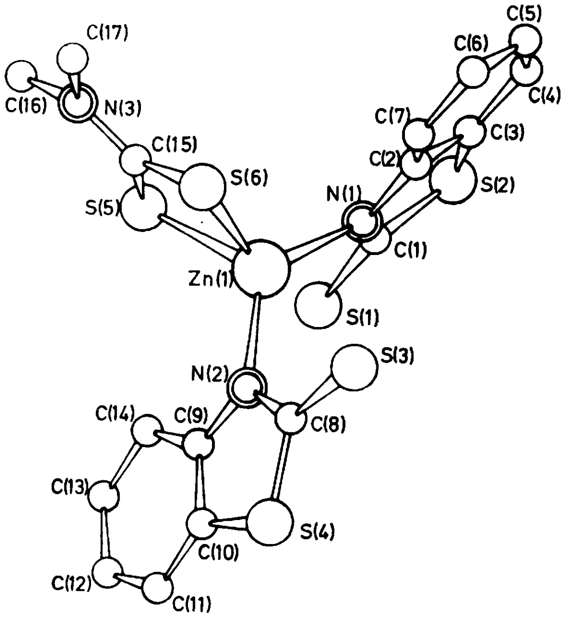


FIGURE 4 Structure and atom labelling for the anion $[Zn(S_2CNMe_2)(C_7H_4NS_2)_2]^-$

Structural Studies.—The structures of the four anions in $[NEt_4][Zn(S_2CNMe_2)_3]$, $[NBu^n{}_4][Zn(C_7H_4NS_2)_3(OH_2)]$, $[NBu^n{}_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]\cdot EtOH$, and $[NBu^n{}_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]$ are shown in Figures 1—4, respectively, in each case with the atomic labelling used in the corresponding Tables. The bond lengths and angles (together with estimated standard deviations), and details of planar fragments, are given, for the four separate structures, in Tables 8—15.

In general, in all four structures, the formal co-ordination number of the zinc atoms is less than six.

TABLE 5

Atomic positional parameters and estimated standard deviations for $[NBu^n{}_4][Zn(C_7H_4NS_2)_3(OH_2)]$

Atom	*X/a*	*Y/b*	*Z/c*
Zn(1)	0.110 11(6)	0.197 31(4)	0.165 37(3)
S(1)	0.320 12(14)	0.199 44(12)	0.258 01(6)
S(2)	0.099 51(15)	0.203 77(11)	0.329 44(6)
S(3)	0.244 23(15)	0.300 81(11)	0.133 42(7)
S(4)	0.249 31(21)	0.381 98(12)	0.034 19(8)
S(5)	0.172 86(16)	0.056 18(10)	0.162 21(7)
S(6)	0.085 05(20)	−0.095 48(11)	0.104 73(8)
O(1)	−0.066 7(3)	0.202 5(2)	0.121 3(1)
N(1)	0.052 5(4)	0.216 5(3)	0.234 6(2)
N(2)	0.026 7(5)	0.324 1(3)	0.066 1(2)
N(3)	−0.034 6(4)	0.045 9(3)	0.089 5(2)
N(4)	−0.361 4(4)	−0.026 4(3)	0.198 8(2)
C(1)	0.154 4(5)	0.207 3(3)	0.269 5(2)
C(2)	−0.073 5(5)	0.221 3(3)	0.254 3(2)
C(3)	−0.069 3(5)	0.214 4(3)	0.305 6(2)
C(4)	−0.187 9(6)	0.214 7(4)	0.330 9(2)
C(5)	−0.311 5(6)	0.223 5(4)	0.303 1(2)
C(6)	−0.315 5(5)	0.233 9(4)	0.252 4(2)
C(7)	−0.198 0(5)	0.232 5(3)	0.226 7(2)
C(8)	0.156 8(6)	0.332 3(4)	0.079 1(2)
C(9)	−0.007 5(7)	0.358 3(4)	0.019 4(2)
C(10)	0.100 6(7)	0.393 5(4)	−0.004 3(2)
C(11)	0.079 2(9)	0.431 3(5)	−0.050 4(3)
C(12)	−0.049 7(10)	0.432 6(5)	−0.071 7(3)
C(13)	−0.158 3(9)	0.397 2(5)	−0.049 6(3)
C(14)	−0.138 7(8)	0.359 7(4)	−0.003 1(3)
C(15)	0.062 8(6)	0.011 4(4)	0.116 9(2)
C(16)	−0.098 0(6)	−0.010 2(4)	0.054 8(2)
C(17)	−0.045 9(6)	−0.090 4(4)	0.057 8(2)
C(18)	−0.097 0(8)	−0.153 6(4)	0.025 7(3)
C(19)	−0.197 4(8)	−0.131 4(5)	−0.009 0(3)
C(20)	−0.251 6(7)	−0.051 7(5)	−0.012 5(3)
C(21)	−0.202 0(6)	0.010 2(4)	0.019 8(2)
C(22)	−0.442 2(6)	−0.064 6(4)	0.239 2(2)
C(23)	−0.449 4(6)	−0.012 3(4)	0.285 4(2)
C(24)	−0.543 8(7)	−0.051 6(5)	0.319 3(3)
C(25)	−0.553 2(9)	−0.004 2(7)	0.366 9(3)
C(26)	−0.222 6(5)	0.005 1(4)	0.220 1(2)
C(27)	−0.131 4(6)	−0.059 5(4)	0.247 0(3)
C(28)	−0.022 3(6)	−0.012 2(4)	0.280 9(3)
C(29)	0.070 1(8)	−0.064 9(5)	0.310 3(3)
C(30)	−0.337 5(6)	−0.092 3(4)	0.160 0(2)
C(31)	−0.465 3(7)	−0.122 2(4)	0.130 8(2)
C(32)	−0.427 3(8)	−0.193 1(6)	0.096 5(3)
C(33)	−0.540 1(11)	−0.226 9(7)	0.065 8(3)
C(34)	−0.441 2(5)	0.048 1(4)	0.177 2(2)
C(35)	−0.383 9(6)	0.089 0(4)	0.132 3(2)
C(36)	−0.472 8(6)	0.163 1(4)	0.117 0(3)
C(37)	−0.426 3(8)	0.209 8(5)	0.073 7(3)
H(1A)	−0.051(6)	0.248(4)	0.098(2)
H(1B)	−0.077(6)	0.165(4)	0.107(2)

Atoms C(22)—C(25), C(26)—C(29), C(30)—C(33), and C(34)—C(37) comprise the atoms of the four n-butyl groups with the lowest numbered atom in each group bonded to the central nitrogen atom N(4).

