The Molecular Structure and Magnetic Properties of the Dimeric *N,N'*-Ethylenebis(salicylamine)Fe(III)-μ-methoxo-*N,N'*-Ethylene(*o*-hydroxylphenylglycine)salicylamine Fe(III): a Complex with a μ-Monodentate Acetato Bridge

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Abstract

We have prepared and characterized a dimeric complex of the formula $Fe_2L(OCH_3)L'\cdot$solvent where L = *N,N'*-ethylenebis(salicylamine) and L' = *N,N'*-ethylene(*o*-hydroxylphenylglycine)salicylamine. Crystals of the methanol solvate were found to be orthorhombic, space group $P2_1nb$, with $a = 13.748$ (5), $b = 22.426(9)$, $c = 11.762(6)$ Å and $d_{calc} = 1.41$ g/cm^3. Least squares refinement of 966 reflections gave a final R factor of 0.066. The structure shows that the two iron atoms are coordinated to two different ligands and are bridged by a methoxide ion and a μ-monodentate acetate oxygen from the pendant arm of L'. The magnetic susceptibility was measured over the range 2–300 K and gave a spin coupling constant $J = -8.3$ cm^{-1}. The significance of acetate bridges to the exchange coupling pathway is discussed.

Introduction

The continuing interest in oxygen bridged dimers of Fe(II) and Fe(III) is largely due to their biological relevance [1–6]. Oxo, and hydroxo bridges are believed to occur in the core structures of hemerythrin [7], purple acid phosphatases [8], ribonucleotide reductase [9] and possibly other metalloproteins. Such features are also thought to be important in ferritin core formation [10]. Considerable effort has been devoted to an understanding of the effect of structure on the magnetic behavior of these dimers. Unfortunately, in contrast to similar copper complexes, simple magnetostructural relationships have not been forthcoming. It is clear, however, that a simple oxo bridge mediates the largest antiferromagnetic exchange coupling ($-J = 80$–150 cm^{-1}) which is considerably reduced ($-J = 5$–20 cm^{-1}) when the oxygen is protonated or alkylated. The extent, however, to which ancillary bridging ligands, such as bidentate carboxylates, affect the coupling is unclear.

In the course of our investigations of new quinquedentate ligands as models for the binding sites in the unrelated monomeric iron–tyrosinate proteins [11] we have isolated and characterized a novel mixed ligand dimeric complex. In this work, we report the structure and magnetic properties of this complex which contains a μ-alkoxy as well as a monodentate carboxylate bridge.

Experimental

Preparation

To a basic aqueous solution of *N,N'*-ethylenebis(salicylamine), H_2SALEN, was added a neutralized solution containing one equivalent of monochloroacetic acid. The solution was heated to 60 °C for one hour and was then stirred overnight. After removal of a considerable quantity of an undesired O-alkylated product* by precipitation at low pH, the reaction mixture was treated with an excess of $FeCl_3$ in methanol and the resulting dark red solution extracted with $CHCl_3$ and 0.1 M sodium carbonate. The dark red chloroform extract was dried, concentrated and then overlayered with methanol. For X-ray analysis the deep red crystals which deposited overnight were briefly dipped in methanol to remove adhering mother liquor, and mounted in glass capillaries**. The bulk sample was washed repeatedly with ether and air dried. *Anal.* Calc. for $Fe_2L(OCH_3)L'\cdot C_4H_{10}O$: C, 57.5; H, 5.8; N, 6.9; Fe, 13.7. Found: C, 57.1; H, 6.0; N, 6.0; Fe, 13.4%.

X-ray Crystallography

A dark rhombohedral crystal was mounted in a glass capillary on an Enraf-Nonius CAD4 diffractometer which employed Mo radiation and a graphite crystal monochromator. Data collection parameters were the same as those previously described [12].

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*This material, which is the major product, has been identified by ^{1}H and ^{13}C NMR and mass spectrometry to be the monophenylacetic acid of H_2SALEN.

