Acta Cryst. (1980). B**36**, 2143–2145

The Structure of Aqua[3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazonato)]zinc(II)

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(*Received* 5 *November* 1979; *accepted* 21 *April* 1980)

Abstract. $[Zn(C_8H_{14}N_6OS_2)(H_2O)]$, $C_8H_{16}N_6O_2S_2Zn$, triclinic, $P\bar{1}$, a = 8·769 (7), b = 9·388 (7), c = 8·866 (7) Å, α = 100·87 (5), β = 94·47 (5), γ = 83·22 (5)° [this is the reduced cell; Donnay's conventional reduced cell may be obtained by applying the transformation: $(001/0\bar{1}0/100)$], Z = 2, D_m = 1·61 (3), D_c = 1·64 Mg m^{-3}. The Zn^{2+} ion is coordinated to one $C_8H_{14}N_6OS_2^{2-}$ ligand (at two S and two N atoms) and O of one water molecule in an irregular arrangement that lies between ideally trigonal biprismatic and square pyramidal. Hydrogen bonding is very weak, as it is in other metal complexes of this ligand; only two of the four amino H atoms form hydrogen bonds. (The final R_w is 0·066 for 3665 data.)

Introduction. Crystals of aqua[3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazonato)]zinc(II) (ZnKTS) were obtained as yellow needles by slow evaporation of a 50:50 water:ethanol solution of a sample supplied by Dr H. G. Petering (Crim, Buskirk & Petering, 1967). The crystal system was established as triclinic by photographic methods. Unit-cell dimensions and intensity data were measured on a Supper automatic two-circle diffractometer using graphite-monochromated Mo $K\alpha$ X-radiation (λ = 0·71069 Å). The unit-cell dimensions were calculated from data obtained from the zero levels of three crystals mounted about the three crystallographic axes. The intensity data were collected with the $\theta/2\theta$ scan technique using one crystal mounted about $\mathbf{a}^*$ (0·050 × 0·125 × 0·025 mm) for layers h = 0–4, and another mounted about $\mathbf{c}^*$ (0·075 × 0·075 × 0·300 mm) for layers l = 0–6. Absorption corrections were not applied (μ = 2·01 mm^{-1}). The intensities of 5873 reflections were scaled and averaged (Rae, 1965) to give data for 3962 unique reflections of which 297 had a net intensity less than zero. Statistical tests showed the space group to be $P\bar{1}$.

The structure was solved by using Patterson and Fourier methods, and refined by full-matrix least-squares calculations minimizing $\sum w(\Delta F)^2$ where $w = \sigma^{-2}(F_o)$. The values for $\sigma(F_o)$ were obtained from a combination of counting statistics and mean deviations for those reflections measured more than once, and counting statistics alone for the remainder. Although the positions of some H atoms were not clearly defined in difference maps, they were all placed at reasonable positions on regions of positive electron density. Scattering factors for Zn^{2+}, S, O, N, C, and H were taken from *International Tables for X-ray Crystallography* (1974); the curve used for H was that calculated by Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections were used for Zn^{2+} (f' = 0·222, f'' = 1·431) and S (f' = 0·110, f'' = 0·124). The refined parameters included a scale factor, positional and anisotropic temperature factor coefficients for non-hydrogen atoms and positional and isotropic thermal parameters for H(1), H(2), H(3), H(4), and H(5). The final R value was 0·085 and R_w was 0·066 for the 3665 non-zero reflections included in the refinement. There are regions of positive electron density of 1·0 to 1·3 e Å^{-3} in the final difference map near O, C(5), and C(8). These probably arise from some disorder in the side chain, as does the abnormally long C(5)—C(6) bond length of 1·615 Å. The thermal parameters of the side-chain atoms are much larger than those of the other atoms in the structure. Final

Table 1. *Atomic coordinates for the non-hydrogen atoms*

	x	y	z
Zn	0·1967 (1)	0·3518 (1)	0·3556 (1)
S(1)	0·1357 (1)	0·6059 (1)	0·3772 (2)
S(2)	0·0395 (1)	0·1973 (1)	0·1869 (2)
C(1)	0·2703 (4)	0·6539 (4)	0·5267 (5)
C(2)	0·3284 (5)	0·3389 (4)	0·6705 (6)
C(3)	0·2784 (5)	0·1939 (4)	0·6099 (6)
C(4)	0·0755 (4)	0·0516 (4)	0·2836 (5)
C(5)	0·3660 (6)	0·3835 (5)	0·8433 (7)
C(6)	0·2108 (7)	0·4563 (6)	0·9263 (7)
C(7)	0·5747 (6)	0·2047 (7)	0·8624 (8)
C(8)	0·6423 (9)	0·1184 (13)	0·9775 (14)
N(1)	0·3034 (4)	0·7932 (3)	0·5540 (5)
N(2)	0·3423 (4)	0·5690 (3)	0·6194 (4)
N(3)	0·3108 (4)	0·4267 (3)	0·5746 (4)
N(4)	0·2124 (4)	0·1753 (3)	0·4770 (4)
N(5)	0·1561 (4)	0·0460 (3)	0·4158 (5)
N(6)	0·0122 (5)	−0·0717 (4)	0·2190 (5)
O	0·4186 (4)	0·2689 (4)	0·9155 (4)
O(w)	0·4010 (3)	0·3058 (3)	0·2405 (4)