TABLE 6

Atomic positional parameters with estimated standard deviations for $[NBu^n{}_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]\cdot C_2H_5OH$

Atom	X/a	Y/b	Z/c
Zn(1)	0.014 76(8)	0.014 27(8)	−0.249 00(8)
S(1)	0.084 3(2)	−0.197 5(2)	−0.214 0(2)
S(2)	−0.094 6(2)	−0.260 2(2)	−0.270 0(2)
S(3)	−0.046 6(2)	0.098 1(2)	−0.396 8(2)
S(4)	0.119 2(2)	0.012 1(2)	−0.314 4(2)
S(5)	−0.047 8(2)	0.127 0(2)	−0.177 4(2)
S(6)	0.105 4(2)	0.020 8(2)	−0.095 0(2)
O(1)	0.387 9(7)	0.092 7(7)	−0.331 7(6)
N(1)	−0.057 8(5)	−0.097 7(5)	−0.268 4(5)
N(2)	0.077 9(5)	0.103 2(5)	−0.460 2(5)
N(3)	0.035 1(5)	0.117 8(5)	−0.008 0(5)
N(4)	0.333 7(5)	−0.194 0(5)	−0.284 9(5)
C(1)	−0.021 2(6)	−0.175 6(6)	−0.249 9(6)
C(2)	−0.147 7(6)	−0.104 3(7)	−0.295 2(6)
C(3)	−0.178 2(6)	−0.188 2(7)	−0.299 9(6)
C(4)	−0.264 5(7)	−0.204 0(8)	−0.324 3(7)
C(5)	−0.318 7(7)	−0.134 2(9)	−0.343 2(8)
C(6)	−0.291 0(7)	−0.048 6(8)	−0.339 8(8)
C(7)	−0.202 9(6)	−0.033 1(8)	−0.316 1(7)
C(8)	0.053 5(6)	0.075 1(6)	−0.397 1(6)
C(9)	0.020 4(8)	0.154 7(8)	−0.529 9(6)
C(10)	0.162 5(7)	0.083 5(7)	−0.458 8(7)
C(11)	0.031 2(6)	0.092 7(6)	−0.085 7(6)
C(12)	−0.028 6(8)	0.177 4(8)	0.001 5(8)
C(13)	0.101 3(7)	0.086 2(7)	0.070 5(6)
C(14)	0.299 3(6)	−0.141 4(6)	−0.227 3(6)
C(15)	0.314 4(6)	−0.181 2(7)	−0.139 7(6)
C(16)	0.293 1(7)	−0.114 7(7)	−0.083 1(6)
C(17)	0.290 5(8)	−0.155 5(9)	−0.000 9(7)
C(18)	0.311 5(7)	−0.142 2(6)	−0.366 0(6)
C(19)	0.335 2(8)	−0.186 8(8)	−0.435 8(7)
C(20)	0.291 8(9)	−0.143 0(8)	−0.521 0(7)
C(21)	0.298 7(11)	−0.187 1(9)	−0.595 4(8)
C(22)	0.430 5(7)	−0.208 2(7)	−0.240 7(7)
C(23)	0.482 9(7)	−0.126 0(8)	−0.208 2(8)
C(24)	0.576 6(7)	−0.147 9(9)	−0.166 8(9)
C(25)	0.629 9(9)	−0.069 1(11)	−0.132 3(11)
C(26)	0.294 6(7)	−0.284 8(6)	−0.299 9(6)
C(27)	0.198 1(7)	−0.287 2(6)	−0.353 2(7)
C(28)	0.165 6(7)	−0.379 6(7)	−0.358 9(8)
C(29)	0.070 7(8)	−0.387 5(8)	−0.408 9(9)
C(30)	0.395 9(10)	0.098 8(10)	−0.415 1(9)
C(31)	0.475 2(10)	0.064 0(13)	−0.411 4(13)

Atoms C(14)—C(17), C(18)—C(21), C(22)—C(25), and C(26)—C(29) are the atoms 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). Atoms C(31), C(30), and O(1) are the atoms of the solvent ethanol molecule.

However, in three of these it is greater than four, but by varying degrees, as is shown below.

$[NEt_4][Zn(S_2CNMe_2)_3]$. The anion (Figure 1) is comprised of one symmetrically bidentate dimethyldithiocarbamate ligand (Zn–S 2.422—2.456 Å) and two formally unidentate S_2CNMe_2 ligands (mean Zn–S 2.306 Å). The latter form, in addition, long intramolecular Zn $\cdots$ S contacts (mean 3.138 Å) which are significantly shorter than the van der Waals distance (3.27 Å). However, it is not clear from this structure whether this weak interaction is bonding or antibonding.

The co-ordination geometry of the zinc can be referred to as a tetrahedron (with, inevitably, one small angle) with the remotely interacting S atoms capping the two enlarged faces. Alternatively, the geometry can be viewed as distorted trigonal prismatic with the S_2CNMe_2 ligands asymmetrically occupying the three 'vertical' edges. The zinc atom is displaced by varying extents from the mean planes of the S_2CNMe_2 ligands (see Table 9). The ligand geometries reflect the greater degree of electron localisation in the formally unidentate ligands, and are otherwise unexceptionable, as is the geometry of the cation. The co-ordination geometry of the zinc atom contrasts markedly with those of other tris-(dithiocarbamato)-complexes,[5] including an analogous cadmium species, $[Cd(S_2CNEt_2)_3]^-$.[6]

$[NBu^n{}_4][Zn(C_7H_4NS_2)_3(OH_2)]$. The anion (Figure 2) is comprised of two $C_7H_4NS_2$ ligands which are co-ordinated to the zinc *via* their exocyclic S atoms (mean Zn–S 2.338 Å). These ligands are also hydrogen-bonded to a co-ordinated water molecule (Zn–O 2.037 Å) through their N atoms (mean N $\cdots$ O 2.67 Å). The third

TABLE 7

Atomic positional parameters and estimated standard deviations for $[NBu^n{}_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]$

Atom	X/a	Y/b	Z/c
Zn(1)	0.104 96(4)	0.110 74(8)	0.247 22(7)
S(1)	0.188 4(1)	−0.089 6(2)	0.150 9(1)
S(2)	0.254 8(1)	0.141 4(2)	0.079 4(1)
S(3)	0.175 3(1)	0.212 7(2)	0.384 5(1)
S(4)	0.159 5(1)	−0.058 2(2)	0.452 8(1)
S(5)	0.012 2(1)	0.041 1(2)	0.178 4(1)
S(6)	0.021 4(1)	0.277 7(2)	0.268 8(1)
N(1)	0.175 9(3)	0.171 6(6)	0.183 6(3)
N(2)	0.122 0(3)	−0.007 6(6)	0.329 5(3)
N(3)	−0.082 5(3)	0.226 7(7)	0.187 9(4)
N(4)	−0.087 4(3)	0.034 9(7)	0.436 7(4)
C(1)	0.202 5(4)	0.077 7(7)	0.144 1(4)
C(2)	0.196 4(3)	0.299 7(7)	0.165 2(4)
C(3)	0.238 4(4)	0.304 3(7)	0.106 8(4)
C(4)	0.261 6(4)	0.426 0(8)	0.079 1(5)
C(5)	0.240 3(5)	0.541 2(8)	0.110 4(5)
C(6)	0.199 3(4)	0.540 5(8)	0.168 9(6)
C(7)	0.176 9(4)	0.417 9(8)	0.197 2(5)
C(8)	0.150 4(4)	0.053 1(7)	0.382 1(4)
C(9)	0.106 5(4)	−0.143 1(7)	0.340 7(4)
C(10)	0.123 7(4)	−0.189 3(8)	0.406 2(4)
C(11)	0.113 3(5)	−0.322 8(9)	0.425 9(5)
C(12)	0.083 4(5)	−0.407 6(8)	0.379 3(5)
C(13)	0.065 3(4)	−0.361 7(8)	0.314 2(5)
C(14)	0.077 0(4)	−0.227 8(8)	0.293 1(5)
C(15)	−0.022 6(4)	0.185 8(8)	0.208 6(4)
C(16)	−0.120 6(4)	0.152 7(11)	0.135 1(6)
C(17)	−0.110 2(5)	0.355 0(10)	0.210 1(6)
C(18)	−0.024 1(4)	0.113 3(9)	0.447 8(5)
C(19)	−0.021 5(5)	0.184 6(10)	0.518 9(6)
C(20)	0.043 2(6)	0.260 3(13)	0.527 2(8)
C(21)	0.045 9(8)	0.333 6(15)	0.596 8(9)
C(22)	−0.148 3(4)	0.124 9(9)	0.447 7(5)
C(23)	−0.151 7(6)	0.248 0(11)	0.400 6(6)
C(24)	−0.207 3(6)	0.334 8(11)	0.422 4(8)
C(25)	−0.218 8(7)	0.449 9(14)	0.379 0(9)
C(26)	−0.094 7(5)	−0.080 1(9)	0.489 9(5)
C(27)	−0.036 1(8)	−0.175 6(9)	0.491 7(9)
C(28)	−0.048 9(6)	−0.295 0(9)	0.540 4(5)
C(29)	−0.088 5(7)	−0.404 2(10)	0.502 4(10)
C(30)	−0.084 9(5)	−0.019 7(10)	0.362 8(5)
C(31)	−0.144 9(15)	−0.094 0(17)	0.341 4(8)
C(32)	−0.148 2(8)	−0.145 0(13)	0.266 2(6)
C(33)	−0.129 9(15)	−0.294 9(14)	0.263 3(10)
C(34)	−0.114 7(20)	−0.192 7(21)	0.285 6(9)
C(35)	−0.171 7(34)	−0.254 0(28)	0.243 7(12)