**The crystal used for the X-ray data analysis proved to be that of the methanol solvate.

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TABLE I. Bond Distances (Å)

Atom 1	Atom 2	Distance[a]
Fe1	O1′	1.89(2)
Fe1	O2′	1.90(2)
Fe1	O3	2.04(2)
Fe1	O4	2.17(2)
Fe1	N1′	2.16(2)
Fe1	N2′	2.14(2)
Fe2	O1	1.92(2)
Fe2	O2	1.83(2)
Fe2	O3	1.94(2)
Fe2	O4	2.03(2)
Fe2	N1	2.20(2)
Fe2	N2	2.15(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE II. Bond Angles (°)

Atom 1	Atom 2	Atom 3	Angle
O1′	Fe1	O2′	103.8(8)
O1′	Fe1	O3	98.3(8)
O1′	Fe1	O4	166.4(8)
O1′	Fe1	N1′	89.4(8)
O1′	Fe1	N2′	99.6(8)
O2′	Fe1	O3	97.7(7)
O2′	Fe1	O4	87.6(7)
O2′	Fe1	N1′	163.0(8)
O2′	Fe1	N2′	88.8(8)
O3	Fe1	O4	72.5(7)
O3	Fe1	N1′	90.7(8)
O3	Fe1	N2′	158.8(8)
O4	Fe1	N1′	80.9(8)
O4	Fe1	N2′	87.8(8)
N1′	Fe1	N2′	78.4(9)
O1	Fe2	O2	100.8(8)
O1	Fe2	O3	103.0(8)
O1	Fe2	O4	166.4(8)
O1	Fe2	N1	86.3(8)
O1	Fe2	N2	98.2(8)
O2	Fe2	O3	97.5(8)
O2	Fe2	O4	92.4(8)
O2	Fe2	N1	169.9(9)
O2	Fe2	N2	89.4(9)
O3	Fe2	O4	77.8(8)
O3	Fe2	N1	87.7(8)
Fe1	O4	Fe2	101.0(8)
Fe1	O3	Fe2	108.7(9)

The crystal was found to be orthorhombic, space group $P2_1nb$. Cell dimensions, as determined from 25 accurately centered relatively high angle reflections, were a = 13.748(5), b = 22.426(9), c = 11.762(6) Å with $Z = 4$ and a calculated density of 1.41 g/cm^3. Of a total of 3228 reflections measured in the range $3° > 2\theta > 48°$, only 966 had $I > 3\sigma(I)$ and were considered observed and used in the refinement. Lorentz polarization corrections were made in the usual manner but no absorption or decay corrections were applied. The structure was solved using the direct methods program MULTAN and successive difference Fourier maps. Refinement was by full matrix least squares procedures to a final R value of 0.0663 and R_w of 0.0764. The irons and the coordinated atoms were allowed to refine with anisotropic thermal parameters, while all the other non hydrogen atoms were refined isotropically. The hydrogen atoms were not located or refined. The final difference map was featureless with the largest residual peak of 0.43 e/Å^3. Selected bond lengths and angles are found in Tables I and II. See also Supplementary Material.

Physical Measurements

Magnetization measurements were recorded using the S.H.E. SQUID magnetometer at the Francis Bitter Magnet Laboratory, M.I.T. The magnetic moment of the sample was measured as a function of temperature from 2 K to 300 K in applied fields of 2.5 T and 5 T. Solution moments were measured at room temperature using the Evans NMR technique [13]. Room temperature moments on the solid were also measured on a Johnson-Matthey MSB-1 susceptibility balance. Mössbauer spectra were taken in zero applied field and in 6 T applied parallel to the gamma beam on a spectrometer of conventional design. Electrochemical, optical and IR data were obtained as previously described [14].

Results and Discussion

Description of Structure

The structure of the methanol solvate* is shown in Fig. 1 where the mixed ligand complex has Fe1 bonded to a tetradentate H_2SALEN molecule and Fe2 is coordinated to the new quinquedentate ligand. The formation of the mixed ligand complex is clearly the result of incomplete alkylation of the parent H_2SALEN molecule by the chloroacetic acid. The two iron atoms are bridged by a methoxide ion (O3) and the monodentate carboxylate oxygen (O4) from the pendant acetate arm of the *N*,*N*′-ethylene-(*o*-hydroxylphenylglycine)salicylamine to give each iron a distorted octahedral geometry. The distortion from regular octahedral geometry is evident from the O1′–Fe1–N2′ angle of 163° and the O1–Fe2–N2 angle of 170°. The more regular geometry is found around Fe2 where the pyramidalization of N2 provides increased flexibility relative to the planar

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*The methanol of solvation was poorly defined as indicated by its large isotropic thermal parameters, and contributed to the relatively high R factor. Nevertheless, there can be no doubt as to the general correctness of the overall structure.

