Inorganica Chimica Acta, 18 (1976) L13 - L14

The Crystal and Molecular Structure of Iron(III) Compounds of the Sexadentate Ligand N,N′-Ethylenebis-(*o*-hydroxyphenylglycine)

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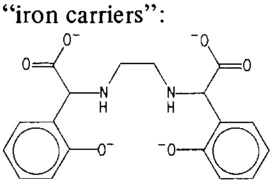
Received January 28, 1976

We have recently taken an interest in the bonding to iron(III) of the tetra-anionic ligand I (abbreviated to ehpg^{4-}) because the stability constant of this compound[1] is of the same order of magnitude as that observed for transferrin[2] and the other biological "iron carriers":



I

In a preliminary study, various salts of the anion [Fe(ehpg)]$^-$ were isolated for X-ray structural studies using the commercially available ligand (ehpgH$_4$, obtained from Fluka AG). Powder patterns show that these compounds fall into two distinct isomorphous series; the first (labelled α) has been characterised for Li$^+$, Na$^+$, K$^+$, Ca^{2+} and Ba^{2+}, the second (labelled β) has so far only been found for Mg^{2+} and for Na$^+$ (in the latter case crystallising from the reaction mixture after the α-form). Clearly, since both Li$^+$ and Ba^{2+} are able to fit into essentially the same crystalline structure (the α-form), this must be defined by the [Fe(ehpg)]$^-$ ion and involve cation disorder sites.

For the X-ray analyses we chose the Na$^+$ salt (α-form, A) and the Mg^{2+} salt (β-form, B). The former crystallises as thin red rectangular plates, the latter as irregular polyhedra.

Crystal Data

A. [$C_{18}H_{16}N_2O_6Fe$]Na·4H$_2$O; M = 507.2. Orthorhombic, a = 37.66(2), b = 7.12(1), c = 24.44(1) Å, U = 6555(6) Å^3. D$_m$(flotation) = 1.53 gcm^{-3}, Z = 12, D$_c$ = 1.542 gcm^{-3}. Space group *Pbcn* (D_{2h}^{14}, No. 60) from systematic absences. μ(Mo-K$_\alpha$) = 7.72 cm^{-1}; mean crystal dimensions 0.32 × 0.28 × 0.03 mm.

B. [$C_{18}H_{16}N_2O_6Fe$]$_2$Mg·9H$_2$O; M = 1010.8. Triclinic, a = 17.20(1), b = 21.52(1), c = 12.388(9) Å, α = 92.433(5), β = 91.865(5), γ = 110.768(4)°, U = 4277(5) Å^3. D$_m$(flotation) = 1.54 gcm^{-3}, Z = 4, D$_c$ = 1.570. Space group $I_{\bar{1}}$ (a non-standard setting of $P_{\bar{1}}$, C_i^1, No. 2), proved by the analysis; μ(Mo-K$_\alpha$) = 7.75 cm^{-1}, estimated minimum and maximum transmission coefficients, respectively, 0.70 and 0.92.

Solution of the Structure

X-ray intensity data were measured on a Stoe Stadi-2 diffractometer. Lorentz and polarisation corrections were applied for both structures, and absorption corrections for A only. The structures were solved by conventional Patterson and Fourier methods, and refined by block diagonal least-squares as follows: A) R = 0.103 with anisotropic thermal parameters for the two iron atoms and disorder of sodium ions and water molecules over several sites; B) R = 0.058 with anisotropic thermal parameters for all metal atoms.

The figure shows the crystal packing of A viewed down the b-axis (Fig. 1). The asymmetric unit contains one [Fe(*meso*-ehpg)]$^-$ ion in a general position, with the expected all-*cis* configuration of the ligand, and also a [Fe(*rac*-ehpg)]$^-$ ion with *trans* carboxylate groups lying across a crystallographic 2-fold axis. Mean bond lengths within the coordination polyhedra are Fe–N 2.16(1), Fe–O (phenolic 1.92(1) and Fe–O (carboxylate) 2.05(1) Å, with only minor differences between bond lengths of the same type.

The crystal lattice contains distinct hydrophilic channels – bounded by the carboxylate fragments at, for example, (0,y,0.5) – which contain disordered water molecules and Na$^+$ ions (three sites): the former in positions suitable for hydrogen bonding and the latter in sites allowing coordination by oxygen atoms. The remainder of the structure comprises an extended, essentially hydrophobic region bounded by phenyl groups but containing localised small hydrophilic pockets occupied by full-population water molecules which are hydrogen bonded to NH groups of the [Fe(*meso*-ehpg)]$^-$ ion.