Atoms C(18)—C(21), C(22)—C(25), C(26)—C(29), and C(30)—C(33) are the atoms 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). Atoms C(34) and C(35), together with atoms C(30) and C(31), comprise an alternative conformation for the fourth n-butyl group with a smaller occupancy (40%) than the major conformer. The estimated standard deviations of atoms C(27)—C(29) and C(31)—C(35) were derived from those of the refined group translational and rotational parameters which were used to locate them.

TABLE 8

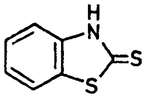
Bond lengths (Å) and angles (°) with estimated standard deviations for $[NEt_4][Zn(S_2CNMe_2)_3]$

Zn(1)–S(1)	3.151(2)	S(1)–C(1)	1.677(8)
Zn(1)–S(2)	2.312(2)	S(2)–C(1)	1.732(8)
Zn(1)–S(3)	2.422(2)	S(3)–C(4)	1.729(7)
Zn(1)–S(4)	2.457(2)	S(4)–C(4)	1.708(7)
Zn(1)–S(5)	2.299(2)	S(5)–C(7)	1.720(8)
Zn(1)–S(6)	3.115(3)	S(6)–C(7)	1.681(8)
		N(1)–C(1)	1.356(10)
N(4)–C(10)	1.500(11)	N(2)–C(4)	1.318(9)
N(4)–C(12)	1.508(11)	N(3)–C(7)	1.346(10)
N(4)–C(14)	1.511(11)	N(1)–C(2)	1.468(11)
N(4)–C(16)	1.527(11)	N(1)–C(3)	1.439(11)
C(10)–C(11)	1.499(15)	N(2)–C(5)	1.469(12)
C(12)–C(13)	1.518(15)	N(2)–C(6)	1.458(11)
C(14)–C(15)	1.511(15)	N(3)–C(8)	1.454(12)
C(16)–C(17)	1.511(15)	N(3)–C(9)	1.453(12)
S(1)–Zn(1)–S(2)	64.05(7)	S(1)–C(1)–S(2)	122.1(5)
S(5)–Zn(1)–S(6)	64.18(8)	S(3)–C(4)–S(4)	116.8(4)
S(3)–Zn(1)–S(4)	73.71(7)	S(5)–C(7)–S(6)	120.8(4)
S(2)–Zn(1)–S(5)	125.18(9)	S(1)–C(1)–N(1)	121.4(6)
S(2)–Zn(1)–S(3)	110.45(8)	S(2)–C(1)–N(1)	116.6(5)
S(2)–Zn(1)–S(4)	110.48(8)	S(3)–C(4)–N(2)	120.4(5)
S(3)–Zn(1)–S(5)	111.89(8)	S(4)–C(4)–N(2)	122.8(5)
S(4)–Zn(1)–S(5)	113.60(8)	S(5)–C(7)–N(3)	117.4(6)
		S(6)–C(7)–N(3)	121.8(6)
C(10)–N(4)–C(12)	111.4(6)	C(1)–N(1)–C(2)	120.7(6)
C(10)–N(4)–C(14)	105.2(6)	C(1)–N(1)–C(3)	122.4(7)
C(10)–N(4)–C(16)	111.3(6)	C(4)–N(2)–C(5)	122.9(7)
C(12)–N(4)–C(14)	112.0(6)	C(4)–N(2)–C(6)	121.9(7)
C(12)–N(4) C(16)	105.6(6)	C(7)–N(3)–C(8)	123.1(7)
C(14)–N(4)–C(16)	111.6(6)	C(7)–N(3)–C(9)	122.6(7)
N(4)–C(10)–C(11)	115.5(8)	C(2)–N(1)–C(3)	116.9(7)
N(4)–C(12)–C(13)	114.7(8)	C(5)–N(2)–C(6)	115.1(7)
N(4)–C(14)–C(15)	114.7(8)	C(8)–N(3)–C(9)	114.3(7)
N(4)–C(16)–C(17)	115.7(8)		
S(1)–Zn(1)–S(3)	80.06(7)	Zn(1)–S(2)–C(1)	100.2(3)
S(1)–Zn(1)–S(4)	149.16(7)	Zn(1)–S(3)–C(4)	85.0(2)
S(1)–Zn(1)–S(5)	90.95(7)	Zn(1)–S(4)–C(4)	84.4(2)
S(1)–Zn(1)–S(6)	122.57(7)	Zn(1)–S(5)–C(7)	99.8(3)
S(2)–Zn(1)–S(6)	88.41(7)		
S(3)–Zn(1)–S(6)	156.10(8)		
S(4)–Zn(1)–S(6)	86.22(7)		

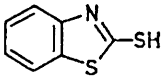
$C_7H_4NS_2$ ligand is attached to the zinc *via* a bond to the nitrogen atom (Zn–N 2.019 Å) and, again, the exocyclic S atom is involved in a short Zn · · · S contact (3.125 Å) which is well within the van der Waals distance. The Zn–N–C angles at the nitrogen atom [N(1)] of this uniquely bound $C_7H_4NS_2$ ligand strongly suggest that the interaction of the exocyclic S atom with the zinc is weakly bonding in nature since the zinc is significantly displaced from the external bisector of the ring bond angle in a direction which *reduces* the Zn · · · S distance. This displacement would seem to be more than is necessary to accommodate any conceivable intramolecular steric problems (see below).

The co-ordination geometry around the zinc atom can either be closely related to a tetrahedron [maximum deviation +11.5°, root-mean-square (r.m.s.) deviation 6.9°] or, less satisfactorily, to a trigonal bipyramid (including the long Zn · · · S interaction) in which the remote S and O atom of the co-ordinated water molecule occupy axial sites. The molecule has approximate C_s symmetry. The zinc atom lies, to varying extents, out of the mean planes of the $C_7H_4NS_2$ ligands (0.43, 0.78, and 0.10 Å, the first being the displacement from the plane of the uniquely co-ordinated ligand).