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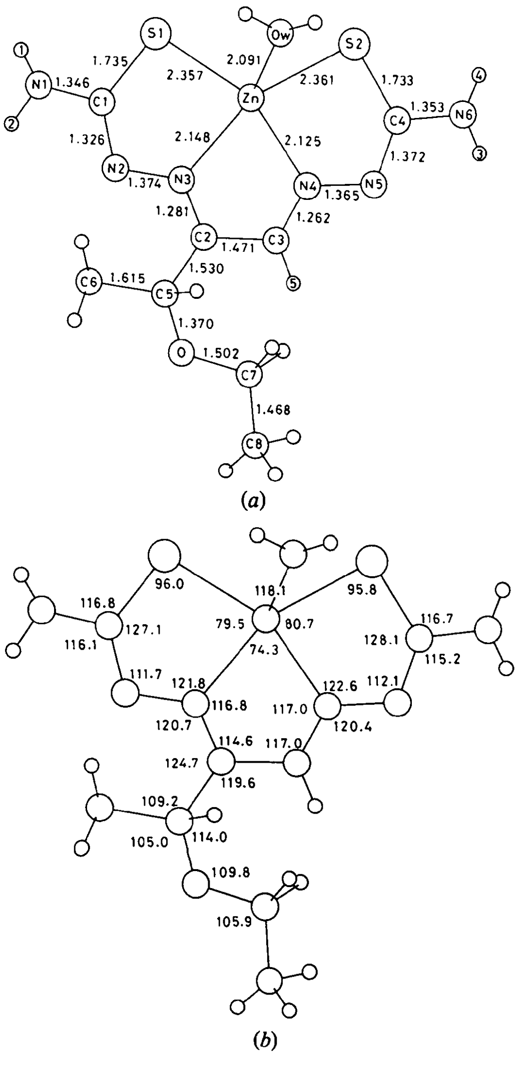
0567-7408/80/092143-03$01.00

atomic coordinates are listed in Table 1.* Atom labelling, and bond lengths and angles are shown in Fig. 1. The final refinement cycles were calculated with *ICRFMLS* (Carrell, 1975).

Discussion. The chemistry of metal complexes of 3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazone) (H_2KTS) has been of interest since it was shown that the copper(II) complex is an active anti-tumor agent and that the zinc(II) complex also is active (Crim, Buskirk & Petering, 1967). The structures of [3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazonato)]-copper(II) (CuKTS) (Taylor, Glusker, Gabe & Minkin, 1974) and H_2KTS (Gabe, Taylor, Glusker, Minkin & Patterson, 1969) have been determined. This structure analysis is part of a continuing investigation of structure–activity relationships in metal complexes of KTS and related ligands.

The KTS^{2-} ligand is bound to the Zn^{2+} ion by two S and two N atoms in a roughly planar configuration. A fifth coordination site of the Zn^{2+} ion is occupied by a water molecule. The arrangement of ligand atoms around Zn is irregular. Because the bulk of the KTS^{2-} ligand lies in one plane there is a tendency to describe the arrangement as distorted square-pyramidal, but if the five ligand atoms are examined in isolation it appears that the arrangement could equally well be described as trigonal bipyramidal (Figs. 2 and 3). The observed stereochemistry lies somewhere between the two ideal configurations and is a compromise resulting from competing energetic and geometrical factors such as the retention of resonance energy by the planar KTS^{2-} ligand, the bite of the ligand, and the tendency of Zn to be surrounded by a spherically symmetrical arrangement of electrostatic charge. Fig. 2 illustrates that while the majority of the atoms of the chelate rings



(*a*)

(*b*)

Fig. 1. (*a*) Interatomic distances (Å). Standard deviations are: Zn–S, 0·001; Zn–N(O), 0·004; C–S, 0·004; C–C(N), 0·006 Å. (*b*) Interbond angles. Standard deviations: 0·2°. Angles at Zn subtended by O(*w*) and S(1) = 104·7; S(2) = 100·0; N(3) = 93·7; N(4) = 101·2°.

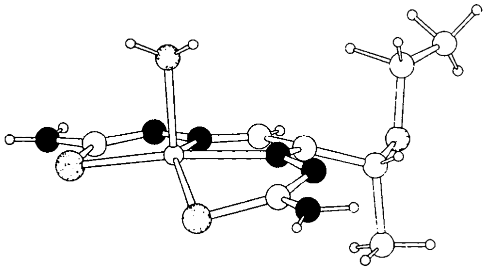


Fig. 2. A perspective view of the molecule showing deviations from planarity in the ligand.

