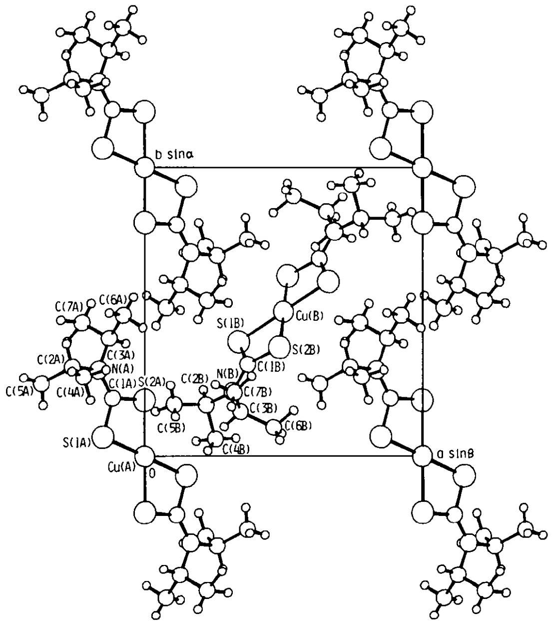

Fig. 1. The crystal structure projected along the *c* axis.

An octahedral configuration as seen around atom Cu(*A*) has also been noticed in $[Cu(S_2CNMe_2)_2]$ and $[Cu(S_2CNEt_2)_2]_2$. In the case of the methyl analog the fifth and sixth octahedral positions are occupied by weakly bonded S atoms in the polymeric chain mentioned above. In the ethyl analog the sixth position is occupied by one of the methylene H atoms at 2·86 Å. Thus, the Cu atom in dithiocarbamate complexes may essentially favor an octahedral site, although this is not realized for molecule *B* of the present crystal.

The difference in the modes of molecular aggregation in diethyl- and diisopropyldithiocarbamates might, at first sight, be considered to result entirely from the difference in bulkiness of the alkyl groups. However, it should be noted that the closely related zinc isopropyldithiocarbamate (Miyamae, Ito & Iwasaki, 1979) is isostructural with zinc diethyldithiocarbamate (Bonamico, Mazzone, Vaciago & Zambonelli, 1965), both being dimeric in the crystalline state. Zinc dimethyldithiocarbamate is monomeric, as in the case of the Cu complex (Klug, 1966), although the crystal and molecular structures are not similar. Thus the change of molecular-aggregation modes of the copper dithiocarbamate series on varying the alkyl group is not paralleled by that of the corresponding Zn series. Obviously the dimeric nature of $[Zn(S_2CN\mathit{i}Pr_2)_2]_2$ cannot be explained by the bulkiness of the isopropyl group. Thus, the molecular association in the solid must be determined by alkyl effects combined with some processes involving the electronic structure of the metal atom.

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# Structure of Tris(*N*,*N*-dimethyldithiocarbamato)cobalt(III)

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**Abstract.** $C_9H_{18}CoN_3S_6$, $[Co(C_3H_6NS_2)_3]$, $M_r$ = 419·6, monoclinic, $P2_1/n$, $a$ = 13·992 (7), $b$ = 9·770 (3), $c$ = 13·555 (6) Å, $\beta$ = 101·50 (4)°, $U$ = 1815·8 Å$^3$, $D_x$ = 1·535 Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 1·60 mm$^{-1}$, $Z$ = 4. The structure was refined to $R$ = 0·050 for 2532 independent reflexions by the block-diagonal least-squares method. The molecule has approximate 32 symmetry. The Co atom is surrounded by six S atoms at distances of 2·254 (2)–2·273 (2) Å.

