Synthesis and Magnetism of Trinuclear Copper(II) Complexes with a Salen-like Schiff Base and a Tertiary Diamine

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Synopsis. Trinuclear Copper(II) complexes [{Cu(sb)}$_2$Cu(da)](ClO$_4$)$_2$ have been synthesized by the use of a copper(II) complex with a salen analog ([Cu(sb)]) and a diamine (da) such as bpy or phen. Cryomagnetic investigations revealed the operation of an antiferromagnetic spin-exchange interaction ($-J$=26—78 cm^{-1}) between the adjacent copper ions.

Binuclear copper(II) complexes of the type [Cu(sb)CuX$_2$] (H$_2$sb denotes salen-like Schiff bases; H$_2$salen=*N*,*N*′-di-salicylideneethylenediamine) have been synthesized and magnetically studied by Gruber *et al.*[1] Recently Patel and Bhattacharya[2] have reported the synthesis of binuclear copper(II) complexes of the type [Cu(sb)Cu(da)](ClO$_4$)$_2$ by the use of a diamine (da) such as 2,2′-bipyridyl (bpy) or 1,10-phenanthroline (phen). According to them, the magnetic moments of the complexes at room temperature fall in the range 0.83—1.19 BM†, which are considerably lower than the moments of [Cu(sb)CuX$_2$].[1] The configuration around the copper coordinated by [Cu(sb)] and da must be much distorted to tetrahedron because of a steric hinderance between these ligands.[1] Since antiferromagnetic spin-exchange interaction generally becomes weaker when the >Cu<$\overset{O}{\underset{O}{}}$>Cu< configuration is distorted from a coplane,[3] such low magnetic moments (which suggest a fairly strong antiferromagnetic spin-exchange interaction) observed for [Cu(sb)Cu(da)](ClO$_4$)$_2$ seem quite unusual. In this study we have reinvestigated the synthesis of the complexes by the use of [Cu(salen)], *N*,*N*′-disalicylidene-1,2-propanediaminatocopper(II) ([Cu(salpn)]), or *N*,*N*′-bis(5-methylsalicylidene)ethylene-diaminatocopper(II) ([Cu(5-Mesalen)]) as [Cu(sb)] and bpy or phen as da. Contrary to the Patel and Bhattacharya's result,[2] we have obtained the complexes of the type [{Cu(sb)}$_2$Cu(da)](ClO$_4$)$_2$. The characterization and the magnetism of the complexes have been reported in this paper.

Experimental

Syntheses. The synthesis of the complexes was carried out in nearly the same way as that of the literature.[2] However, the products obtained by the method often contaminated with some impurities. It was found in this study that the same complexes were obtained without the contamination of impurities when [Cu(sb)], [Cu(H$_2$O)$_6$](ClO$_4$)$_2$, and da were reacted in the 2:1:1 mole ratio.

Magnetic Measurements. Magnetic susceptibilities were measured by the Faraday method in the temperature range 80—300 K. The apparatus was calibrated by the use of [Ni(en)$_3$]S$_2$O$_3$.[4]

Results and Discussion

The elemental analyses were invariably consistent with the formulation of [{Cu(sb)}$_2$Cu(da)](ClO$_4$)$_2$ (see Table 1). No complexes of the stoichiometry [Cu(sb)Cu(da)](ClO$_4$)$_2$ as reported in the literature[2] were obtained in spite of our all efforts. We believe that [{Cu(sb)}$_2$Cu(da)](ClO$_4$)$_2$ is the most stable among possible oligonuclear complexes when [Cu(sb)] and da are utilized as the ligands. It is to be noted that tetranuclear complexes [Cu(sb)Cu(ta)]$_2$(ClO$_4$)$_4$ are obtainable when a triamine (ta) is utilized instead of a diamine.[5]

The sketetal band near 1525 cm^{-1} of [Cu(sb)] shifted to 1540 cm^{-1} in [{Cu(sb)}$_2$Cu(da)](ClO$_4$)$_2$, suggesting that the phenolic oxygens are acting as the bridges in the present complexes.[6] Magnetic moments (per copper atom) at room temperature are lower than the spin-only value, implying an operation of antiferromagnetic spin-exchange interaction. The plausible structure is supposed to be trinuclear as shown in Fig. 1, since such a structure has been demonstrated for [{Cu(sb)}$_2$M(H$_2$O)$_2$](ClO$_4$)$_2$.[7]

