The Influence of Solvents on Formation of the Molecular Geometry of [{Fe(salphen)}₂O]

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Abstract

The crystal structure and magnetic properties of the complex (I)=[{Fe(salphen)}₂-O]·(C_4H_8SO) and (II)=[{Fe(salphen)}₂O]·($C_4H_8O_2$) (salphen H_2=N,N'-o-phenylenebis-(salicylidene-imine)) were recently reported [1, 2]. This complex crystallized with the solvents of dimethyl sulfoxide and dioxane. In this paper, we investigate the influence of the solvents on the formation of the molecular geometry and study the orbital mechanism of the magnetic super-exchange interactions of this complex.

1. Introduction

Recently the crystal structures and magnetic properties of [{Fe(salphen)}₂O]· X (X = dimethylsulfoxide and dioxane) were reported [1, 2]. [{Fe(salphen)}₂O]· X crystallized with the same space group as P2₁/c. The present investigation was undertaken to determine whether the solvents play important roles in the formation of the molecular geometry or not. We also investigated the orbital mechanism of the magnetic super-exchange interactions. These complexes are interest because of their occurrence at the active centers of the haemerythin and haem proteins and magnetic properties which arise from strong spin exchange via the oxygen atom in the Fe-O-Fe systems [3, 4, 5].

2. Calculations

A perspective drawing of the molecules is shown in Figure 1. For simplicity only the coordination of iron(III) are labeled and hydrogen atoms are omitted. The comparison of the selected bond lengths, angles and conformational data are summarized in Table 1 and Table 2, respectively. The parameters are given and defined in Figure 2 and in Table

2 for each [{Fe(salphen)}$_2$O] moiety (NOON is the torsion angle, d is the displacement from the coordination plane of iron(III) atom, the degree of bending can conveniently be described by the angles α and β between the coordination planes) the geometrical parameters of the molecule were computed with the XANADU program [5]. Molecular orbital calculations at the extended Hückel level were performed using the CACAO 4.0 [6] program.
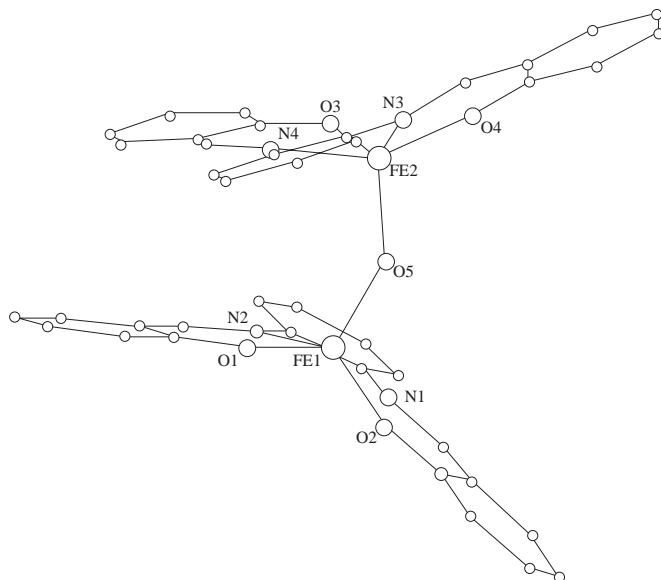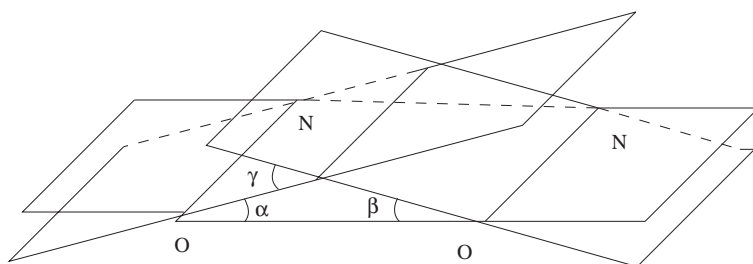

Figure 1. Molecular viex of [{Fe(salphen)}$_2$O] complex [7].

Figure 2. Plane angles between coordination sphere and chelate rings.