The six- and five-membered rings of the three $C_7H_4NS_2$ ligands are each closely planar, and only S(5) deviates significantly from the plane of its thiazole ring. On the basis of the observed variations in $C_7H_4NS_2$ bond lengths, it would seem possible to formally represent the unique $C_7H_4NS_2$ ligand as the anion derived from (A), while the other two ligands could be described as derivatives of (B). However, the ligand geometries are not sufficiently precise to *prove* the validity of these representations of the electron distribution in the ligands.



(A)



(B)

The reason for the difficulty in dehydrating $[Zn(C_7H_4NS_2)_3(OH_2)]^-$ is now apparent. The water molecule is not only bound directly to the metal atom but is also strongly hydrogen-bonded to the N atom of two $C_7H_4NS_2$ ligands.

The geometry of the cation shows no important features: two carbon–methyl bonds are rather short, which probably reflects a degree of thermal motion associated with rather loose packing.

$[NBu^n_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]$. The anion (Figure 3) contains two bidentate S_2CNMe_2 ligands which exhibit a wide spread of Zn–S distances (2.384—2.628 Å) with one ligand being considerably more symmetrically bonded than the other. The co-ordination sphere of the zinc atom is completed by a $C_7H_4NS_2$ ligand which is

TABLE 9

Planar fragments of $[NEt_4][Zn(S_2CNMe_2)_3]$. 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*. Where relevant, 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(3)	0.3750	−0.9128	0.1617	−1.1147
[Zn(1) 0.057, S(1) −0.020, S(2) 0.034, N(1) −0.014, C(1) −0.013, C(2) 0.039, C(3) −0.026]				
Plane B: S(3), S(4), N(2), C(4), C(5), C(6)	0.6782	0.6872	0.2603	3.7971
[Zn(1) 0.215, S(3) 0.008, S(4) 0.009, N(2) −0.022, C(4) −0.017, C(5) 0.011, C(6) 0.010]				
Plane C: S(5), S(6), N(3), C(7), C(8), C(9)	−0.4463	0.2680	−0.8538	−2.5741
[Zn(1) 0.463, S(5) −0.060, S(6) 0.049, N(3) −0.003, C(7) 0.015, C(8) 0.066, C(9) −0.067]				
Plane D: N(4), C(10), C(11)	0.1963	0.6148	0.7638	4.9571
Plane E: N(4), C(12), C(13)	−0.8077	−0.3537	0.4717	−1.1087
Plane F: N(4), C(14), C(15)	0.2070	0.5966	0.7754	5.0892
Plane G: N(4), C(16), C(17)	−0.7931	−0.3786	0.4771	−0.9875

Angles (°) between planes: D–E 90.9; D–F 1.4; D–G 91.4; E–F 90.7; E–G 1.7; F–G 91.2.

N-bonded [Zn-N 2.061 Å; see mode (A) above]. The zinc co-ordination geometry is best described as rectangular-based pyramidal, which is similar to that observed in $[\{Zn(S_2CNMe_2)_2\}_2(\mu\text{-}OCOMe)]^-$ but different to that found in $[Zn(py)(S_2CNMe_2)_2]$ (py = pyridine).[7] The deviations from local C_{2v} symmetry are relatively small. There is no interaction of significance between the zinc and the exocyclic S atom of the $C_7H_4NS_2$ ligand (3.43 Å, well in excess of the van der Waals distance) and the Zn–N–C bond angles are more similar than in $[Zn(C_7H_4NS_2)_3(OH_2)]^-$; residual differences are probably steric in origin. It seems likely that the variations in the four Zn-S distances reflect a degree of overcrowding in this genuinely five-co-ordinate complex and there is no opportunity or need for the formation of such weak and long zinc–sulphur interactions.

The bond lengths in the S_2CNMe_2 ligands do not reflect any variations in the strength of Zn–S bonding, and the bond lengths in the $C_7H_4NS_2$ ligand are again consistent with bonding mode (A) (above). The S_2CNMe_2 ligands are fairly planar with the zinc lying 0.16 and 0.36 Å from the mean planes. The $C_7H_4NS_2$ ligand is rather less planar but the zinc atom lies only 0.02 Å from the mean plane.

The geometry of the cation is, in the main, unexceptionable. The molecule of ethanol in the crystal lattice is not well defined and, indeed, may be disordered end-to-end since it seems not to interact *via* hydrogen-bond formation with any part of the anion. The identification of only one site for a hydrogen substituent allowed assignment of the O atom, at least of the major orientational form. The only contact worthy of note is of 3.30 Å to S(4) but the determined position of the hydrogen atom does not lie near to the line between S(4) and O(1).

TABLE 10

Bond lengths (Å) and angles (°) with estimated standard deviations for $[NBu^n{}_4][Zn(C_7H_4NS_2)_3(OH_2)]$

Zn(1)–S(1)	3.125(2)	S(1)–C(1)	1.690(6)
Zn(1)–S(3)	2.327(2)	S(2)–C(1)	1.747(6)
Zn(1)–S(5)	2.348(2)	S(2)–C(3)	1.746(6)
Zn(1)–O(1)	2.037(4)	N(1)–C(1)	1.331(7)
Zn(1)–N(1)	2.019(4)	N(1)–C(2)	1.390(6)
		C(2)–C(3)	1.387(7)
O(1)–H(1A)	0.98(6)	C(3)–C(4)	1.397(8)
O(1)–H(1B)	0.72(6)	C(4)–C(5)	1.388(8)
N(2) ··· H(1A)	1.71(6)	C(5)–C(6)	1.376(8)
N(3) ··· H(1B)	2.02(6)	C(6)–C(7)	1.395(8)
		C(2)–C(7)	1.398(7)
N(4)–C(22)	1.526(7)	S(3)–C(8)	1.720(6)
C(22)–C(23)	1.511(9)	S(4)–C(8)	1.761(6)
C(23)–C(24)	1.493(10)	S(4)–C(10)	1.741(7)
C(24)–C(25)	1.501(12)	N(2)–C(8)	1.310(8)
N(4)–C(26)	1.529(7)	N(2)–C(9)	1.394(8)
C(26)–C(27)	1.520(9)	C(9)–C(10)	1.400(9)
C(27)–C(28)	1.556(10)	C(10)–C(11)	1.388(11)
C(28)–C(29)	1.438(11)	C(11)–C(12)	1.354(12)
N(4)–C(30)	1.519(7)	C(12)–C(13)	1.385(12)
C(30)–C(31)	1.512(9)	C(13)–C(14)	1.393(11)
C(31)–C(32)	1.531(11)	C(9)–C(14)	1.387(10)
C(32)–C(33)	1.441(13)	S(5)–C(15)	1.729(6)
N(4)–C(34)	1.522(7)	S(6)–C(15)	1.761(6)
C(34)–C(35)	1.523(8)	S(6)–C(17)	1.742(7)
C(35)–C(36)	1.515(9)	N(3)–C(15)	1.292(7)
C(36)–C(37)	1.489(11)	N(3)–C(16)	1.409(7)
		C(16)–C(17)	1.385(9)
		C(17)–C(18)	1.401(10)
		C(18)–C(19)	1.357(11)
		C(19)–C(20)	1.386(11)
		C(20)–C(21)	1.384(10)
		C(16)–C(21)	1.380(9)

