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Novel Tetranuclear Copper(II) Complexes with a Quadridentate Schiff Base and a Tridentate Amine†

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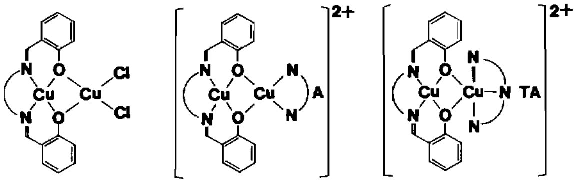
Abstract

New metal complexes of the type Cu(SB)Cu(TA)-$(ClO_4)_2$ were synthesized, where SB^{2-} denotes N,N′-disalicylideneethylenediaminate anion or N,N′-disalicylidene-1,2-propanediaminate anion and TA denotes 2,2′:6′,2″-terpyridine, N,N-di(2-aminoethyl)-amine, or N,N-di(3-aminopropyl)amine. Based on infrared and electronic spectra and cryomagnetic properties, the complexes are suggested to be tetranuclear, where each Cu(SB) forms bonds with two Cu(TA) molecules through the phenolic oxygens. It is shown that an antiferromagnetic spin-exchange interaction operates between Cu(SB) and Cu(TA) of $-J = 28 \sim 64\ cm^{-1}$.

Introduction

It is known that N,N′-disalicylideneethylenediaminatocopper(II) (Cu(salen) and its homologs (abbreviated as Cu(SB) in general) can act as bidentate chelating agents through their phenolic oxygens to form binuclear and trinuclear metal complexes [2]. Sinn *et al.* prepared $Cu(SB)CuCl_2$ (Fig. 1a) and investigated their cryomagnetic properties in detail [3–5]. Recently, Patel and Bhattacharya [6] reported binuclear complexes of the type $[Cu(SB)Cu(A)](ClO_4)_2$ (Fig. 1b) with a bidentate ligand (A) such as 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen). In these complexes the copper ion coordinated to Cu(SB) adopts a distorted pseudotetrahedral configuration, because of the steric hindrance between the 3-hydrogen on the ring (the hydrogen adjacent to the phenolic oxygen) and chloride ion or the ring hydrogen of the ligand A.



(a) (b) (c)

Fig. 1. Chemical structures of (a) $Cu(SB)CuCl_2$, (b) $[Cu(SB)Cu(A)]^{2+}$ (A = bip or phen), and (c) $[Cu(SB)Cu(TA)]^{2+}$ (TA = triamine).

If a tridentate ligand (TA) such as 2,2′:6′,2″-terpyridine (tpy), N,N-di(2-aminoethyl)amine (dien), or N,N-di(3-aminopropyl)amine (ditn) is utilized instead of bipy or phen, it is expected to synthesize new binuclear copper(II) complexes consisting of planar and trigonal bipyramidal copper ions which share the phenolic oxygens in their equatorial planes (Fig. 1c). Because of interest in the magnetic properties of such complexes, we have attempted in this study to synthesize and characterize the metal complexes of the type $[Cu(SB)Cu(TA)]^{2+}$ with Cu(salen) or Cu(salpn) ($salpn^{2-}$ = N,N′-disalicylidene-1,2-propanediaminate anion) as Cu(SB) and tpy, dien, or ditn as TA.

Experimental

Syntheses

Cu(salen), Cu(salpn), and Ni(salen) were prepared by a literature method [7]. Dien and ditn were obtained from Wako Chemical Co. and tpy from Nakarai Chemical Co.

$Cu(salen)Cu(tpy)(ClO_4)_2$

A solution of copper(II) perchlorate hexahydrate (89 mg) in absolute ethanol (20 cm^3) and ethyl orthoformate (4 g) was refluxed for 3 h. Then, Cu(salen) (66 mg) was added and the mixture was refluxed for 1 h. To the resulting red solution was added tpy (47 mg), and the mixture was refluxed for 1 h to give a gray crystalline powder. This was separated, washed with ethanol, and dried over P_2O_5 in vacuum desiccator. The yield was ca. 150 mg. *Anal.* Found: C, 43.70; H, 3.22; N, 8.34; Cu, 15.1%.

[†] Part LVI.Binuclear Metal Complexes, for Part LV, see ref. [1].

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Calcd. for $C_{31}H_{25}N_5O_{10}Cl_2Cu_2 \cdot H_2O$: C, 44.14; H, 3.23; N, 8.30; Cu, 15.1%.

