Crystal Structure of Diaquobisglycollatozinc(II)

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EXCEPT for the recent structural study of bisglycollatocopper(II) and other similar copper(II) carboxylate complexes[1,2] very little is known of the structure of glycollato-complexes with other bivalent ions of the first transition series. I.r. studies of bisglycollatocobalt(II) and other ion-series ions[3] suggest that a low symmetry may be present around the metal such as *cis*-square-planar or tetrahedral and that the glycollate ligand co-ordinates through both the hydroxy- and carboxy-oxygens. Visible spectra of the anhydrous glycollates of Mn^{II}, Co^{II}, Ni^{II}, and Cu^{II},[4] the diaquobisglycollato-complexes of Mn^{II}, Co^{II}, and Ni^{II} and of single crystals of diaquobisglycollatozinc(II) doped with Mn^{II}, Fe^{II}, Co^{II}, and Ni^{II} [5] indicate that the ion possesses an approximately octahedral environment, but give little information on the nature of the bidentate ligand or water co-ordination. To clarify these issues and to establish the exact site symmetry of the metal ion for further possible spectral studies, an investigation of the crystal structure of these complexes was undertaken. Preliminary optical studies indicate that crystals of Mn^{II}, Co^{II}, and Zn^{II} bisglycollato-dihydrates are isomorphous. Because of its relatively low linear absorption coefficient, a zinc glycollate dihydrate crystal was chosen for a three-dimensional *X*-ray diffraction analysis.

Crystals of the zinc complex are monoclinic, space group $P2_1/c$ (C_{2h}^5) with $a = 11{\cdot}425 \pm 0{\cdot}002$, $b = 5{\cdot}856 \pm 0{\cdot}001$, $c = 12{\cdot}505 \pm 0{\cdot}002$ Å, $\beta = 91{\cdot}028° \pm 0{\cdot}007°$, and $Z = 4$. Intensities of 1513 independent non-zero reflections were collected manually with a Picker diffractometer and Cu-K_α radiation. The structure was solved by the symbolic addition method[6] and refined by full-matrix least-squares. Water hydrogens were not found but hydrogens in reasonable positions on the glycollate rings were located by difference synthesis and included in the final least-squares cycle. *R* (assuming anisotropic temperature factors for all atoms except the hydrogens) is 0·059. Standard deviations in interatomic distances varied from 0·005 to 0·008 Å for bonds not involving the hydrogens.

In contrast to the *trans*-chelate arrangement found in copper glycollate and other related α-hydroxy-carboxylate complexes,[2] the zinc complex has a distorted *cis*-configuration with Zn–H_2O contacts of unequal length (2·09 and 2·05 Å). Moreover, the Zn–O hydroxyl and carboxyl bond lengths are unequal for the two chelate rings, leading to further asymmetry around the zinc ion (Figure, a). The bond lengths and angles within the glycollate rings themselves are nearly identical to those found in copper glycollate[2] and in anhydrous[7] and monohydrated lithium glycollate.[8] The distorted *cis*-configuration with its unequal Zn–O bonds appears to be stabilized by an

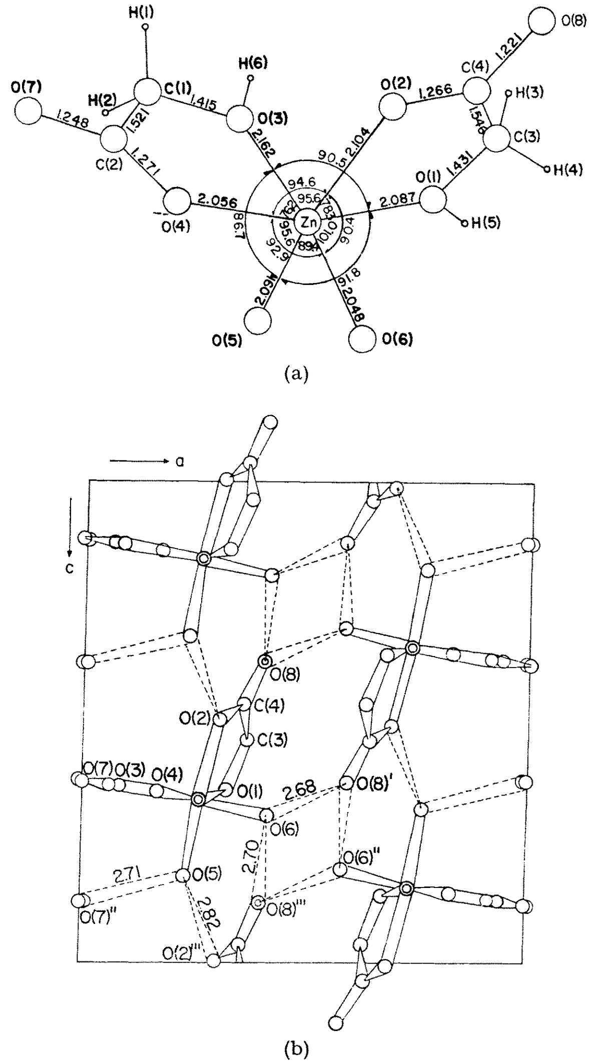

FIGURE. (a) *The geometry of the zinc*(II) *glycollate dihydrate molecules showing* cis-*configuration. The numbering of the atoms corresponds to that of* (b).

(b) *Molecular arrangement projected down* b-*axis showing layers of molecules parallel to the* c-*axis and held together by hydrogen bonding of each water molecule to two carboxyl oxygens. The single, double, and triple primes after the oxygen numbers designate the inversion, screw axis, and* c-*glide transformations of the unprimed positions. A single turn of the continuous spiral of hydrogen bonds begins at* O(8)''' (*small circle*) *and ends at the* O(8)''' *above* (*large circle*).

intermolecular network of hydrogen bonds which affects each ligand differently. As shown in the Figure, b, one glycollate is involved in a relatively simple hydrogen-bonding system with a single water across the unit-cell boundary, while the other glycollate is hydrogen bonded to both waters.

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