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The Coordination Chemistry of Amino Acid Schiff Bases. Part I. Hexaaquoiron(II) Bis(N-Salicylideneglycinato)ferrate(III) Trihydrate

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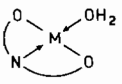
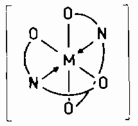
A reinvestigation of the reaction between ferrous sulphate, glycine and salicylaldehyde has shown that the reaction product is the title compound, and not as had previously been reported a binuclear ferric N-salicylideneglycinato complex containing a bridging glycinato ligand.

Introduction

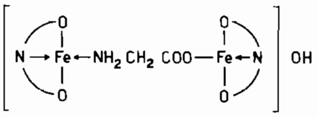
Salicylaldehyde and glycine form Schiff bases which produce complexes with a range of transition metal ions *e.g.*, M^{II} (Sal:gly)·nH_2O, (I), ($M^{II} = Co^{II}$, Ni^{II} or Cu^{II}) and $M^I[M^{III}$(Sal:gly)$_2$], (II) (M^I = Na or K; $M^{III} = Co^{III}$, Fe^{III} or Rh^{III}) [1–6]. In view of this, there is some doubt about the structure (III) proposed for the reaction product from $FeSO_4$, glycine and salicylaldehyde, and we have reinvestigated this reaction as part of a general study of the coordination chemistry of amino acid Schiff bases.



I



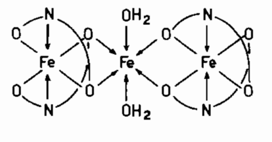
II



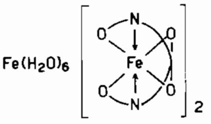
III

Results and Discussion

The reaction product, complex IV, forms deep red crystals which are sparingly soluble in water and alcohol in contrast to the very water soluble salts K[Fe(N–Salicylideneaminoacidato)$_2$]·nH_2O (n = 0.5–3.0) [4, 8]. However the presence of the [Fe(Sal:gly)$_2$]$^-$ unit in (IV) is indicated by its i.r. spectrum which is identical to that of K[Fe(Sal:gly)$_2$]·2H_2O [4, 8] over the range 600–2000 cm^{-1}. The ν(C=N) band at 1620 cm^{-1} is 20–30 cm^{-1} lower than that of Co^{II}(Sal:gly)H_2O [9] reflecting the increased charge on the metal. This band lies within the narrow range 1613–1626 cm^{-1} for a series of more than thirty amino acid-Schiff base complexes of Fe^{III} [8]. The assignment of the 1620 cm^{-1} band to $\delta(NH_2)$ of coordinated glycine is excluded by the absence of a sharp $\nu(NH_2)$ band near 3200 cm^{-1}. A sharp medium-intensity band at 3620 cm^{-1} is assigned to lattice water; the small band width suggests that the lattice water molecules are not engaged in hydrogen bonding. However there is evidence of hydrogen bonding in the shape of a weak broad band centered on *ca.* 3250 cm^{-1}. This is assigned tentatively to the hydrogen-bonded water ligands of the $[Fe(H_2O)_6]^{2+}$ ion (*vide infra*).



IVa



IVb

The electronic spectrum of the complex is typical of the [Fe^{III}N-(Salicylideneaminoacidato)$_2$]$^-$ unit [8]; there are two intense absorptions at 420 nm ($\log\epsilon_{max}$ = 3.1) and 487 nm ($\log\epsilon_{max}$ = 3.3) assigned to the $t_{2g} \longleftarrow n$ and $t_{2g} \longleftarrow p_\pi$ oxygen-to-metal charge-transfer transitions.

