Acta Cryst. (1978). B**34**, 2859–2860

Bis(2-amino-1,1-dimethylethanethiolato-*N*,*S*)zinc

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(*Received* 7 *March* 1978; *accepted* 12 *April* 1978)

Abstract. $Zn[SC(CH_3)_2CH_2NH_2]_2$, orthorhombic, $C222_1$, *a* = 5·5755 (7), *b* = 10·585 (1), *c* = 21·741 (3) Å, *Z* = 4, D_o = 1·41 (1), D_c = 1·417 g cm^{-3}. The structure consists of discrete $Zn[SC(CH_3)_2CH_2NH_2]_2$ molecules with point symmetry 2. Each Zn atom is ligated by two N and two S atoms which yield a distorted tetrahedral coordination geometry. The Zn—S and Zn—N bond lengths are 2·297 (4) and 2·06 (1) Å, respectively, while *L*—Zn—*L*′ angles within the coordination polyhedron range from 91·5 (3) to 137·1 (2)°.

Introduction. Colorless, slightly elongated six-sided plates of the title complex were prepared as described previously (Mastropaolo, Thich, Potenza & Schugar, 1977). A single crystal of dimensions 0·68 × 0·39 × 0·075 mm, mounted on a glass fiber, was used. Weissenberg photographs showed systematic absences for *hkl*, $h + k = 2n + 1$ and 00*l*, $l = 2n + 1$ along with *mmm* reciprocal-lattice symmetry, fixing the space group as $C222_1$. Assuming four molecules per unit cell, the observed (flotation) and calculated densities agreed well. Data were collected at 20 ± 2°C with a CAD-3 automated diffractometer (θ–2θ scan) using graphite-monochromated Mo *Kα* radiation (λ = 0·71069 Å). Of the 934 intensities recorded ($4 < 2\theta < 50°$), 562 with $F^2 \geq 3\sigma(F^2)$ were considered observed, corrected for Lp and absorption effects (μ = 22·3 cm^{-1} for Mo *Kα* radiation), and used in the refinement.

Inspection of the data showed that the title complex and the recently characterized Co^{II} analog (Mastropaolo, Thich, Potenza & Schugar, 1977) were isostructural. Refinement of the non-hydrogen atoms was initiated using atomic coordinates from the Co^{II} complex. Neutral atom scattering factors and anomalous dispersion corrections for Zn and S were obtained from *International Tables for X-ray Crystallography* (1974). At a later stage, H atoms were included in the refinement with fixed isotropic temperature factors equal to those of the heavy atoms to which they are bonded; trial coordinates for the CH_2 and NH_2 protons were calculated, while those for the methyl groups were obtained from the Co^{II} complex. Refinement was based on *F* and a weighting scheme $[w = 1/\sigma^2(F)]$ was chosen by an analysis of variance (Ricci, Eggers & Bernal, 1972) to make $|\Delta F|/\sigma$ independent of $|F_o|$. This led to the following assignments: $\sigma(F_o) = 3{\cdot}52 - 0{\cdot}031|F_o|$, $|F_o| < 43{\cdot}7$; $\sigma(F_o) = 1{\cdot}07 + 0{\cdot}025|F_o|$, $|F_o| > 43{\cdot}7$. Full-matrix least-squares refinement of all non-hydrogen atomic coordinates and anisotropic thermal parameters gave final values of $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}063$ and R_{wF}

Table 1. *Final atomic coordinates*

Estimated standard deviations, obtained from the least-squares refinement, are given in parentheses.

	x	*y*	*z*
Zn	0	0·1878 (2)	¼
S	0·2722 (5)	0·1084 (3)	0·1809 (2)
N	0·182 (5)	0·2812 (9)	0·3190 (5)
C(1)	0·038 (2)	0·274 (1)	0·3764 (6)
C(2)	−0·248 (3)	0·157 (2)	0·4440 (7)
C(3)	0·097 (3)	0·041 (1)	0·3968 (7)
C(4)	−0·078 (2)	0·146 (1)	0·3871 (6)
H(1)	0·235	0·364	0·314
H(2)	0·337	0·238	0·327
H(3)	−0·053	0·342	0·375
H(4)	0·128	0·284	0·411
H(5)	−0·348	0·080	0·453
H(6)	−0·355	0·233	0·427
H(7)	−0·156	0·172	0·471
H(8)	−0·005	−0·040	0·400
H(9)	0·175	0·058	0·473
H(10)	0·198	0·040	0·362

Table 2. *Bond distances* (Å) *and angles* (°)

Zn–S	2·297 (4)	Zn–S–C(4)	93·0 (4)
Zn–N	2·06 (1)	Zn–N–C(1)	108·7 (8)
N–C(1)	1·48 (2)	S–C(4)–C(2)	106·5 (8)
C(1)–C(4)	1·52 (2)	S–C(4)–C(3)	109·4 (9)
C(2)–C(4)	1·56 (2)	S–C(4)–C(1)	108·4 (9)
C(3)–C(4)	1·49 (2)	C(2)–C(4)–C(3)	110 (1)
S–C(4)	1·88 (1)	C(2)–C(4)–C(1)	109 (1)
N–Zn–N′	122·8 (6)	C(3)–C(4)–C(1)	114 (1)
S–Zn–S′	137·1 (2)	C(4)–C(1)–N	114 (1)
S–Zn–N′	108·9 (3)	S′–Zn–S/N′–Zn–N	79·5 (3)
S–Zn–N	91·5 (3)	S′–Zn–N/S–Zn–N′	63·7 (4)
		S′–Zn–N′/S–Zn–N	73·0 (5)