Table 1. Elemental analyses, magnetic moments at room temperature, and magnetic parameters of complexes

	Found/% (Calcd/%)				g	J/cm^{-1}	μ_{eff}/BM (T/K)
	C	H	N	Cu			
[{Cu(salen)}$_2$Cu(bpy)](ClO$_4$)$_2$·H$_2$O	46.03 (46.01)	3.32 (3.49)	7.90 (7.67)	17.1 (17.4)	2.07	−30	1.70(297.6)
[{Cu(salen)}$_2$Cu(phen)](ClO$_4$)$_2$·H$_2$O	47.09 (47.17)	3.49 (3.42)	7.29 (7.50)	16.7 (17.0)	2.05	−70	1.55(297.8)
[{Cu(salpn)}$_2$Cu(bpy)](ClO$_4$)$_2$·H$_2$O	47.10 (47.00)	3.69 (3.76)	7.43 (7.47)	17.0 (17.0)	2.09	−32	1.72(297.8)
[{Cu(salpn)}$_2$Cu(phen)](ClO$_4$)$_2$·H$_2$O	48.26 (48.11)	3.56 (3.69)	7.36 (7.32)	17.0 (16.6)	2.05	−78	1.60(297.6)
[{Cu(5-Mesalen)}$_2$Cu(bpy)](ClO$_4$)$_2$	48.46 (48.70)	4.06 (3.91)	7.28 (7.41)	16.6 (16.8)	2.09	−66	1.68(297.8)
[{Cu(5-Mesalen)}$_2$Cu(phen)](ClO$_4$)$_2$	49.57 (49.77)	4.09 (3.83)	7.01 (7.25)	16.5 (16.6)	2.09	−26	1.74(297.6)

† 1BM=9.274078(36)×10^{-24} Am^2.

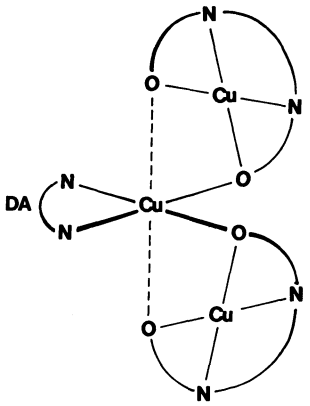

Fig. 1. Schematic representation of trinuclear structure for $[\{Cu(sb)\}_2Cu(da)]^{2+}$.

The magnetic susceptibilities of the complexes were examined in the temperature range 80—300 K. Based on the spin Hamiltonian, $\mathcal{H}=-2J(\hat{S}_1\cdot\hat{S}_2+\hat{S}_2\cdot\hat{S}_3)$, the susceptibility equation for the linear trinuclear system is given by

$$\chi_A=\frac{Ng^2\beta^2}{12kT}\times\frac{\exp(2J/kT)+10\exp(3J/kT)+1}{\exp(2J/kT)+2\exp(3J/kT)+1}+N\alpha,$$

where J is the exchange integral between the adjacent copper ions and other symbols have their conventional meanings. As exemplified in Fig. 2, the magnetisms of the complexes can be well explained with this equation. The magnetic parameters determined by the best-fit technique are given in Table 1, together with the moments at room temperature. Thus, the magnetical investigations clearly demonstrate the trinuclear structure for the present complexes.

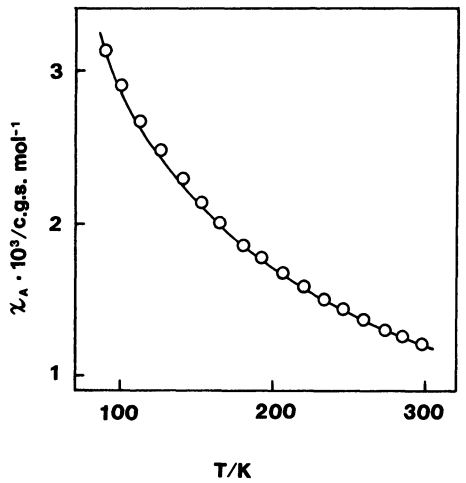

Fig. 2. Temperature variation of magnetic susceptibility of $[\{Cu(salen)\}_2Cu(bpy)](ClO_4)_2\cdot H_2O$. Solid curve is drawn on the basis of the expression in the text using the parameters, $J=-30\,cm^{-1}$, g=2.07, and $N\alpha=0$.

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