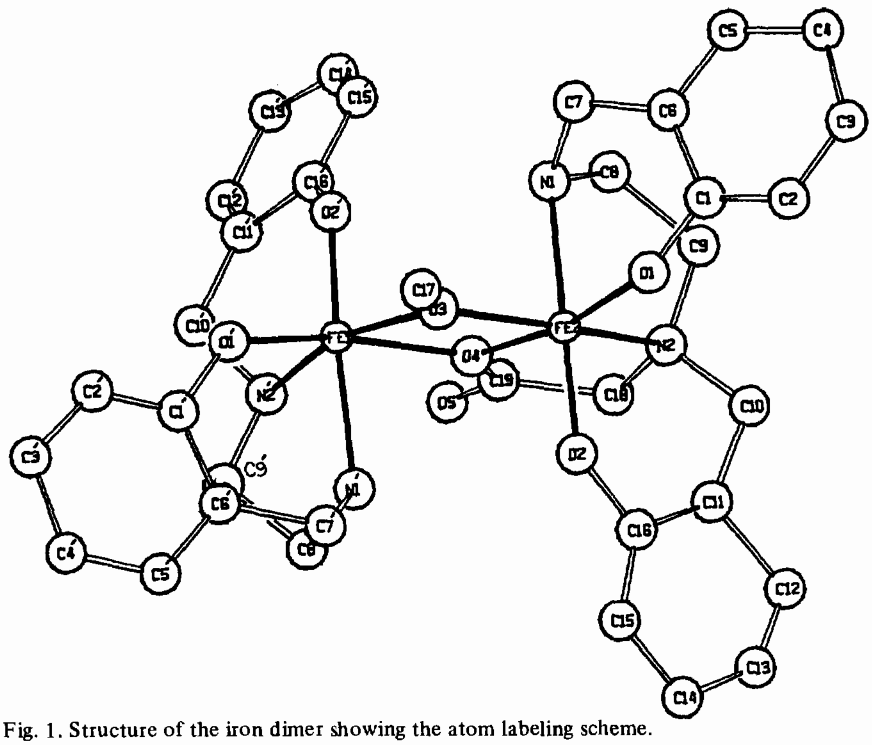


Fig. 1. Structure of the iron dimer showing the atom labeling scheme.

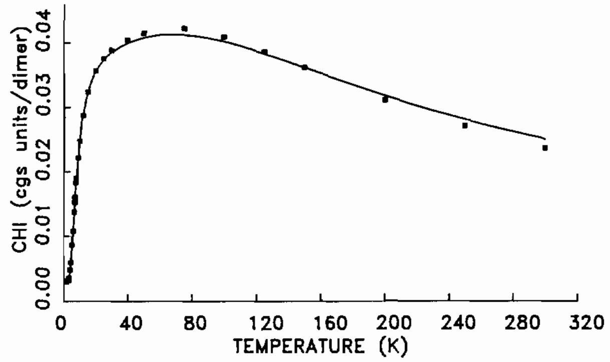
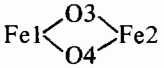


Fig. 2. Plot of the molar susceptibility per dimer as a function of temperature for the ether solvate. The solid line shows the best fit to the data as explained in the text.

imino nitrogen found around Fe1. The Fe1–O3-(methoxide)–Fe2 angle of 109° and the Fe1–O4-(acetate)–Fe2 angle of 101° are in the range seen for other oxygen bridged dimers [1]. The



$$\mathrm{Fe1}\overset{\mathrm{O3}}{\underset{\mathrm{O4}}{\langle\;\rangle}}\mathrm{Fe2}$$

unit is planar with O1 and N2 about 0.3 Å below the plane and O1′ and N2′ a similar distance above. The unusual monodentate bridging mode of the acetate is presumably the result of steric effects resulting from its attachment to N2 which precludes the bidentate bridging mode more commonly seen. The Fe–Fe separation of 3.24 Å is clearly too large to permit direct orbital overlap and is in line with that found in similar complexes [1].