Molecular models indicate two possible configurations of similar energy for the [Fe(*rac*-ehpg)]$^-$ ion involving either *trans* carboxylates or *trans* phenoxyls.

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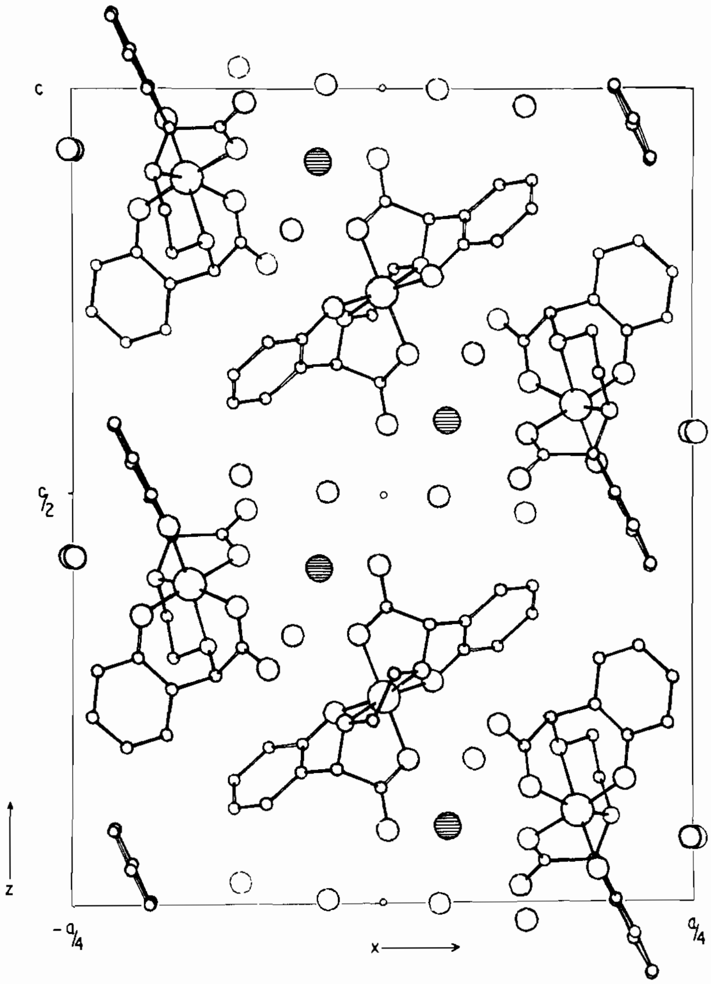

Figure 1. The crystal packing in Na[Fe(ehpg)] $\cdot 4H_2O$ (structure A), showing half the unit cell viewed down the *b* axis. The empty circles represent Fe, O, N and C atoms in descending order of size. The shaded circles represent three sites occupied by Na^+, all of which have closely similar x and z coordinates. Only the major sites occupied by waters of crystallisation are shown.

The observation of the former in both this structure and in B (see below) may well be a result of more favourable crystal-packing forces. It is particularly noticeable in this structure that the hydrophilic (carboxylate) fragments are separated by an essentially hydrophobic plane.

Structure B contains two [Fe(*rac*-ehpg)]$^-$ ions in general positions, both ions having the same configuration as that observed in the corresponding molecular anion in A (mean bond lengths Fe–N 2.172(8), Fe–O (phenolic) 1.907(7) and Fe–O (carboxylate) 2.041(7) Å.) Once again the crystal structure contains distinct hydrophilic and hydrophobic regions, with an ordered octahedral hexaaquamagnesium(II) cation (Mg–O, 2.051 → 2.158 Å, mean 2.085 Å, average esd. 0.009 Å), and waters of crystallisation which are hydrogen-bonded at three other sites in the crystal lattice.

The preparation of the magnesium salt provides a method of obtaining the pure *rac* form of the ligand. Such crystals (especially the α-form) may offer useful models for the study of passive ion transport through channels which may, in some of their aspects, resemble those within cell membranes.

Acknowledgment

We thank S.R.C. for a grant for the diffractometer, a studentship (for D.C.) and a fellowship (for J.M.W.).

References

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