Cu(salpn)Cu(tpy)(ClO$_4$)$_2$

This complex was obtained as a gray crystalline powder by a method similar to that for Cu(salen)-Cu(tpy)(ClO_4)$_2$, except for the use of Cu(salpn) instead of Cu(salen). *Anal.* Found: C, 44.28; H, 3.38; N, 8.11; Cu, 14.8%. Calcd. for $C_{32}H_{27}N_5O_{10}Cl_2Cu_2 \cdot 2H_2O$: C, 43.90; H, 3.57; N, 8.00; Cu, 14.5%.

Cu(salen)Cu(dien)(ClO$_4$)$_2$

Dien (1.04 g) and copper(II) perchlorate hexahydrate (3.7 g) were dissolved in absolute ethanol (30 cm^3), and to this was added Cu(salen) (2.74 g). The mixture was stirred under reflux for 3 h to give purple crystals, which were separated, washed with absolute ethanol, and dried over P_2O_5 in a vacuum desiccator. The yield was 5.3 g. *Anal.* Found: C, 34.33; H, 3.92; N, 10.04; Cu, 18.2%. Calcd. for $C_{20}H_{27}N_5O_{10}Cl_2Cu_2$: C, 34.54; H, 3.91; N, 10.07; Cu, 18.3%.

Cu(salpn)Cu(dien)(ClO$_4$)$_2$

This complex was obtained as purple crystals in the same way as that for Cu(salen)Cu(dien)-(ClO_4)$_2$. *Anal.* Found: C, 35.51; H, 4.20; N, 9.78; Cu, 17.9%. Calcd. for $C_{21}H_{29}N_5O_{10}Cl_2Cu_2$: C, 35.55; H, 4.12; N, 9.87; Cu, 17.9%.

Cu(salen)Cu(ditn)(ClO$_4$)$_2$

An ethanolic solution (10 cm^3) of copper(II) perchlorate hexahydrate (0.43 g) was added dropwise to an ethanolic solution of ditn (0.13 g) and Cu(salen) (0.33 g) to give blue-purple crystals. They were separated, washed with absolute ethanol, and dried over P_2O_5 in a vacuum desiccator. The yield was 0.7 g. *Anal.* Found: C, 35.85; H, 4.31; N, 9.38; Cu, 17.2%. Calcd. for $C_{22}H_{31}N_5C_{10}Cl_2Cu_2 \cdot H_2O$: C, 35.65; H, 4.49; N, 9.44; Cu, 17.1%.

Cu(salpn)Cu(ditn)(ClO$_4$)$_2$

A solution of copper(II) perchlorate hexahydrate (0.37 g) and 2,2-dimethoxypropane (1 g) in ethanol (30 cm^3) was refluxed for 3 h and then mixed with an ethanolic solution of Cu(salpn) (0.34 g). To the resulting reddish solution was added dropwise an ethanolic solution of ditn (0.13 g) with stirring under reflux. After the addition was completed, the refluxing was continued for an additional 3 h and the mixture was left to stand at room temperature. After a few days purple crystals separated, which were collected, washed with absolute ethanol, and dried over P_2O_5 in a vacuum desiccator. The yield was 0.4 g. *Anal.* Found: C, 37.39; H, 4.49; N, 9.39; Cu, 17.3%. Calcd. for $C_{23}H_{33}N_5O_{10}Cl_2Cu_2$: C, 37.46; H, 4.51; N, 9.50; Cu, 17.2%.

Ni(salen)Cu(dien)(ClO$_4$)$_2$

This complex was obtained as yellowish-green crystals by the reaction of Ni(salen) (0.27 g), copper(II) perchlorate hexahydrate (0.4 g), and dien (0.1 g) in absolute ethanol (30 cm^3). The yield was 0.6 g. *Anal.* Found: C, 34.56; H, 3.95; N, 10.30; Cu, 9.6; Ni, 8.2%. Calcd. for $C_{20}H_{27}N_5O_{10}Cl_2CuNi$: C, 34.78; H, 3.94; N, 10.14; Cu, 9.2; Ni, 8.5%.

Measurements

Infrared spectra were recorded on a Hitachi Infrared Spectrometer Model 215 on KBr disks. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrophotometer Model MPS-5000 on powder samples. Magnetic susceptibilities were measured by the Faraday method in the range from liquid nitrogen temperature to room temperature. The apparatus was calibrated by the use of [Ni-(en)$_3$]S_2O_3 [8]. Diamagnetic corrections were made with Pascal's constants [9] and effective magnetic moments were calculated by the equation, $\mu_{\text{eff}} = 2.828 (\chi_A \times T)^{1/2}$.