TABLE 10 (*Continued*)

S(3)–Zn(1)–S(5)	120.98(7)	Zn(1)–N(1)–C(1)	112.9(3)
S(3)–Zn(1)–O(1)	103.82(11)	Zn(1)–N(1)–C(2)	133.2(3)
S(3)–Zn(1)–N(1)	116.23(12)	S(1)–C(1)–S(2)	122.6(3)
S(5)–Zn(1)–O(1)	103.52(11)	S(1)–C(1)–N(1)	124.5(4)
S(5)–Zn(1)–N(1)	105.89(12)	S(2)–C(1)–N(1)	112.9(4)
O(1)–Zn(1)–N(1)	104.36(15)	C(1)–S(2)–C(3)	90.5(3)
S(1)–Zn(1)–S(3)	85.92(6)	C(1)–N(1)–C(2)	112.6(4)
S(1)–Zn(1)–S(5)	83.07(5)	N(1)–C(2)–C(3)	114.7(4)
S(1)–Zn(1)–O(1)	162.48(11)	N(1)–C(2)–C(7)	125.2(5)
S(1)–Zn(1)–N(1)	58.12(12)	C(3)–C(2)–C(7)	120.1(5)
		S(2)–C(3)–C(2)	109.4(4)
Zn(1)–O(1)–H(1A)	104(4)	S(2)–C(3)–C(4)	129.0(4)
Zn(1)–O(1)–H(1B)	111(5)	C(2)–C(3)–C(4)	121.6(5)
H(1A)–O(1)–H(1B)	107(6)	C(3)–C(4)–C(5)	118.0(5)
O(1)–H(1A) ··· N(2)	162(6)	C(4)–C(5)–C(6)	120.5(5)
O(1)–H(1B) ··· N(3)	153(7)	C(5)–C(6)–C(7)	122.1(5)
H(1A) ··· N(2)–C(8)	114(2)	C(6)–C(7)–C(2)	117.7(5)
H(1A) ··· N(2)–C(9)	131(2)		
H(1B) ··· N(3)–C(15)	116(2)	Zn(1)–S(3)–C(8)	105.3(2)
H(1B) ··· N(3)–C(16)	132(2)	S(3)–C(8)–S(4)	117.9(4)
		S(3)–C(8)–N(2)	128.0(5)
C(22)–N(4)–C(26)	111.3(4)	S(4)–C(8)–N(2)	114.1(4)
C(22)–N(4)–C(30)	109.3(4)	C(8)–S(4)–C(10)	90.1(3)
C(22)–N(4)–C(34)	107.9(4)	C(8)–N(2)–C(9)	111.6(5)
C(26)–N(4)–C(30)	108.0(4)	N(2)–C(9)–C(10)	115.5(6)
C(26)–N(4)–C(34)	107.9(4)	N(2)–C(9)–C(14)	123.8(6)
C(30)–N(4)–C(34)	112.5(4)	C(10)–C(9)–C(14)	120.7(6)
N(4)–C(22)–C(23)	115.3(5)	S(4)–C(10)–C(9)	108.7(5)
C(22)–C(23)–C(24)	110.1(5)	S(4)–C(10)–C(11)	130.2(6)
C(23)–C(24)–C(25)	113.1(7)	C(9)–C(10)–C(11)	121.1(6)
N(4)–C(26)–C(27)	115.8(5)	C(10)–C(11)–C(12)	117.5(7)
C(26)–C(27)–C(28)	107.8(5)	C(11)–C(12)–C(13)	122.8(8)
C(27)–C(28)–C(29)	114.8(6)	C(12)–C(13)–C(14)	120.4(7)
N(4)–C(30)–C(31)	114.5(5)	C(13)–C(14)–C(9)	117.5(7)
C(30)–C(31)–C(32)	108.6(6)		
C(31)–C(32)–C(33)	114.4(7)	Zn(1)–S(5)–C(15)	105.8(2)
N(4)–C(34)–C(35)	115.6(5)	S(5)–C(15)–S(6)	117.1(3)
C(34)–C(35)–C(36)	108.3(5)	S(5)–C(15)–N(3)	128.9(5)
C(35)–C(36)–C(37)	113.8(6)	S(6)–C(15)–N(3)	114.0(4)
		C(15)–S(6)–C(17)	89.7(3)
		C(15)–N(3)–C(16)	112.4(5)
		N(3)–C(16)–C(17)	114.3(5)
		N(3)–C(16)–C(21)	125.0(5)
		C(17)–C(16)–C(21)	120.7(6)
		S(6)–C(17)–C(16)	109.6(5)
		S(6)–C(17)–C(18)	129.0(5)
		C(16)–C(17)–C(18)	121.4(6)
		C(17)–C(18)–C(19)	116.5(7)
		C(18)–C(19)–C(20)	123.0(7)
		C(19)–C(20)–C(21)	120.1(7)
		C(20)–C(21)–C(16)	118.1(6)

$[NBu^n{}_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]$. The anion (Figure 4) is comprised of two $C_7H_4NS_2$ ligands which are nitrogen-bonded (mean Zn–N 1.997 Å) to the zinc atom [mode (A)], and a bidentate S_2CNMe_2 ligand (mean Zn–S 2.408 Å). The zinc-to-exocyclic ($C_7H_4NS_2$) sulphur distances are again within the van der Waals distance (mean length 3.19 Å) but are larger than similar contacts of this type observed in $[Zn(S_2CNMe_2)_3]^-$ and $[Zn(C_7H_4NS_2)_3(OH_2)]^-$; a similar asymmetry in the Zn–N–C angles is also observed.

The co-ordination geometry around the zinc atom is again best referred to as a tetrahedron but with the inevitable small S_2CNMe_2 chelate bite angle (75.1°) counterbalanced by a large N–Zn–N angle (122.7°) which must be sterically favourable. Two remote exocyclic S atoms asymmetrically cap the two enlarged faces of the tetrahedron and the molecule has approximate C_2

symmetry. The two $C_7H_4NS_2$ ligands are fairly planar with the Zn atom lying 0.36 and 0.08 Å from the mean planes. The S_2CNMe_2 ligand is slightly non-planar with the zinc atom lying 0.22 Å out of the mean plane. Bond lengths in these ligands continue the pattern observed in the previous three structures.

The cation showed some disorder and geometric constraints were applied during the later stages of refinement (see Experimental section); otherwise, the geometry is acceptable.