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Table 1. *Atomic parameters with estimated standard deviations in parentheses*

Positional parameters for non-hydrogen atoms are multiplied by $10^4$; those for H by $10^3$. *B* values for non-hydrogen atoms are equivalent isotropic temperature factors.

| | *x* | *y* | *z* | *B* (Å$^2$) |
|---|---|---|---|---|
| Co | 2261 (1) | 2648 (1) | −149 (1) | 3·2 |
| S(1) | 2001 (1) | 1260 (1) | 1118 (1) | 4·0 |
| S(2) | 1909 (1) | 607 (2) | −912 (1) | 4·3 |
| S(3) | 729 (1) | 3482 (2) | −515 (1) | 4·4 |
| S(4) | 2205 (1) | 3794 (1) | −1615 (1) | 3·9 |
| S(5) | 2864 (1) | 4429 (1) | 861 (1) | 4·1 |
| S(6) | 3893 (1) | 2298 (1) | 166 (1) | 4·1 |
| N(1) | 1720 (3) | −1328 (5) | 436 (3) | 4·5 |
| N(2) | 436 (3) | 4939 (5) | −2230 (3) | 4·5 |
| N(3) | 4820 (3) | 4308 (5) | 1326 (3) | 4·5 |
| C(1) | 1853 (3) | −29 (6) | 249 (3) | 3·6 |
| C(2) | 1033 (4) | 4191 (5) | −1557 (4) | 3·6 |
| C(3) | 3989 (4) | 3764 (5) | 861 (3) | 3·6 |
| C(4) | 1722 (5) | −1809 (7) | 1450 (4) | 5·9 |
| C(5) | 1565 (5) | −2342 (7) | −371 (4) | 6·2 |
| C(6) | −553 (4) | 5264 (7) | −2128 (5) | 5·9 |
| C(7) | 754 (5) | 5484 (7) | −3106 (4) | 6·0 |
| C(8) | 4847 (5) | 5565 (7) | 1884 (5) | 6·8 |
| C(9) | 5744 (4) | 3662 (7) | 1293 (5) | 6·0 |
| H(41) | 202 (4) | −271 (7) | 156 (4) | 9 (2) |
| H(42) | 200 (4) | −119 (6) | 194 (4) | 7 (2) |
| H(43) | 109 (4) | −206 (7) | 148 (4) | 8 (2) |
| H(51) | 212 (3) | −230 (5) | −57 (3) | 5 (1) |
| H(52) | 130 (4) | −314 (5) | −10 (4) | 5 (1) |
| H(53) | 117 (3) | −213 (5) | −107 (4) | 5 (1) |
| H(61) | −76 (4) | 485 (6) | −150 (4) | 6 (1) |
| H(62) | −94 (4) | 473 (7) | −255 (4) | 8 (2) |
| H(63) | −69 (4) | 623 (7) | −216 (5) | 8 (2) |
| H(71) | 141 (3) | 532 (5) | −324 (4) | 5 (1) |
| H(72) | 77 (3) | 639 (5) | −298 (4) | 5 (1) |
| H(73) | 34 (3) | 513 (5) | −377 (4) | 5 (1) |
| H(81) | 446 (4) | 601 (5) | 167 (4) | 5 (1) |
| H(82) | 541 (5) | 612 (7) | 184 (5) | 10 (2) |
| H(83) | 506 (6) | 544 (9) | 262 (6) | 13 (3) |
| H(91) | 577 (4) | 325 (6) | 73 (4) | 7 (2) |
| H(92) | 606 (6) | 322 (10) | 184 (7) | 15 (3) |
| H(93) | 614 (5) | 429 (8) | 118 (5) | 11 (2) |

**Introduction.** The crystal structure analysis of the title compound was undertaken as part of a series of studies on coordination compounds with metal–sulfur bonds. The compound was prepared by adding cobaltous chloride to an aqueous solution of potassium *N*,*N*-dimethyldithiocarbamate; recrystallization from an acetone solution produced dark-green prismatic crystals.

A specimen of approximate dimensions 0·4 × 0·3 × 0·3 mm was mounted on a Rigaku automated four-circle diffractometer. Intensities of reflexions up to $2\theta < 55°$ were measured with Mo $K\alpha$ radiation monochromated by a graphite plate. Measurement was made in the $\omega$–$2\theta$ scan mode with a scanning speed of 2° min$^{-1}$ in $2\theta$, and 2532 independent reflexions with $|F_o|$ values greater than three times their standard deviations were obtained. The intensities were corrected for Lorentz and polarization factors, but not for absorption.