Evidence for the presence of two different iron environments in (IV), was provided by its Mössbauer spectrum which had two doublet signals with temperature-independent area ratios close to 2:1. The spectroscopic parameters of the more intense signal: I.S./mms^{-1} = 0.495 (77K), 0.455 (298K); Q.S./mms^{-1} = 0.950 (77K), 0.870 (298K), are at the high end of the range for high-spin Fe^{III} implying a substantial degree of asymmetry in the environment of the metal atom. The I.S. and Q S. values for the less intense signal: I.S./mms^{-1} = 1.370 (77K), 1.320 (298K); Q.S./mms^{-1} = 3.400 (77K), 3.620 (298 K) are characteristic of high-spin Fe^{II}; they are close to those of the $[Fe(H_2O)_6]^{2+}$ ion *e.g.*, $Fe(H_2O)_6SO_4 \cdot H_2O$, I.S./mms^{-1} = 1.261, Q.S./mms^{-1} = 3.217 [10], but do not distinguish between this ion and other possible $Fe^{II}O_6$ units. The two structures IVa and IVb are consistent with the spectroscopic and analytical data. Of these, we prefer the ionic structure IVb

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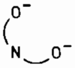
*  = Sal:gly = N-Salicylideneglycinato dianion.

on the grounds that a compound with i.r. and Mössbauer spectra identical to those of IV was obtained by adding concentrated aqueous solution of ferrous sulphate and $K[Fe(Sal{:}gly)_2]2H_2O$, and that an analogous ionic compound has been prepared from $CoSO_4$, glycine and salicylaldehyde [11]. In view of the proposed ionic formulation of IV, it exhibits a surprisingly low conductivity λ_m = 58.1 mhos cm^2 mol^{-1} in methanol – the only solvent in which it is sufficiently soluble for conductivity measurements. The crystal structure of the cobalt complex $[Co^{II}(H_2O)_6][Co^{III}(Sal{:}gly)_2]_2 2H_2O$ [11] shows that this low conductivity could occur because of ion–ion association through hydrogen bonding between the water ligands of the cation and the carboxylate oxygens of the anion. Such hydrogen bonding in (IV) is indicated by the i.r. band at 3250 cm^{-1}. It could also account for the increased value of I.S. in (IV) compared with 0.32 mms^{-1} (298K) for $K[Fe^{III}(Sal{:}gly)_2]2H_2O$ which may reflect a decrease in the s-electron density at the Fe^{III} centre of (IV) brought about by the diminished donor power of the carboxylate oxygens.

The magnetic moment of (IV) μ_{eff} (298K) = 5.38 B.M. calculated on the basis of the stoichiometry $Fe_3(Sal{:}gly)_4 9H_2O$ is close to the value of 5.58 B.M. required for a combination of one high-spin Fe^{II} and two high-spin Fe^{III} ions.

Experimental

I.r., electronic and Mössbauer spectra were recorded on Perkin–Elmer model 621, Beckman Acta M IV, and Harwell 6000-Series instruments respectively. The Mössbauer source was $^{57}Co/Rh$ (298K); the velocity scale and I.S. standard was natural iron foil.

Magnetic susceptibility was determined by the Gouy method. Conductance measurements were made with a Cambridge instruments bridge.

The addition of a solution of salicylaldehyde (3.5 g, 0.029 mol) in 1:1 aqueous ethanol (30 cm^3) to a solution of $FeSO_4 \cdot 7H_2O$ (7.0 g, 0.025 mol) and glycine (2.0 g, 0.027 mol) in water (40 cm^3) caused a colour change from sandy-yellow to an intense red–purple. The mixture was heated for 2 hr at *ca.* 60 °C with continuous aeration, the volume being maintained approximately constant by the addition of 1:1 aqueous ethanol. Dark-red lustrous crystals of Complex IV separated on cooling; they were filtered off, washed with warm water, acetone and ether and dried *in vacuo* over P_4O_{10}.

Complex was also precipitated from a deep-red aqueous solution of $K[Fe(Sal{:}gly)_2]2H_2O$ by the addition of a concentrated aqueous solution of $FeSO_4 \cdot 7H_2O$. *Anal.* Found: C, 41,6; H, 4.5; N, 5.5. Calculated for $C_{36}H_{46}O_{21}Fe_3$: C, 41.6; H, 4.6; N, 5.4%.

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