The arrangement of the various donor atoms in the above four structures may be compared with the geometric environment of zinc in crystalline ZnS_2 (tetrahedral) where *four* sulphur atoms (or S^{2-} ions) almost totally encapsulate the Zn^{2+}. In the S_2CNMe_2–$C_7H_4NS_2$ complexes, the donor atoms usually occur either in SS pairs or in SN groups which are constrained by ligand geometry to form four-membered chelate rings. Thus the relatively small cone angle subtended by these donor atom sets would seem to leave the zinc atom slightly co-ordinatively unsaturated. This must presumably occur to a sufficient extent that vacancies can be created which are radially close to the first co-ordination sphere. Thus, further interacting groups can be allowed to ap-

TABLE 11

Planar fragments of $[NBu^n_4][Zn(C_7H_4NS_2)_3(OH_2)]$. 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: C(2)—C(7)				
	0.0695	0.9922	0.1033	4.1564
[C(2) −0.016, C(3) 0.013, C(4) 0.003, C(5) −0.016, C(6) 0.013, C(7) 0.003, S(2) 0.022, N(1) −0.058]				
Plane B: C(9)—C(14)				
	0.1978	−0.8747	−0.4424	−5.2723
[C(9) −0.004, C(10) 0.005, C(11) 0.001, C(12) −0.007, C(13) 0.007, C(14) −0.002, S(4) −0.018, N(2) −0.033]				
Plane C: C(16)—C(21)				
	0.7271	0.2464	−0.6409	−1.7727
[C(16) 0.004, C(17) 0.004, C(18) −0.010, C(19) 0.008, C(20) −0.001, C(21) −0.005, S(6) 0.042, N(3) 0.029]				
Plane D: S(1), S(2), N(1), C(1)—C(3)				
	0.0859	0.9936	0.0729	3.9124
[S(1) −0.004, S(2) 0.006, N(1) 0.000, C(1) 0.002, C(2) 0.005, C(3) -0.009, Zn(1) -0.381]				
Plane E: S(3), S(4), N(2), C(8)—C(10)				
	0.2052	−0.8853	−0.4172	−5.3222
[S(3) −0.007, S(4) 0.008, N(2) 0.008, C(8) 0.002, C(9) −0.003, C(10) −0.008, Zn(1) 0.818, O(1) 0.901]				
Plane F: S(5), S(6), N(3), C(15)—C(17)				
	0.7007	0.2306	−0.6751	−1.8020
[S(5) 0.022, S(6) −0.018, N(3) −0.022, C(15) −0.014, C(16) 0.013, C(17) 0.018, Zn(1) 0.049, O(1) −0.288]				
Plane G: C(22)—C(25)				
	−0.7307	0.5257	−0.4356	0.2001
[C(22) −0.010, C(23) 0.009, C(24) 0.011, C(25) −0.010, N(4) 0.144]				
Plane H: C(26)—C(29)				
	−0.6703	−0.0082	0.7420	6.1583
[C(26) 0.011, C(27) −0.010, C(28) −0.014, C(29) 0.012, N(4) 0.477]				
Plane I: C(30)—C(33)				
	0.2104	0.6658	−0.7158	−4.8422
[C(30) 0.004, C(31) −0.004, C(32) −0.005, C(33) 0.004, N(4) −0.107]				
Plane J: C(34)—(C37)				
	−0.5273	−0.5876	−0.6137	−0.8935
[C(34) −0.005, C(35) 0.005, C(36) 0.006, C(37) −0.006, N(4) −0.053]				

Selected angles (°) between planes: A–D 2.0; B–E 1.6; C–F 2.6.

TABLE 12

Bond lengths (Å) and angles (°) with estimated standard deviations for $[NBu^n_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]\cdot C_2H_5OH$

Zn(1)–S(1)	3.430(4)	S(1)–C(1)	1.679(10)
Zn(1)–S(3)	2.628(3)	S(2)–C(1)	1.736(10)
Zn(1)–S(4)	2.384(3)	S(2)–C(3)	1.709(11)
Zn(1)–S(5)	2.541(4)	N(1)–C(1)	1.328(13)
Zn(1)–S(6)	2.454(3)	N(1)–C(2)	1.411(13)
Zn(1)–N(1)	2.061(8)	C(2)–C(3)	1.378(14)
		C(3)–C(4)	1.374(16)
N(4)–C(14)	1.522(13)	C(4)–C(5)	1.365(18)
N(4)–C(18)	1.492(13)	C(5)–C(6)	1.389(18)
N(4)–C(22)	1.531(13)	C(6)–C(7)	1.403(17)
N(4)–C(26)	1.521(13)	C(2)–C(7)	1.391(15)
C(14)–C(15)	1.516(15)		
C(15)–C(16)	1.521(15)	S(3)–C(8)	1.721(10)
C(16)–C(17)	1.523(17)	S(4)–C(8)	1.710(10)
C(18)–C(19)	1.526(16)	N(2)–C(8)	1.334(12)
C(19)–C(20)	1.495(18)	N(2)–C(9)	1.441(14)
C(20)–C(21)	1.456(20)	N(2)–C(10)	1.444(14)
C(22)–C(23)	1.519(16)		
C(23)–C(24)	1.503(19)	S(5)–C(11)	1.693(10)
C(24)–C(25)	1.488(22)	S(6)–C(11)	1.715(10)
C(26)–C(27)	1.532(15)	N(3)–C(11)	1.330(13)
C(27)–C(28)	1.510(16)	N(3)–C(12)	1.461(15)
C(28)–C(29)	1.505(18)	N(3)–C(13)	1.451(14)
O(1)–C(30)	1.449(19)		
C(30)–C(31)	1.415(24)		
S(3)–Zn(1)–S(4)	71.15(10)	Zn(1)–N(1)–C(1)	121.3(6)
S(3)–Zn(1)–S(5)	91.19(11)	Zn(1)–N(1)–C(2)	127.6(6)
S(3)–Zn(1)–S(6)	146.77(12)	S(1)–C(1)–S(2)	119.9(6)
S(4)–Zn(1)–S(5)	136.64(12)	S(1)–C(1)–N(1)	126.8(8)
S(4)–Zn(1)–S(6)	101.72(11)	S(2)–C(1)–N(1)	113.3(7)
S(5)–Zn(1)–S(6)	71.60(11)	C(1)–S(2)–C(3)	91.2(5)
N(1)–Zn(1)–S(3)	104.9(2)	C(1)–N(1)–C(2)	110.9(8)
N(1)–Zn(1)–S(4)	114.1(2)	N(1)–C(2)–C(3)	114.6(9)
N(1)–Zn(1)–S(5)	108.6(2)	N(1)–C(2)–C(7)	123.9(9)
N(1)–Zn(1)–S(6)	107.4(2)	C(3)–C(2)–C(7)	121.4(10)
		S(2)–C(3)–C(2)	109.9(8)
C(14)–N(4)–C(18)	105.3(7)	S(2)–C(3)–C(4)	129.4(9)
C(14)–N(4)–C(22)	110.8(7)	C(2)–C(3)–C(4)	120.7(10)
C(14)–N(4)–C(26)	110.5(7)	C(3)–C(4)–C(5)	118.0(11)
C(18)–N(4)–C(22)	112.0(8)	C(4)–C(5)–C(6)	123.3(12)
C(18)–N(4)–C(26)	113.0(7)	C(5)–C(6)–C(7)	118.3(11)
C(22)–N(4)–C(26)	105.4(7)	C(6)–C(7)–C(2)	118.2(10)
N(4)–C(14)–C(15)	115.3(8)		
C(14)–C(15)–C(16)	109.5(9)	Zn(1)–S(3)–C(8)	81.9(3)
C(15)–C(16)–C(17)	112.0(9)	Zn(1)–S(4)–C(8)	89.9(3)
N(4)–C(18)–C(19)	113.9(9)	S(3)–C(8)–S(4)	116.8(5)
C(18)–C(19)–C(20)	110.5(10)	S(3)–C(8)–N(2)	121.5(7)
C(19)–C(20)–C(21)	115.8(12)	S(4)–C(8)–N(2)	121.6(7)
N(4)–C(22)–C(23)	115.2(9)	C(8)–N(2)–C(9)	120.2(8)
C(22)–C(23)–C(24)	110.3(10)	C(8)–N(2)–C(10)	120.5(8)
C(23)–C(24)–C(25)	111.9(12)	C(9)–N(2)–C(10)	119.3(8)
N(4)–C(26)–C(27)	114.6(8)		
C(26)–C(27)–C(28)	109.8(9)	Zn(1)–S(5)–C(11)	83.7(4)
C(27)–C(28)–C(29)	113.3(10)	Zn(1)–S(6)–C(11)	86.1(4)
		S(5)–C(11)–S(6)	118.1(6)
O(1)–C(30)–C(31)	110.8(13)	S(5)–C(11)–N(3)	121.9(8)
		S(6)–C(11)–N(3)	120.0(7)
		C(11)–N(3)–C(12)	120.9(9)
		C(11)–N(3)–C(13)	121.8(8)
		C(12)–N(3)–C(13)	117.2(9)