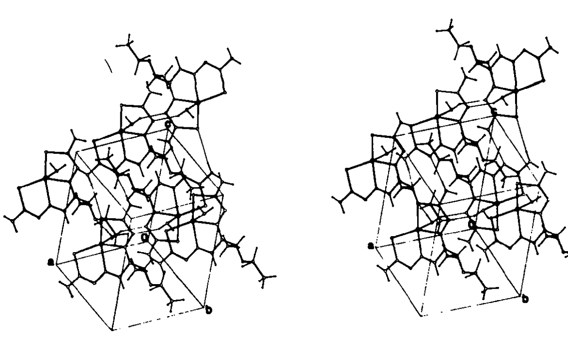


Fig. 3. Stereoscopic diagram of the structure drawn by *VIEW* (Carrell, 1976). Circles are at arbitrary sizes. Hydrogen bonds are shown as fine lines similar to the unit-cell outline.

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* Lists of structure factors, H atom parameters, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35297 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

are coplanar one thioamide group is out of this plane with S(1) in a position that tends to balance the coordination sphere.

The bite of the ligand leaves the Zn^{2+} ion in an exposed position. The smaller Cu^{2+} ion for which the average Cu—N bond length in CuKTS is 1·97 Å is more completely enclosed by the ligand than is the Zn^{2+} ion in ZnKTS where the Zn—N distances average 2·136 Å. This, along with inherently weaker Zn—ligand bonds, is a reason why the stability of ZnKTS [log K = 6·0 at pH = 7·4, Petering (1974)] is lower than that of CuKTS [log K = 18·6 at pH = 7·4, Petering (1974)].

The interatomic distances in the ligand are similar to those in related complexes. The weaker Zn—ligand binding leads to smaller perturbations in the KTS^{2-} ligand bonds than is observed in Cu complexes. In particular, the C—S bonds retain more of their double-bond character in ZnKTS than they do in CuKTS (1·746 Å) or in [benzil bis(thiosemicarbazonato)]copper(II) (1·755 Å) (Bushnell & Tsang, 1979).

The molecules are linked together in sheets within the plane of the KTS^{2-} ligands by a few weak hydrogen bonds in a pattern that is similar to that found in CuKTS (Fig. 3). Not all the amino H atoms form hydrogen bonds. One, H(1) of the amino group that is proximal to the side chain, is hydrogen bonded to N(5) of another molecule at a distance of 2·98 Å (*cf.* 2·96 Å in CuKTS). This is coupled with a N—H···S intermolecular interaction of 3·59 Å (Fig. 3) compared to a similar one of 3·70 Å in CuKTS. There appears to be a growing body of evidence that indicates that the hydrogen-bonding potential of the amino protons in these complexes is very low. This is consistent with the observation that a number of these complexes are soluble in weakly polar solvents. Hydrogen bonds of the water molecules link molecules of the complex related by a center of symmetry in pairs [O(w)···N(2)] and within sheets [O(w)···O].

PEB thanks the Commonwealth of Australia for a Postgraduate Award. This work was supported by a research grant from the Flinders University of South Australia and was completed at The Institute for Cancer Research, Fox Chase, Philadelphia, with support from grants BC-242 from the American Cancer Society, and CA-22780 and CA-06927 from the National Institutes of Health.

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Acta Cryst. (1980). B**36**, 2145–2147

The Structure of Disodium *catena*-Bis(μ-oxalato)-cuprate(II) Dihydrate

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(*Received* 19 *November* 1979; *accepted* 21 *April* 1980)

Abstract. $\{Na_2[Cu(C_2O_4)_2].2H_2O\}_n$, $(C_4CuO_8^{2-})_n.2nNa^+.2nH_2O$, $M_r = 321{\cdot}6$; triclinic, $P\bar{1}$, $a = 3{\cdot}583$ (7), $b = 9{\cdot}649$ (6), $c = 7{\cdot}549$ (6) Å, $\alpha = 109{\cdot}07$ (1), $\beta = 76{\cdot}38$ (1), $\gamma = 103{\cdot}32$ (1)°, $V = 236$ Å^3; $D_m = 2{\cdot}25$, $Z = 1$, $D_c = 2{\cdot}26$ Mg m^{-3}. The final R value for 604 independent data is 0·052. The compound was produced as an unknown product during oxygenation reactions with cupric complexes. It is recorded for comparison with its ammonium and potassium analogues from which it differs in having the water molecules absent from the coordination sphere. The distorted octahedral geometry about each Cu atom is completed by the formation of oxalate bridges and by the sharing of individual oxygen donors.

Introduction. During studies of the interaction of copper(II) complexes with molecular oxygen it was noticed that after reduction with ascorbic acid a small

0567-7408/80/092145-03$01.00