

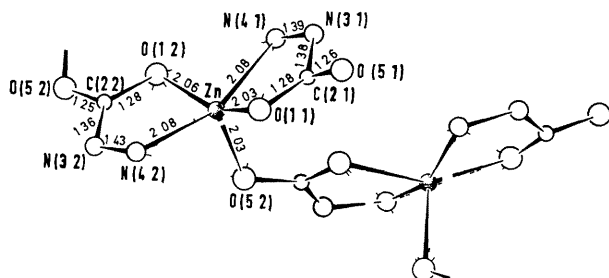
Pentaco-ordination in Bis(hydrazinecarboxylato-*N'O*)-zinc

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Summary A five-co-ordinate chelate complex has been found in the crystal structure of bis(hydrazinecarboxylato-*N'O*)-zinc, with the basal atoms in *trans*-positions and the sixth apical position completely free

THE importance of the structures of hydrazinecarboxylato-complexes¹ lies mainly in their similarity to complexes of α -amino-acids². The only known pentaco-ordinated complex of an amino-acid is *cis*-Cu(L-Ala)₂³ where O- and N-donor atoms of the same ligand are in *cis* positions at the basal corners of a square pyramid



FIGURE

The crystal structure of bis(hydrazinecarboxylato-*N'O*)-zinc, $Zn(N'H_2-NH-CO_2)_2$, has been determined by X-ray methods. The crystals are monoclinic and the unit cell parameters, obtained photographically by Cu- K_{α} radiation, are $a = 6.87(1)$, $b = 5.08(1)$, $c = 9.10(1)$ Å, $\beta = 111.2(1)^\circ$, $U = 296.5$ Å³, $M = 215.48$, $Z = 2$, $D_m = 2.38$, $D_c = 2.41$ g cm⁻³, space group $Pc(C_2^2, No. 7)$ (from systematic absences

and structure determination). Intensities of 665 independent reflections (out of 677 possible) have been measured photographically on integrated Weissenberg photographs, by rotation around [010] and [001]. The structure has been solved by Patterson and Fourier methods and refined by differential syntheses (final $R = 7.9\%$). Further refinement is in progress. In other compounds⁴ with bivalent transition metals studied in this laboratory, the hydrazinecarboxylic acid forms octahedral chelate complexes, while in the present compound the co-ordination around the metal is pyramidal and not octahedral (Figure). The same situation is probably present in the copper complex which from the comparison of the powder photographs seems isostructural with the zinc compound. The N(2) and O(1) atoms belonging to two ligand molecules, in the *trans* position, are at the four corners of the pyramid base, whereas the apex is occupied by the O(5) of another complex. The zinc atom lies $+0.47$ Å above the mean plane passing through the atoms of the pyramid base. The atoms at the basal corners deviate significantly below or above the mean plane: N(4 1) $+0.34$, N(4 2) $+0.42$, O(1 1) -0.24 , O(1 2) -0.24 Å.

The sixth position of the co-ordination polyhedron is completely free, while in *cis*-Cu(L-Ala)₂ it was reported³ to be occupied by an H(methyl). There are two chelate rings which are not crystallographically equivalent, the distances in them, however, are very similar. All the important distances are reported in the Figure. Different complexes are held together by a Zn-O(5) bond to form chains along [001]. No hydrogen bonding has been found between different chains.

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¹ A. Ferrari, A. Braibanti, G. Bighardi, and A. M. Lanfredi, *Z. Krist.* 1965, **122**, 259; A. Braibanti, G. Bighardi, A. M. Manotti Lanfredi, and A. Tiripicchio, *Nature*, 1966, **211**, 1174; A. Braibanti, A. M. Manotti Lanfredi, and A. Tiripicchio, *Z. Krist.* 1967, **124**, 335; A. Braibanti, A. Tiripicchio, A. M. Manotti Lanfredi, and M. Camellini, *Acta Cryst.*, 1967, **23**, 248; A. Braibanti, A. Tiripicchio, A. M. Manotti Lanfredi, and F. Bigoli, *Z. Krist.*, 1968, **126**, 307; A. Braibanti, A. M. Manotti Lanfredi, A. Tiripicchio, and F. Bigoli, *Acta Cryst.*, 1969, **B25**, 100; A. Braibanti, A. M. Manotti Lanfredi, A. Tiripicchio, and F. Bigoli, *Acta Cryst.*, in the press.

² H. C. Freeman, *Adv. Protein Chem.*, 1967, **22**, 257.

³ R. D. Gillard, R. Mason, N. C. Payne, and G. B. Robertson, *Chem. Comm.*, 1966, 155.