Magnetochemistry

The measured room temperature moment corrected for diamagnetism, $\mu_{\mathrm{eff}} = 5.23$ BM, of **I** is smaller than the spin-only value of 5.96 expected for an unperturbed $S = 5/2$ ion and indicates antiferromagnetic exchange coupling between the iron atoms. The degree of exchange coupling was determined from fits of the temperature dependence of the susceptibility (Fig. 2) to the Heisenberg exchange Hamiltonian, $\mathcal{H} = -2J\vec{S}_1\cdot\vec{S}_2$ with $S_1 = S_2 = 5/2$. Best fits to the data gave $J = -8.3$ cm^{-1} and a temperature-independent paramagnetic correction (TIP) of 3.1×10^{-3} c.g.s. emu. The raw data were corrected for diamagnetism using a diamagnetic susceptibility of -380×10^{-6} c.g.s. emu calculated from Pascal's constants [15]. Solution moments in DMF and methylene chloride averaged 5.12(7) BM. The good agreement between the solid state and solution moments indicates that the dimer remains intact in solution.

A Mössbauer spectrum of the complex at 4.2 K in 6 T field applied longitudinally to the gamma beam (Fig. 3) was fitted by computer to a phenomenological model in which an internal magnetic hyperfine field is assumed to act upon the ^{57}Fe in addition to the applied field. Best fits to the data gave $\Delta E = 0.98$ mm/s, $\delta = 0.58$ mm/s (with respect to metallic Fe) and an internal field of -1.1 T. This relatively small but non-zero hyperfine field is consistent with the magnetization measurements in 5 T which show that even at 4.2 K the dimer has a net magnetic moment as the first excited (triplet) state becomes appreciably populated. In zero applied

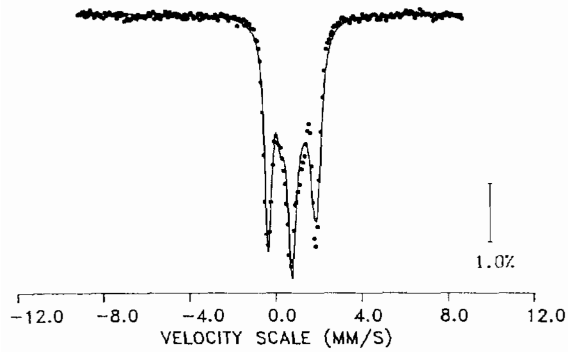


Fig. 3. Mössbauer spectrum of the ether solvate at 4.2 K in 6 T applied parallel to the gamma beam. The solid line represents the best fit to the data in the effective field approximation.

field, the Mössbauer spectrum shows a single quadrupole pattern showing that the two iron sites are equivalent.

Electrochemistry and Optical Spectroscopy

As expected the complex absorbs strongly at 530 nm with an ϵ_m of 3847 due to a phenolate to metal charge transfer transition. This is in the same range as is seen for many other chelated iron–phenolates and gives rise to the characteristic red coloration. The complex also displays irreversible electrochemistry as monitored by cyclic voltammetry. Upon scanning in the negative direction, only a single reduction wave (–0.92 V) is seen which has no complementary return oxidation at scan rates up to 1.0 V/s. However, upon scan reversal two product oxidation waves are seen at –0.078 and –0.29 V. This electrochemical behavior is consistent with the dimer maintaining its integrity in solution in the oxidized form while dissociating into two electrochemically active products upon reduction. Similar effects have been reported for other dimeric iron complexes [5].

Conclusion

A new mixed ligand μ-methoxy-μ-acetato iron dimer has been isolated and characterized. This complex displays a novel μ-monodentate mode of acetate bridging by virtue of the covalent attachment of the acetate group to the ligand backbone. A comparison of the exchange coupling constant J in iron dimers, bridged by similar groups but differing only in their mode of coordination (denticity), might shed some light on the contribution, if any, of the acetate bridge to the exchange coupling pathway. We have seen that μ-hydroxo, μ-alkoxo, and now μ-monodentate acetato groups all mediate nearly identical exchange coupling ($-J = 8$ cm^{-1}). The stronger exchange coupling ($-J = 17$ cm^{-1}) observed in μ-hydroxo-μ-bis bidentate acetato complexes [5] suggests that the bidentate mode of coordination by acetate provides a small additional contribution to the exchange coupling. This is consistent with the observation that the coupling between iron atoms found for the μ-oxo-μ-bis bidentate acetate complex ($-J = 121$ cm^{-1}) is also somewhat stronger than in other typical nonheme oxo bridged dimers ($-J = 80$–105 cm^{-1}). It is possible that these differences arise from different ligand backbones or from other structural factors, but this seems unlikely given the apparent insensitivity of J to iron ligand bond lengths or the Fe–O–Fe angle [16].

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Supplementary Material

More complete data along with positional and thermal parameters and observed and calculated structure factors are available as supplementary material.

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