Inorganica Chimica Acta, 65 (1982) L35–L36

Versatility of Iron(III) upon Coordination with the Binucleating Ligand N,N'-bis(2-hydroxy, 3-carboxybenzilidene)1,2-diaminoethane

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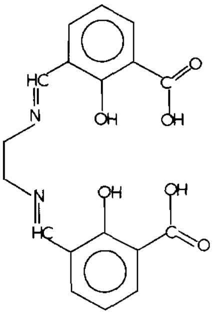
Received April 1, 1982

The ligand N,N'-bis(2-hydroxy, 3-carboxybenzilidene) 1,2-diaminoethane *1*, noted hereafter $H_4(fsa)_2en$, has been used recently to obtain asymmetrical homobimetallic [1, 2] and heterobimetallic [3] complexes.



The first step in the synthesis of heterobimetallic species consists of preparing the mononuclear species. In all the reported cases but $Li_2[UO_2(fsa)_2en]\cdot 2H_2O$ [4], the metal ion occupies the inside-N_2O_2 site. In fact, by analyzing the IR spectra of several mononuclear compounds formed with $H_4(fsa)_2en$, we have deduced that the hard Lewis acids (Cr^{3+}, Fe^{3+}, VO_2^{2+}) are located in the $-O_2O_2$ site and the borderline ones (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) in the $-N_2O_2$ site. However, with Fe(III), two complexes have been isolated.

Their formulae are $[H_2Fe(fsa)_2en(H_2O)_2]Cl\cdot 3H_2O$ (termed A) and $FeH_2(fsa)_2enCl(CH_3OH)\cdot H_2O$ (termed B). In the former compound, Fe(III) occupies the outside site and in the latter the inside site. We report here the synthesis, characterization and the magnetic properties of both complexes, as also the crystal structure of A.

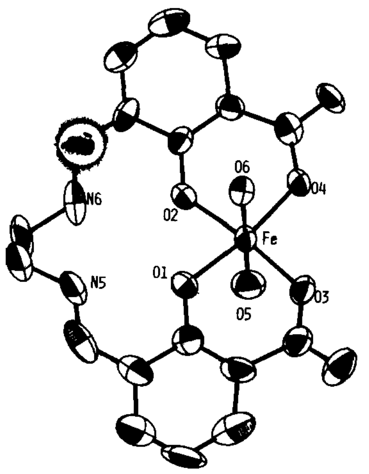


Fig. 1. Perspective view of $[H_2Fe(fsa)_2en(H_2O)_2]^+$.

Syntheses

A. To a suspension of $H_4(fsa)_2en$ (200 mg) in methanol (60 ml) heated under reflux was added dropwise a solution of $FeCl_3\cdot 6H_2O$ (152 mg) in methanol (60 ml). Refluxing was continued for 1½ h. The solution was filtered and NH_4Cl (≅60 mg) added to the filtrate. Dark red, well shaped single crystals of A were obtained by slow evaporation. *Anal.* Calcd. for $C_{18}H_{24}N_2O_{11}ClFe$: C, 40.36; H, 4.52; N, 5.23; Cl 6.62%. Found: C, 39.35; H, 4.65; N, 5.23; Cl, 6.87%.

B. To a suspension of $H_4(fsa)_2en$ (200 mg) and NH_4Cl (180 mg) in methanol (60 ml) heated under reflux was added dropwise a solution of $FeCl_3\cdot 6H_2O$ (152 mg) in methanol (60 ml). B precipitated as a red polycrystalline powder. B can be also obtained from A by displacing the Fe(III) ion from the outside towards the inside site, according to the reaction:

$$H_2Fe(fsa)_2en(H_2O)_2]^+ + Cl^- \xrightarrow[\text{excess of Cl ions}]{} \underline{FeH_2(fsa)_2enCl(CH_3OH)}\downarrow$$

Here, 200 mg of A and 200 mg of NH_4Cl in ≅80 ml of methanol are heated under reflux and B precipitates. *Anal.* Calcd. for $C_{19}H_{20}N_2O_7ClFe$: C, 46.04; H, 4.07; N, 5.65; Cl, 7.15%. Found: C, 46.51; H, 4.08, N, 5.42; Cl, 7.52%.