The structure was solved by the heavy-atom method, and refined by the block-diagonal least-squares method with the weighting scheme $w = 0{\cdot}3$ if $|F_o| < 25$, $w = 1$ if $25 \le |F_o| < 70$ and $w = (70/F_o)^2$ if $|F_o| \ge 70$. All the H positions were located on a difference Fourier map, and they were included in the refinement with isotropic temperature factors. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final *R* value was 0·050. The calculations were performed on a FACOM 230-75 computer of this Institute using the *UNICS*-3 program system (Sakurai & Kobayashi, 1979). The atomic coordinates are shown in Table 1.*

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with estimated standard deviations in parentheses*

| | | | | | |
|---|---|---|---|---|---|
| Co–S(1) | 2·273 (2) | Co–S(3) | 2·254 (2) | Co–S(5) | 2·271 (2) |
| Co–S(2) | 2·254 (2) | Co–S(4) | 2·269 (2) | Co–S(6) | 2·264 (2) |
| S(1)–C(1) | 1·709 (5) | S(3)–C(2) | 1·702 (5) | S(5)–C(3) | 1·703 (5) |
| S(2)–C(1) | 1·708 (5) | S(4)–C(2) | 1·703 (5) | S(6)–C(3) | 1·705 (5) |
| C(1)–N(1) | 1·315 (7) | C(2)–N(2) | 1·327 (6) | C(3)–N(3) | 1·319 (6) |
| N(1)–C(4) | 1·453 (8) | N(2)–C(6) | 1·452 (8) | N(3)–C(8) | 1·439 (8) |
| N(1)–C(5) | 1·459 (8) | N(2)–C(7) | 1·451 (8) | N(3)–C(9) | 1·448 (8) |
| S(1)–Co–S(2) | 76·5 (1) | S(3)–Co–S(4) | 76·4 (1) | S(5)–Co–S(6) | 76·2 (1) |
| S(1)–Co–S(3) | 95·4 (1) | S(3)–Co–S(5) | 94·5 (1) | S(5)–Co–S(1) | 95·6 (1) |
| S(1)–Co–S(4) | 166·8 (1) | S(3)–Co–S(6) | 167·2 (1) | S(5)–Co–S(2) | 167·2 (1) |
| S(2)–Co–S(3) | 96·2 (1) | S(4)–Co–S(5) | 95·4 (1) | S(6)–Co–S(1) | 94·3 (1) |
| S(2)–Co–S(4) | 94·0 (1) | S(4)–Co–S(6) | 95·6 (1) | S(6)–Co–S(2) | 94·2 (1) |
| Co–S(1)–C(1) | 86·2 (2) | Co–S(3)–C(2) | 86·9 (2) | Co–S(5)–C(3) | 86·5 (2) |
| Co–S(2)–C(1) | 86·9 (2) | Co–S(4)–C(2) | 86·4 (2) | Co–S(6)–C(3) | 86·7 (2) |
| S(1)–C(1)–S(2) | 110·2 (3) | S(3)–C(2)–S(4) | 110·4 (3) | S(5)–C(3)–S(6) | 110·5 (3) |
| S(1)–C(1)–N(1) | 125·5 (4) | S(3)–C(2)–N(2) | 124·6 (4) | S(5)–C(3)–N(3) | 125·0 (4) |
| S(2)–C(1)–N(1) | 124·3 (4) | S(4)–C(2)–N(2) | 125·1 (4) | S(6)–C(3)–N(3) | 124·6 (4) |
| C(1)–N(1)–C(4) | 121·4 (5) | C(2)–N(2)–C(6) | 122·5 (5) | C(3)–N(3)–C(8) | 121·6 (5) |
| C(1)–N(1)–C(5) | 121·1 (5) | C(2)–N(2)–C(7) | 120·7 (5) | C(3)–N(3)–C(9) | 121·2 (5) |
| C(4)–N(1)–C(5) | 117·5 (5) | C(6)–N(2)–C(7) | 116·8 (5) | C(8)–N(3)–C(9) | 117·3 (5) |

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35202 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