3. Discussion

The structure of [{Fe(salphen)}$_2$O] is composed of μ-OXO bridged ferric salphen dimers. Each Fe(III) environment is that of a square-based pyramid linked by Fe-O bonds. In the structure, each complex has the asymmetric umbrella conformation often observed in

penta-coordinated species. In this arrangement the phenylenediamine bridge has a gauge conformation and the two salicylaldimine groups of the each ligand are both bent.

The bond lengths and angles are given in Table 1, which includes only the coordination spheres. The Fe-Fe distance, Fe-O, Fe-N bond lengths and O-Fe-O, O-Fe-N, N-Fe-N bond angles show small differences within experimental error. In Table 2 some conformational data are given and there are no significant differences between (I) and (II) complexes. In particular, the comparison revealed that the conformational data show small differences and the influence of the solvent on the gauge formation is not important.

Table 1. Selected bond lengths and angles (Å and degrees) for the samples.

Bond length			Angle		
	(I)	(II)		(I)	(II)
Fe(1)...Fe(2)	3.408(2)	3.409(1)	Fe(1)-O(5)-Fe(2)	146.7(4)	145.0(3)
Fe(1) - O(1)	1.911(7)	1.911(5)	O(1)-Fe(1)-O(2)	91.8(3)	91.5(2)
Fe(1) - O(2)	1.919(7)	1.916(5)	O(1)-Fe(1)-N(1)	86.8(3)	86.9(2)
Fe(1) - O(5)	1.776(7)	1.788(4)	O(1)-Fe(1)-N(2)	148.6(3)	146.1(2)
Fe(2) - O(5)	1.781(7)	1.786(4)	O(2)-Fe(1)-N(1)	142.5(3)	142.4(2)
Fe(2) - O(3)	1.934(7)	1.901(4)	O(2)-Fe(1)-N(2)	87.3(3)	86.8(2)
Fe(2) - O(4)	1.911(7)	1.893(5)	N(1)-Fe(1)-N(2)	75.4(4)	74.5(2)
Fe(1) - N(1)	2.115(9)	2.132(6)	O(3)-Fe(2)-N(4)	91.1(3)	91.0(2)
Fe(1) - N(2)	2.111(8)	2.104(5)	O(3)-Fe(2)-N(4)	86.4(3)	87.7(2)
Fe(2) - N(3)	2.098(8)	2.093(6)	O(3)-Fe(2)-N(3)	150.1(3)	150.8(2)
Fe(2) - N(4)	2.114(9)	2.103(6)	O(4)-Fe(2)-N(4)	138.8(3)	140.9(2)
			O(4)-Fe(2)-N(3)	85.9(3)	86.8(2)
			N(3)-Fe(2)-N(4)	76.7(4)	76.2(2)

Table 2. Conformational data [{Fe(salphen)}$_2$O].

Complex	NOON(∘)	d(Å)	α(∘)	β(∘)	γ(∘)	μ_{eff}	Magnetic properties
DMSO	5.9	0.585(20)	21.1	12.7	31.6	2.05 μ_B	antiferromag.
dioxane	4.9	0.581(20)	21.3	12.6	31.2	2.90 μ_B	antiferromag.

Another comparison point is the magnetic moment of complexes at the room temperature. The magnetic susceptibility measurements of complex (II) with the powdered sample were performed in the range 4.2 to 286.5 K. The effective magnetic moment of complex (I), however, was measured at room temperature. The effective magnetic moment of complex (II) is 2.90 μ_B at room temperature, and the corresponding value for complex (II) is 2.05 μ_B. This difference could be explained by the measurement errors of the effective magnetic moment at room temperature of complex (I).

We also studied the electronic structure of complexes (I) and (II). The molecular orbital energies, molecular orbital configurations and their effects on the super-exchange interactions of the investigated complex were calculated by using the extended Hückel method. We took the iron and bridge oxygen atoms for the molecular orbital calculations. We used fractional coordinates from the experimental x-ray results of the compounds (I)

and (II). During the theoretical calculations the Hückel constant was taken as 1.75. It can be easily seen from Table 1 that the Fe-Fe distances for both Fe(III) ion complexes are nearly the same and the contribution of direct metal-metal orbital overlaps to the exchange mechanism is considered to be small for such separations. The antiferromagnetic super-exchange interactions occured between d orbitals of the iron ion and the s and p orbitals of the interceded bridging oxygen atom. Antiferromagnetic and ferromagnetic pathways both occur in the case of 180° on the linear super-exchange for the $d_{5/2}$-$d_{5/2}$ systems, but direct overlap between iron and oxygen orbitals dominates and leads to the overall antiferromagnetism. We calculated the smallest energy values of the occupied molecular orbitals, net atomic charges and occupations of the molecular orbitals from the extended Hückel calculations. The results for both complexes are nearly the same. The same atomic orbital overlaps between t_{2g} and e_g orbitals (such as t_{2g}-s-t_{2g}, t_{2g}-p_x-t_{2g}, e_g-p_y-e_g) are given in Figure 3 and Figure 4.

