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# Ferromagnetically Coupled Binuclear Iron(III) Complexes and Antiferromagnetically Coupled Binuclear Copper(II) Complexes. The Importance of the Metal-O-Metal Angle

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Binuclear iron(III) and copper(II) complexes with N-salicylidene-2-hydroxy-5-chloro(or bromo)benzylamine ($H_2L$), $[Fe_2(L)_2(CH_3COO)_2]\cdot 2THF$ (THF = tetrahydrofuran) and $[Cu_2(L)_2(DMSO)_2]\cdot 2DMSO$ (DMSO = dimethyl sulfoxide) have been prepared and characterized by X-ray structure analysis and magnetic susceptibilities (80–300 K).

We have recently reported synthesis, structure, and magnetic properties of a novel manganese(IV) complex with N-salicylidene-2-hydroxy-5-chlorobenzylamine.$^{1)}$ The Schiff-base ligand stabilizes such a high oxidation state owing to the two phenolic-oxygen donor atoms. We have now extended our efforts to iron and copper chemistry and found that isolated compounds are ferromagnetically coupled binuclear iron(III) complexes and antiferromagnetically coupled binuclear copper(II) complexes, respectively. We herein report the preparation and structural characterization of these novel binuclear complexes with N-salicylidene-2-hydroxy-5-bromobenzylamine ($H_2L_a$) or N-salicylidene-2-hydroxy-5-chlorobenzylamine ($H_2L_b$).

The iron(III) complexes were prepared as follows. 2-Hydroxy-5-bromobenzylamine (20 mg) and salicylaldehyde (12 mg) were dissolved in 25 ml of THF (THF=tetrahydrofuran). Then iron(III) acetate (52 mg) was added. The mixture was refluxed for 0.5 h and filtered; a slow evaporation gave black crsytals of $Fe_2(L_a)_2(CH_3COO)_2\cdot 2THF$ (**1**). Anal. Found:C, 53.80; H, 4.72; N, 3.08%. Calcd for $Fe_2Br_2O_{10}N_2C_{40}H_{42}$:C, 53.78; H, 4.74; N, 3.14%. $Fe_2(L_b)_2(CH_3COO)_2\cdot 2THF$ (**2**). Anal. Found:C, 49.49; H, 4.48; N, 2.74%. Calcd for $Fe_2Cl_2O_{10}N_2C_{40}H_{42}$:C, 48.91; H, 4.31; N, 2.85%.

In a similar fashion, the binuclear copper(II) complexes were prepared. A solution of 2-hydroxy-5-bromobenzylamine (20 mg) and salicylaldehyde (12 mg) in DMSO (DMSO=dimethyl sulfoxide) (1 ml) was treated with copper(II) acetate (18 mg) dissolved in DMSO (1 ml). The solution was allowed to stand to produce well-formed dark green crystals of $Cu_2(L_a)_2(DMSO)_2\cdot$-2DMSO (**3**). Anal. Found:C,41.10; H,4.27; N,2.66%. Calcd for $Cu_2Br_2S_4O_8N_2C_{36}H_{44}$:C,41.26; H,4.23; N, 2.67%. $Cu_2(L_b)_2(DMSO)_2\cdot 2DMSO$ (**4**). Anal. Found:C,44.92; H,4.55; N,2.95%. Calcd for $Cu_2Cl_2S_4O_8N_2C_{36}H_{44}$:C,45.09; H,4.62; N,2.92%.

The molecular structure of the iron(III) complex, **1**, was determined by X-ray crystallography.$^{2)}$ The crystal consists of centrosymmetric binuclear units, $[Fe_2(L_a)_2(CH_3COO)_2]$, and crystal solvents, THF. The ORTEP plot of $[Fe_2(L_a)_2(CH_3COO)_2]$ is shown in Fig. 1. The structure shows a dimeric unit where the two iron atoms are bridged by the phenolic-oxygen atoms of the two Schiff-base ligands, $L_a$, forming a $Fe_2O_2$ core. The center of symmetry lies in the center of this core. The Fe-Fe separation and Fe-O-Fe angle are 2.955(3) Å and 92.6(5)°, respectively. It is noteworthy that these values are unusual and the smallest yet found for complexes with $Fe^{III}{}_2(OR)_2$, being closer to values (Fe-Fe 3.06 Å, Fe-O-Fe 97°) found in $Fe_2(salmp)_2{\cdot}2DMF$ ($H_3salmp$=2-bis(salicylideneamino)methylphenol) which has been reported recently.[3] For more than 16 complexes containing the $Fe^{III}{}_2(OR)_2$ bridge, these values fall into the ranges 3.08–3.22 Å and 100–111°, respectively.[3,4] Each iron atom has an $NO_5$ donor set in a distorted octahedron with the Schiff-base ligands and acetate ions. The acetate ions are positioned above and below the equatorial plane containing the Schiff-base moiety and involved in the bridges in a syn-syn configuration. The example of the two-acetate bridging in a similar fashion is found in $Mn_2(spa)_2(CH_3COO)_2$ ($H_2spa$=3-salicylideneamino-1-propanol).[5] It seems likely that the small Fe-O-Fe angle is a result of constraints imposed by the incorporation of the bridging acetate ions.