TABLE 13

Planar fragments of $[NBu^n_4][Zn(S_2CNMe_2)_2(C_7H_4NS_2)]\cdot C_2H_5OH$. Details as Table 11

	p	*q*	*r*	*d*	
Plane A: S(3), S(4), N(2), C(8)—C(10)	−0.1790	−0.8310	−0.5268	1.6910	[Zn(1) −0.162, S(3) −0.006, S(4) 0.012, N(2) 0.002, C(8) −0.010, C(9) 0.011, C(10) −0.010]
Plane B: S(5), S(6), N(3), C(11)—C(13)	0.6338	0.7728	−0.0334	1.7952	[Zn(1) −0.362, S(5) −0.010, S(6) −0.005, N(3) 0.010, C(11) 0.016, C(12) −0.003, C(13) −0.009]
Plane C: S(1), S(2), N(1), C(1)—C(3)	−0.3220	0.0667	0.9444	−4.2249	[Zn(1) 0.022, S(1) 0.011, S(2) −0.017, N(1) −0.024, C(1) 0.007, C(2) 0.012, C(3) 0.011, C(4) 0.056, C(5) 0.106, C(6) 0.101, C(7) 0.034]
Plane D: C(2)—C(7)	−0.2854	0.0587	0.9566	−4.2888	[C(2) 0.009, C(3) 0.000, C(4) −0.006, C(5) 0.004, C(6) 0.005, C(7) −0.011, S(1) 0.159, S(2) 0.031, N(1) 0.027, C(1) 0.089]
Plane E: C(14)—(C16)	−0.8842	−0.3247	−0.3357	−3.8033	[N(4) −0.264, C(17) 0.265]
Plane F: C(18)—C(20)	0.7632	0.6153	0.1972	3.2620	[N(4) −0.341, C(21) −0.204]
Plane G: C(22)—C(25)	−0.4594	−0.1164	0.8806	−6.9241	[N(4) 0.002, C(22) 0.008, C(23) −0.008, C(24) −0.008, C(25) 0.008]
Plane H: C(26)—C(29)	−0.5289	0.1389	0.8372	−8.1019	[N(4) 0.098, C(26) 0.006, C(27) −0.006, C(28) −0.007, C(29) 0.007]

Angle between planes: C–D 2.3°.

TABLE 14

Bond lengths (Å) and angles (°) with estimated standard deviations for $[NBu^n_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]$

Zn(1)–S(1)	3.208(3)	S(1)–C(1)	1.694(8)
Zn(1)–S(3)	3.174(3)	S(2)–C(1)	1.756(8)
Zn(1)–S(5)	2.405(3)	S(2)–C(3)	1.736(8)
Zn(1)–S(6)	2.410(2)	N(1)–C(1)	1.320(10)
Zn(1)–N(1)	1.984(6)	N(1)–C(2)	1.388(10)
Zn(1)–N(2)	2.006(6)	C(2)–C(3)	1.412(11)
		C(3)–C(4)	1.404(12)
N(4)–C(18)	1.518(11)	C(4)–C(5)	1.365(13)
N(4)–C(22)	1.540(12)	C(5)–C(6)	1.402(13)
N(4)–C(26)	1.544(11)	C(6)–C(7)	1.411(13)
N(4)–C(30)	1.525(12)	C(2)–C(7)	1.385(11)
C(18)–C(19)	1.545(14)		
C(19)–C(20)	1.521(17)	S(3)–C(8)	1.667(8)
C(20)–C(21)	1.529(21)	S(4)–C(8)	1.766(8)
C(22)–C(23)	1.526(15)	S(4)–C(10)	1.742(8)
C(23)–C(24)	1.482(18)	N(2)–C(8)	1.312(9)
C(24)–C(25)	1.437(20)	N(2)–C(9)	1.400(9)
C(26)–C(27)	1.523(17)	C(9)–C(10)	1.388(11)
C(27)–C(28) *	1.537(—)	C(10)–C(11)	1.397(13)
C(28)–C(29) *	1.537(—)	C(11)–C(12)	1.374(13)
C(30)–C(31)	1.483(24)	C(12)–C(13)	1.384(13)
C(31)–C(32) *	1.537(—)	C(13)–C(14)	1.413(13)
C(32)–C(33) *	1.537(—)	C(9)–C(14)	1.383(12)
C(31)–C(34)	1.579(36)		
C(34)–C(35) *	1.537(—)	S(5)–C(15)	1.705(8)
		S(6)–C(15)	1.727(8)
		N(3)–C(15)	1.342(10)
		N(3)–C(16)	1.474(12)
		N(3)–C(17)	1.459(13)

TABLE 14 (*Continued*)

S(5)–Zn(1)–S(6)	75.10(8)	Zn(1)–N(1)–C(1)	115.9(5)
S(5)–Zn(1)–N(1)	108.3(2)	Zn(1)–N(1)–C(2)	131.0(5)
S(5)–Zn(1)–N(2)	113.7(2)	S(1)–C(1)–S(2)	120.8(5)
S(6)–Zn(1)–N(1)	114.0(2)	S(1)–C(1)–N(1)	125.6(6)
S(6)–Zn(1)–N(2)	112.9(2)	S(2)–C(1)–N(1)	113.7(6)
N(1)–Zn(1)–N(2)	122.9(2)	C(1)–S(2)–C(3)	90.3(4)
		C(1)–N(1)–C(2)	112.3(6)
C(18)–N(4)–C(22)	111.2(6)	N(1)–C(2)–C(3)	114.5(7)
C(18)–N(4)–C(26)	111.6(6)	N(1)–C(2)–C(7)	125.4(7)
C(18)–N(4)–C(30)	106.6(6)	C(3)–C(2)–C(7)	120.0(7)
C(22)–N(4)–C(26)	105.2(6)	S(2)–C(3)–C(2)	109.2(6)
C(22)–N(4)–C(30)	111.3(7)	S(2)–C(3)–C(4)	128.6(6)
C(26)–N(4)–C(30)	111.1(6)	C(2)–C(3)–C(4)	122.2(7)
N(4)–C(18)–C(19)	112.9(7)	C(3)–C(4)–C(5)	116.8(8)
C(18)–C(19)–C(20)	110.5(9)	C(4)–C(5)–C(6)	122.6(9)
C(19)–C(20)–C(21)	111.1(11)	C(5)–C(6)–C(7)	120.4(8)
N(4)–C(22)–C(23)	114.8(8)	C(6)–C(7)–C(2)	118.0(8)
C(22)–C(23)–C(24)	109.5(10)		
C(23)–C(24)–C(25)	115.1(12)	Zn(1)–N(2)–C(8)	114.6(5)
N(4)–C(26)–C(27)	113.7(8)	Zn(1)–N(2)–C(9)	130.4(5)
C(26)–C(27)–C(28)	111.3(10)	S(3)–C(8)–S(4)	122.9(5)
C(27)–C(28)–C(29) *	110.1(—)	S(3)–C(8)–N(2)	126.4(6)
N(4)–C(30)–C(31)	114.2(11)	S(4)–C(8)–N(2)	110.7(5)
C(30)–C(31)–C(32)	117.6(16)	C(8)–S(4)–C(10)	91.6(4)
C(31)–C(32)–C(33) *	110.1(—)	C(8)–N(2)–C(9)	115.0(6)
C(30)–C(31)–C(34)	100.5(17)	N(2) C(9)–C(10)	113.8(7)
C(31)–C(34)–C(35) *	108.2(—)	N(2)–C(9)–C(14)	125.5(7)
		C(10)–C(9)–C(14)	120.7(7)
Zn(1)–S(5)–C(15)	83.9(3)	S(4)–C(10)–C(9)	109.0(6)
Zn(1)–S(6)–C(15)	83.3(3)	S(4)–C(10)–C(11)	129.4(7)
S(5)–C(15)–S(6)	117.5(5)	C(9)–C(10)–C(11)	121.6(8)
S(5)–C(15)–N(3)	122.0(6)	C(10)–C(11)–C(12)	118.2(9)
S(6)–C(15)–N(3)	120.5(6)	C(11)–C(12)–C(13)	120.5(9)
C(15)–N(3)–C(16)	122.0(7)	C(12)–C(13)–C(14)	121.8(8)
C(15)–N(3)–C(17)	121.8(7)	C(13)–C(14)–C(9)	117.1(8)
C(16)–N(3)–C(17)	115.9(7)		