Results and Discussion

Elemental analyses demonstrate the stoichiometry of the complexes to be Cu(SB)Cu(TA)(ClO_4)$_2$. This does not rule out the possibility of co-precipitation of the components. However, each complex obtained forms uniform prismatic crystals under microscopic observation, suggesting the formation of a pure complex. The complexes are practically insoluble in most non-donating solvents and decompose in pyridine, N,N-dimethylformamide and alcohols. The investigations were therefore carried out on solid samples.

The selected IR bands are given in Table I. The N–H stretching vibrations observed for the dien and ditn complexes shift to a lower frequency by more than 100 cm^{-1} relative to those of free amines, suggesting the coordination of all the amine nitrogens to the copper(II) ion. It is known that one of the skeletal vibrations near 1530 cm^{-1} shifts to higher frequency when the phenolic oxygens of Cu(SB) coordinate to another metal ion [10, 11], and such a shift has often been used as a diagnosis for the formation of binuclear and oligonuclear metal complexes with phenolic oxygen bridge. The skeletal vibration observed for Cu(SB)Cu(TA)(ClO_4)$_2$ is higher than that of the corresponding Cu(SB), by more than 10 cm^{-1}. This fact implies that the phenolic oxygens act as bridges in the present complexes. The vibration due to the perchlorate ion splits into two. This splitting must be caused by a weak interaction of the ion in the crystal lattice rather than the coordination to the metal, judging from its small splitting (25–30 cm^{-1}).

TABLE I. Selected IR Bands and Effective Magnetic Moments at Room Temperature of the Complexes.

Compound	IR			μ_{eff} (T/K)[b]
	N–H	skel[a]	ClO_4^-	
$Cu(salen)Cu(tpy)(ClO_4)_2$		1540	1110, 1080	170(299.0)
$Cu(salpn)Cu(tpy)(ClO_4)_2$		1540	1115, 1080	1.71(294.6)
$Cu(salen)Cu(dien)(ClO_4)_2$	3325, 3250, 3160	1540	1110, 1085	1.68(297.8)
$Cu(salpn)Cu(dien)(ClO_4)_2$	3320, 3250, 3170	1540	1110, 1080	1.55(297.8)
$Cu(salen)Cu(ditn)(ClO_4)_2 \cdot H_2O$	3300, 3220, 3150	1535	1110, 1080	1.72(297.6)
$Cu(salpn)Cu(ditn)(ClO_4)_2$	3325, 3250, 3170	1540	1110, 1080	1.68(287.0)
$Ni(salen)Cu(dien)(ClO_4)_2$	3310, 3260, 3150	1540	1110, 1080	1.84(298.2)[c]

[a] The skeletal vibrations for Cu(salen) and Cu(salpn) being 1520 and 1525 cm^{-1}, respectively. [b] The effective magnetic moment per copper atom. [c] The effective magnetic moment per nickel and copper atoms.

Magnetic moments of the complexes at room temperature fall in the range 1.55–1.72 BM, which is lower than the moment for common mononuclear copper(II) complexes (Table I). Further, the moments decrease when the temperature is lowered to that of liquid nitrogen. It is evident that an antiferromagnetic spin-exchange interaction operates in each molecule. If the complexes are binuclear, the magnetic susceptibility should obey the Bleaney-Bowers equation [12],

$$\chi_A = \frac{Ng^2\beta^2}{kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha,$$

where each symbol has its usual meaning. As is exemplified in Fig. 2, however, the complexes do not obey the Bleaney–Bowers equation. Contrary to our expectation, therefore, the complexes may not be binulcear but oligonuclear. If this is true, Cu(SB) may not coordinate to a metal as a chelate but coordinate to two metals as a bridging group through its phenolic oxygens.

When Cu(SB) binds to two metal ions with its phenolic oxygens, the configuration around the bridging oxygen cannot be planar because of the steric hindrance from the 3-hydrogen on the ring (Fig. 3). Therefore, two bridging modes of Cu(SB) are possible: (1) '*cis*-bridging' with two copper ions at the same side of the Cu(SB) plane, and (2), '*trans*-bridging' with copper ions at the different sides of the plane (Fig. 4). In order to gain an insight into the bridging mode of Cu(SB), electronic spectra of the complexes measured on powder samples were examined (Fig. 5). Parent mononuclear complexes Cu(SB) show a d–d band near 18 × 10^3 cm^{-1}, while the Cu(SB)Cu(TA)-$(ClO_4)_2$ complexes show a d–d band at higher frequency. If Cu(SB) adopts the '*trans*-bridging' mode, the configuration of Cu(SB) may distort to tetrahedral. On the other hand, the planar configuration of Cu(SB) may be strengthened more or less as seen in $Cu(SB)CuCl_2$ [2], when Cu(SB) adopts the '*cis*-bridging'. Since the d–d band of Cu(SB) generally shifts to higher frequency when its configuration becomes more planar [2, 13], the spectral results suggest the '*cis*-bridging' in the present complexes.