The crystal structure of the copper(II) complex, 3, again consists of the centrosymmetric binuclear units, $[Cu_2(L_a)_2(DMSO)_2]$, and crystal solvents, DMSO.[2] The two copper atoms are doubly bridged by phenolic-oxygen atoms of the Schiff-base ligands. The Cu-Cu separation and Cu-O-Cu angle are 3.077(2) Å and 101.6(4)°, respectively. These values are normal for complexes

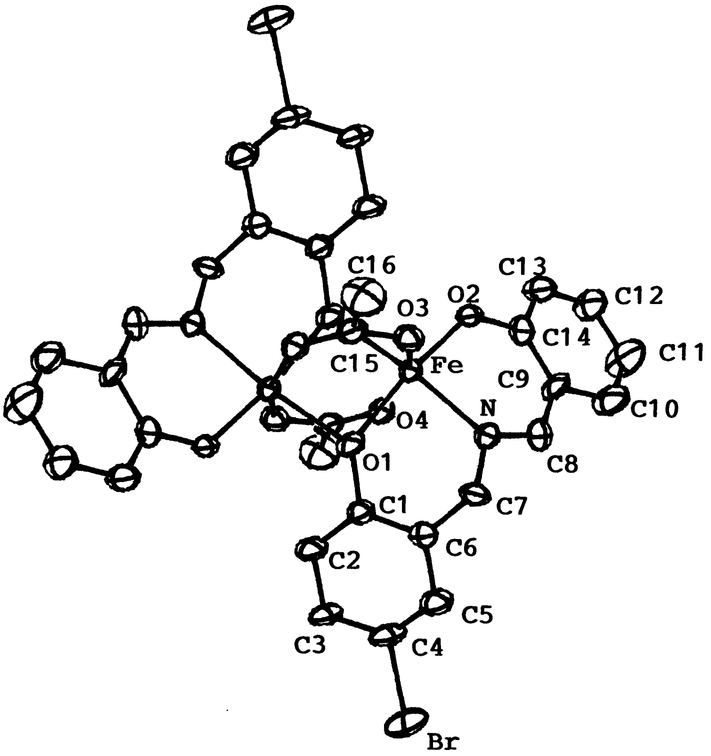

Fig. 1. Perspective view of $[Fe_2(L_a)_2(CH_3COO)_2]$. Selected bond distances (l/Å) and angles (ϕ/°) are: Fe-Fe' 2.955(3), Fe-O1 2.071(14), Fe-O1' 2.016(10), Fe-O2 1.862(14), Fe-O3 2.049(10), Fe-O4 2.041(11), Fe-N 2.091(13); Fe-O-Fe' 92.6(5).

with $Cu^{II}{}_2(OR)_2$.[6] The coordination geometry of each copper ion is a distorted square pyramid; the basal plane is defined by a nitrogen atom and three oxygen atoms of the Schiff-base ligands and an oxygen atom of the solvent DMSO acts as the apical ligand.

Variable temperature magnetic susceptibility data were collected on powdered samples of **1**, **2**, **3**, and **4** in the temperature range 80–300 K. The data were analyzed with the van Vleck equation based on the Heisenberg model ($\mathcal{H}=-2JS_1\cdot S_2$). For complex **1**, the effective magnetic moment per Fe, $\mu_{eff}$, rises gradually from 6.00 B.M. at 285 K to 6.48 B.M. at 81 K. The behavior is characteristic of intramolecular ferromagntic coupling, and the fitting parameters are $J=+2.0$ $cm^{-1}$, $g=2.00$. Complex **2** is also ferromagnetically-coupled ($\mu_{eff}$/Fe=6.02 B.M. (290 K), 6.39 B.M. (81 K); $J=+1.6$ $cm^{-1}$, $g=2.00$). These iron(III) complexes are unique in being ferromagnetic, since the large majority of the structurally characterized iron(III) complexes with the $Fe^{III}{}_2(OR)_2$ bridge are antiferromagnetic and only one example, $Fe_2(salmp)_2$, is known to be ferromagnetic.[3] On the other hand, the magnetic susceptibility data of the copper(II) complexes, **3** and **4**, could be interpreted in terms of the intramolecular antiferromagnetic coupling (**3**: $\mu_{eff}$/Cu=1.14 B.M.(290 K), 0.23 B.M. (81 K), $J=-233$ $cm^{-1}$, $g=2.24$, $N\alpha=60\times10^{-6}$ cgs emu; **4**: $\mu_{eff}$/Cu=1.13 B.M. (294 K), 0.17 B.M. (81 K), $J=-236$ $cm^{-1}$, $g=2.26$, $N\alpha=40\times10^{-6}$ cgs emu). Judging from the structural comparison of the iron(III) and copper(II) complexes, the bridging angle M-O-M seems to be important determining the sign of J, i.e., the nature of the magnetic exchange interaction. In general,