* Constrained during refinement.

TABLE 15

Planar fragments of $[NBu^n_4][Zn(S_2CNMe_2)(C_7H_4NS_2)_2]$. Details as in Table 9

	p	*q*	*r*	*d*	
Plane A: C(2)—C(7)	−0.7993	0.0342	−0.5999	−5.0008	[C(2) 0.007, C(3) 0.003, C(4) −0.012, C(5) 0.011, C(6) −0.001, C(7) −0.008, S(1) 0.169, S(2) −0.002, N(1) 0.083, C(1) 0.076]
Plane B: S(1), S(2), N(1), C(1)—C(3)	−0.7794	0.0701	−0.6226	−4.8667	[Zn(1) 0.317, S(1) 0.013, S(2) −0.017, N(1) 0.001, C(1) −0.011, C(2) −0.013, C(3) 0.027, C(4) 0.077, C(5) 0.119, C(6) 0.065, C(7) −0.008]
Plane C: S(3), S(4), N(2), C(8)—C(14)	0.8989	−0.2647	−0.3493	0.0306	[Zn(1) −0.072, S(3) 0.018, S(4) −0.018, N(2) −0.005, C(8) −0.001, C(9) −0.005, C(10) −0.012, C(11) 0.017, C(12) 0.009, C(13) −0.004, C(14) −0.001]
Plane D: S(5), S(6), C(15)	0.4365	0.5128	−0.7393	−2.2253	[Zn(1) 0.197, N(3) −0.026, C(16) 0.011, C(17) 0.066]
Plane E: N(3), C(16), C(17)	0.5075	0.4669	−0.7242	−2.4190	[S(5) 0.244, S(6) 0.176, C(15) 0.137]
Plane F: C(18)—C(21)	0.4153	−0.8105	0.4131	2.4561	[N(4) 0.003, C(18) −0.007, C(19) 0.006, C(20) 0.007, C(21) −0.007]
Plane G: C(22)—C(25)	0.6110	0.5159	0.6004	4.0088	[N(4) 0.141, C(22) −0.024, C(23) 0.021, C(24) 0.029, C(25) −0.026]

TABLE 15 (*Continued*)

Plane H: C(26)—C(28)

0.3897	0.5166	0.7624	6.0399

[N(4) −0.133, C(29) −1.433]

Plane I: N(4), C(30), C(31)

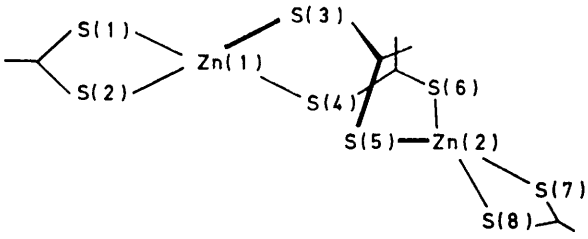
−0.4012	0.8509	−0.3391	−1.8473

[C(32) 0.086, C(33) −1.312, C(34) −0.717, C(35) −0.498]

Angles (°) between planes: A–B 2.7; D–E 4.9.

proach the metal thereby either increasing its co-ordination number, as by formal addition of $C_7H_4NS_2^-$ [form (A)], pyridine, and acetate ion to $[Zn(S_2CNMe_2)_2]$ giving $[Zn(S_2CNMe_2)_2(C_7H_4NS_2)]^-$, $[Zn(py)(S_2CNMe_2)_2]$, and $[\{Zn(S_2CNMe_2)_2\}_2(\mu\text{-}OCOMe)]^-$, respectively, or effectively ' blocking ' the sites with some small additional bonding effect, as in $[Zn(S_2CNMe_2)_3]^-$, $[Zn(C_7H_4NS_2)_3(OH_2)]^-$, and $[Zn(S_2CNMe_2)(C_7H_4NS_2)_2]^-$.

A further comment along the above lines may be made about the structure of $[\{Zn(S_2CNMe_2)_2\}_2]$.[8] This binuclear species contains two terminal and two bridging S_2CNMe_2 ligands. The co-ordination geometry of each zinc atom is described as strongly distorted tetrahedral in which the Zn–S distances [S(1)—S(4)] vary from 2.312 to 2.429 Å and two of the six tetrahedral angles differ greatly from the ideal. An inspection of the structure reveals that within each metal co-ordination sphere an additional S atom [S(5) for Zn(1), S(4) for Zn(2)] lies at a distance of 3.036 Å, which is remarkably similar to those values quoted above for weak Zn · · · S interactions. While the description of the co-ordination geometry about the zinc atom as distorted tetrahedral was preferred,[8] it was suggested that it could also be represented as a strongly distorted trigonal bipyramid. In this alternative description S(2), S(3), and S(4) form the trigonal group and S(1) and S(5) the axial atoms. In view of the results presented in this paper, it would seem perhaps more reasonable to consider each metal atom in $[\{Zn(S_2CNMe_2)_2\}_2]$ to be essentially five-co-ordinate.



The structure determination of $[\{Zn(S_2CNEt_2)_2\}_2]$ [9] has revealed that each zinc atom is more obviously five-co-ordinate with a geometry intermediate between tetragonal pyramidal and distorted trigonal bipyramidal (the latter description was favoured). The Zn–S distances vary from 2.331 to 2.815 Å, the largest bond occurring within each $Zn(S_2CNEt_2)_2$ monomeric unit.

It remains to be seen whether other zinc complexes of sterically constrained sulphur ligands adopt similar unusual structures, and whether a range of distortions will be found which may depend to some extent on the size and nature of the substituents attached to these ligands.

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