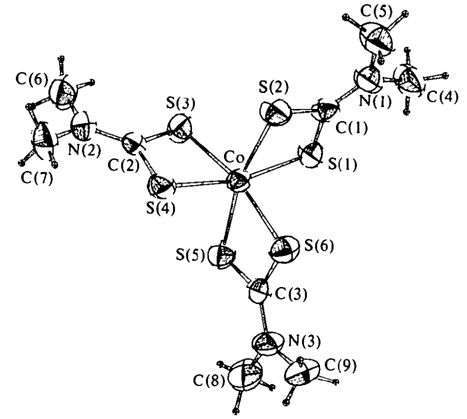

Fig. 1. A perspective view of the molecule along the approximate threefold axis, showing thermal ellipsoids at 50% probability. Hydrogen atoms are represented by spheres of 0·1 Å radius.

**Discussion.** Crystals of the title compound (I) consist of tris-chelate molecules of the complex [$Co(S_2CNMe_2)_3$]. Three dithiocarbamate ligands octahedrally coordinate to a Co atom through S atoms. The bond lengths and angles are listed in Table 2. A perspective view of the molecule is presented in Fig. 1. The molecule assumes 32 symmetry to a good approximation. The dimensions within the ligands are normal. The Co atom lies nearly in the plane of each ligand, the deviations being 0·18 (3), 0·02 (1) and 0·05 (1) Å for the three ligands respectively. The geometry of the $CoS_6$ part of the molecule is similar to those of [$Co(S_2CNH_2)_3$] (II) (Raston, White & Willis, 1975) and [$Co(S_2CNEt_2)_3$] (III) (Merlino, 1968), and is intermediate between (II) and (III). The mean Co—S distances are 2·275, 2·264 and 2·258 Å for (II), (I) and (III) respectively. The molecules of (III) lie on crystallographic twofold axes, and hence the two Co—S lengths in each ligand are equal. In (II), one Co—S bond is significantly shorter than the other, the mean difference being 0·020 Å, and these three short bonds are related by the approximate threefold axis of the molecule. The corresponding difference in (I) is 0·013 Å. In this case, however, the shorter bonds are not related by the approximate threefold axis, and, therefore, the present molecule by no means has strict trigonal symmetry. As Raston *et al.* (1975) have suggested, the difference between the two Co—S distances within a ligand might result from the difference of the sulfur environment, but a close correlation between Co—S distances and intermolecular S—H interactions as reported for (II) could not be found in the present case. Relatively short intermolecular contacts of 2·8 (1)–3·0 (1) Å are observed for S(2)···H(71), S(3)···H(43), S(4)···H(93) and S(5)···H(42), though the H positions have been less accurately determined.

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# The Structure of Tetraaqua(2,2,3,3-tetrafluorosuccinato)zinc(II)

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**Abstract.** [$Zn(C_4F_4O_4)(H_2O)_4$], $C_4H_8F_4O_8Zn$, monoclinic, $P2_1/c$, $a = 10{\cdot}799\ (2)$, $b = 9{\cdot}115\ (5)$, $c = 10{\cdot}995\ (3)$ Å, $\beta = 115{\cdot}53\ (2)°$, $V = 976{\cdot}60$ Å$^3$, $Z = 4$, $d_c = 2{\cdot}20$, $d_m = 2{\cdot}2$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 2·70 mm$^{-1}$, $R = 0{\cdot}034$ and $R_w = 0{\cdot}040$ for 1536 counter-collected reflections. The sixfold, approximately octahedral, coordination polyhedron around the $Zn^{2+}$ ion consists of four water molecules and two carboxylate O atoms (*trans* configuration) from two different tetrafluorosuccinate ions.

**Introduction.** The title compound was prepared from the reaction of zinc(II) carbonate and aqueous tetrafluorosuccinic acid. The compound is hygroscopic, very soluble in water, and single-crystal growth is often difficult. A solution of the compound in deuterium oxide ($D_2O$), which was originally prepared for NMR studies, yielded suitable crystals after slow evaporation over a period of two months. A crystal with approximate dimensions 0·15 × 0·15 × 0·20 mm was placed in a thin-walled capillary tube and used in the X-ray

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