Table 3. *Structural parameters of distorted tetrahedral* ZnS_2N_2 *chromophores*

	$Zn[SC(CH_3)_2CH_2NH_2]_2$	Zn^{II} (dithizonate)$_2$	$[Zn_2Cl_2L_2]_2.2H_2O$
Zn–S (Å)	2·297 (4)	2·220 (9); 2·288 (9)	2·286 (4)
Zn–N (Å)	2·06 (1)	2·11 (2); 2·03 (3)	2·103 (11)
S–Zn–S′ (°)	137·1 (2)	130·9 (4)	148·1 (2)
N–Zn–N′ (°)	122·8 (6)	110 (1)	87·0 (4)
S–Zn–S′/N–Zn–N′ (°)	79·5 (3)	85	75·2 (3)

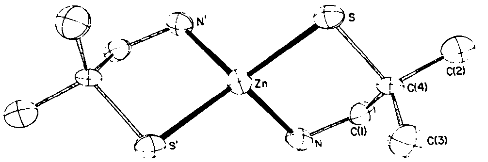

Fig. 1. *ORTEP* (Johnson, 1965) view of $Zn[SC(CH_3)_2CH_2NH_2]_2$ showing the atom-numbering scheme.

$= [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0{\cdot}081$.* For the final cycle, all parameter changes were $\leq 0{\cdot}2\sigma$ where σ is the e.s.d. obtained from the inverse matrix. A final difference map showed a general background of ±0·5 e Å^{-3} and revealed no significant features. Atomic parameters are given in Table 1 while a view of the structure, showing the atom-numbering scheme, is given in Fig. 1. Bond lengths and angles are presented in Table 2.

Discussion. We have been interested in characterizing model M^{II} mercaptide (M = Cu, Co, and Zn) complexes to better understand the features of analogous chromophores present in various proteins. The aliphatic ligand $^-SC(CH_3)_2CH_2NH_2$ was chosen because of its uncomplicated UV spectra and its potentially important structural similarity to the chelating drug penicillamine $[HSC(CH_3)_2CH(NH_3^+)CO_2^-]$. Reported elsewhere are structural and electronic-spectral studies of $Co[SC(CH_3)_2CH_2NH_2]_2$ (Mastropaolo *et al.*, 1977) and of an unusual mixed-valence cluster complex of composition $\{Cu_8^+Cu_6^{2+}[SC(CH_3)_2CH_2NH_2]_{12}Cl\}.\sim 3{\cdot}5SO_4.\sim 19H_2O$ (Schugar, Ou, Thich, Potenza, Lalancette & Furey, 1976). In addition to being a useful d^{10} electronic-spectral reference complex, the title complex represents an ideal host lattice in which to study the EPR and charge-transfer features of the Co^{II} mercaptide chromophore. To aid such studies, the present structural analysis was undertaken.

The structure consists of discrete $Zn[SC(CH_3)_2CH_2NH_2]_2$ molecules (1) with point symmetry 2. Each Zn atom is ligated by two N and two S atoms which yield a distorted tetrahedral coordination geometry. As expected, structural parameters for (1) are nearly identical with those of the Co^{II} analog (Mastropaolo *et al.*, 1977). They may be compared with those reported for zinc(II) dithizonate [(2) Mawby & Irving, 1972] and the tetranuclear zinc cluster complex $[Zn_2Cl_2L_2]_2.2H_2O$ [(3) L = $^-SCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2S^-$; Hu, Barton & Lippard, 1973], both of which also contain distorted tetrahedral ZnS_2N_2 chromophores and five-membered chelate rings with S and N as ligating atoms. As shown in Table 3, the Zn–S and Zn–N distances in (1) compare favorably with those reported for (2) and (3) except for the short Zn–S distance [2·220 (9) Å] in (2). Distortion of the ZnS_2N_2 units from tetrahedral symmetry may be gauged by the S–Zn–S′ and N–Zn–N′ angles as well as the dihedral angle S–Zn–S′/N–Zn–N′ Using either or both of these as criteria, the ZnS_2N_2 units in (1) are less distorted than those in (3) and more distorted than those in (2). Compared with the tertiary mercaptide $^-SC(CH_3)_2CH_2NH_2$ ligand in (1), the tetradentate ligand L in (3) consists of two mercaptoamine fragments linked by an ethylene bridge. The hindered mercaptide group in (1) apparently causes less structural distortion than do the steric restraints associated with the ethylene bridge in (3).

We thank the National Institutes of Health (Grant AM-16412) for financial support and the Center for Computer and Information Services, Rutgers University, for providing computer time.

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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 33544 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.