In summary, the influence of the solvents are not important on the molecular geometry and magnetic properties of these complexes. The differences on the effective magnetic moments of the complexes could not originate from the solvents.
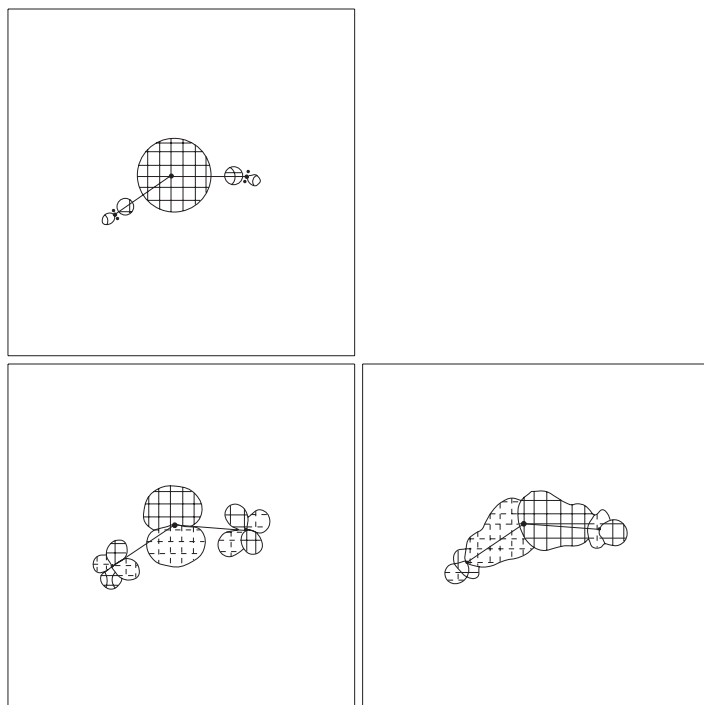

Figure 3. Molecular orbitals of [{Fe(salphen)}$_2$O].dioxan [6].
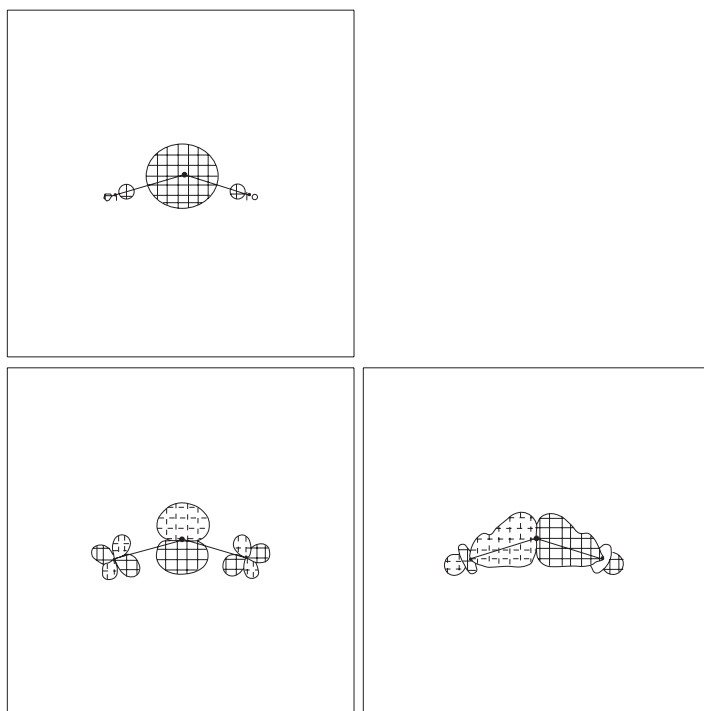
Figure 4. Molecular orbitals of [{Fe(salphen)}$_2$O].DMSO [6].

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