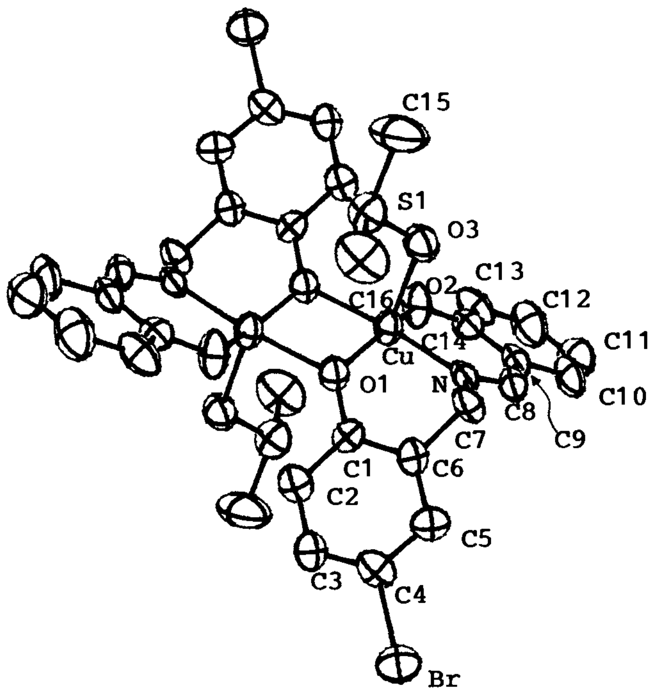

Fig. 2. Perspective view of $[Cu_2(L_a)_2(DMSO)_2]$. Selected bond distances (l/Å) and angles (ϕ/°) are: Cu-Cu' 3.077(2), Cu-O1 2.001(8), Cu-O1' 1.970(9), Cu-O2 1.911(9), Cu-O3 2.480(9), Cu-N 1.912(11); Cu-O-Cu' 101.6(4).

bridging angle M-O-M of 90° will promote ferromagnetic behavior and larger angles will favor antiferromagnetism. A crossover from ferromagnetism to antiferromagnetism was observed in a series of complexes containing the $Cu^{II}_2(OH)_2$ bridge at Cu-O-Cu≈98°[7] and was analyzed in the extended Hückel MO calculations.[8] Although there have been some controversy on the correlation between the Fe-O-Fe bridging angle and J,[3,9-11] some correlation between them should also exist for iron(III) complexes and the unusual small Fe-O-Fe angle may be a major cause of the observed ferromagnetic interaction.

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2) Crystal data for **1**: $Fe_2Br_2O_{10}N_2C_4H_{42}$, F.W.=982.3, triclinic, space group $P\bar{1}$, a=10.005(12), b=13.728(21), c=8.383(12) Å, $\alpha$=107.43(8), $\beta$=107.05(7), $\gamma$=71.92(12)°, V=1018.6(25) $Å^3$, Z=1, $D_m$=1.58, $D_c$=1.60 g $cm^{-3}$, $\mu$(Mo-K$\alpha$)=27.16 $cm^{-1}$, R=0.095, $R_w$=0.118. 3200 reflections were measured in the range $2 \le 2\theta \le 48°$; 1758 with $I \ge 3\sigma(I)$ were assumed observed. For **3**: $Cu_2Br_2S_4O_8N_2C_{36}H_{44}$, F.W.=1047.9, monoclinic, space group $P2_1/n$, a=17.095(12), b=8.547(1), c=16.074(8) Å, $\beta$=111.72(2)°, V=2182.0(19) $Å^3$, Z=2, $D_m$=1.59, $D_c$=1.60 g $cm^{-3}$, $\mu$(Mo-K$\alpha$)=30.22 $cm^{-1}$, R=0.066, $R_w$=0.070. 3680 reflections were measured in the range $2 \le 2\theta \le 48°$; 1620 with $I \ge 3\sigma(I)$ were assumed observed. For the determination of both structures, intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K$\alpha$ radiation. The structures were solved by direct methods and refined by the full-matrix least-squares methods using the SDP program package.

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