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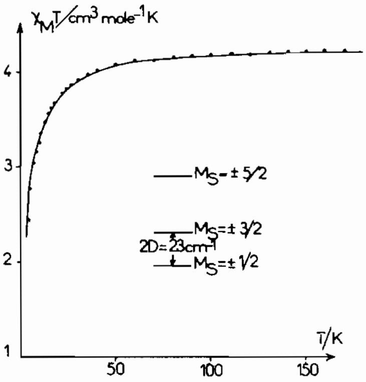


Fig. 2. Temperature dependence of $\chi_M T$ for A. The experimental points are noted • and the theoretical curve is the continuous line.

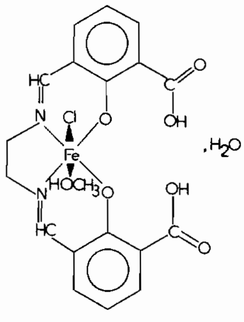
Structures

The compound A crystallizes in the quadratic system, space group $P4_32_12$. The lattice constants are $a = b = 18.732(9)$ Å, $c = 13.520(7)$ Å with $Z = 4$. The structure was determined by Patterson and direct methods using 1806 hkl reflexions collected with an automatic single crystal diffractometer and refined by least squares techniques to a conventional R factor of 0.0805. A perspective view of the cation (heavy atoms only) $[H_2Fe(fsa)_2en(H_2O)_2]^+$ is shown in Fig. 1. The Fe(III) ion is linked to two phenolic oxygen atoms (Fe–O3 = 1.948 Å, Fe–O4 = 1.950 Å) and two water molecules (Fe–O5 = 2.040 Å, Fe–O6 = 2.076 Å). The FeO_6 octahedron is therefore elongated along the O5–O6 direction. The angles around Fe(III) in the equatorial plane are O1FeO2 = 85.2°, O2FeO4 = 89.4°, O4FeO3 = 97.9°, O3FeO1 = 88.0. At the present stage of the investigation, only one of the two phenolic hydrogen atoms has been localized, between N6 and O2. The Cl^- counteranion is disordered on four positions with the respective occupancies of 0.3, 0.3, 0.2 and 0.2. Three additional water molecules are free in the lattice.

The structure of B is unambiguously deduced from the IR spectrum, which exhibits an intense band at 1730 cm^{-1}, characteristic of the free carboxylic group. The insolubility of B in the protic solvents indicates that the chlorine atom is bound to the metal, the coordinence six being achieved by a methanol molecule (under prolonged vacuum, B loses its water molecule). A band at 315 cm^{-1}, which does not exist in A, might be assigned to ν_{Fe-Cl}.

Magnetic Properties

The magnetic behavior for A is shown in Fig. 2 in the form of the product of molar magnetic susceptibility and temperature, *versus* temperature ($\chi_M \cdot T$ *vs.* T). $\chi_M \cdot T$ is constant and equal to 4.21 cm^3 mol^{-1} K in the range 300–60 K. Upon cooling down below 60 K, $\chi_M T$ decreases down to 2.45 cm^3 mol^{-1} K at 4 K. This behavior is characteristic of an isolated high spin Fe(III) with a large zero field splitting leading to a $M_S = \pm\frac{1}{2}$ ground Kramers doublet. The g-factor, assumed to be isotropic, and the axial zero field splitting parameter D of the spin Hamiltonian [5]



$$\mathcal{H} = g\beta\hat{S}\cdot\vec{H} + DS_z^2$$

were determined by least squares fitting and were found equal to g = 1.96 and D = 11.5 cm^{-1}*. The calculated magnetic curve is compared to the experimental data in Fig. 2. The magnetic behavior of B is quite similar to that of A. Again the Fe(III) ion is in a high spin state, with g = 1.97 and D = 8.0 cm^{-1}**.

References

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*Strictly speaking, the symmetry of the FeO_6 chromophore is below axial and a rhombic zero field splitting parameter E should be introduced in the spin Hamiltonian. In other respects, the intermolecular interactions, that we did not take into account, are most probably very weak owing to the large separation between the complex cations.

**The X-band powder E.P.R. spectra for both A and B at 4 K exhibit very broad peaks (4000 G) centered at 1730 G and 2000 G respectively.