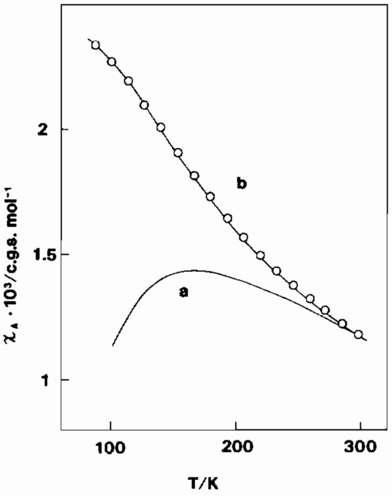


Fig. 2. Temperature variation of magnetic susceptibility of $Cu(salen)Cu(dien)(ClO_4)_2$. The carveture **a** is drawn on the basis of the Bleaney-Bowers equation with magnetic parameters g = 2.10, $-2J$ = 185 cm^{-1}, and $N\alpha$ = 60 × 10^{-6} c.g.s./mol. The carveture **b** is drawn on the basis of the equation for a tetranuclear copper(II) system given in the text, with the parameters g = 2.07, $-J$ = 34 cm^{-1}, and $N\alpha$ = 60 × 10^{-6} c.g.s./mol.

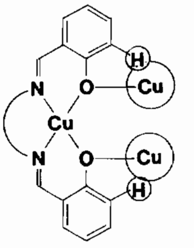
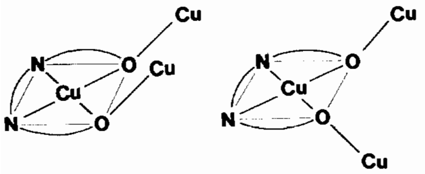


Fig. 3. Cu(SB) binding to two metal ions with its phenolic oxygens.



(a) (b)

Fig. 4. Bridging modes of Cu(SB): (a) *cis*-bridging and (b) *trans*-bridging.

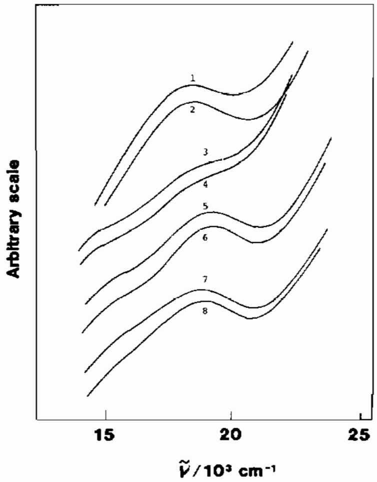


Fig. 5. Reflectance spectra of (1) Cu(salen), (2) Cu(salpn), (3) Cu(salen)Cu(tpy)$(ClO_4)_2$, (4) Cu(salpn)Cu(tpy)$(ClO_4)_2$, (5) Cu(salen)Cu(dien)$(ClO_4)_2$, (6) Cu(salpn)Cu(dien)$(ClO_4)_2$, (7) Cu(salen)Cu(ditn)$(ClO_4)_2$, and (8) Cu(salpn)Cu(ditn)-$(ClO_4)_2$.

A shoulder near 15×10^3 cm^{-1} may be attributed to a d–d band of the Cu(TA) moiety. The low frequency of the band suggests a distorted configuration around the metal ion.

So far we have not succeeded in making crystals suitable for single-crystal X-ray analysis. Therefore, we have assumed a possible structure of the complexes by the use of Dreiding model. The model suggests the most plausible structure with the '*cis*-bridging' to be tetranuclear as schematically shown in Fig. 6.

For the derivation of the magnetic susceptibility equation for the supposed tetranuclear system, three different exchange integrals should be taken into consideration (Fig. 7); that is, the exchange integral J between Cu(SB) and Cu(TA), J' between Cu^1(SB) and Cu^2(SB), and J'' between Cu^1(TA) and Cu^2(TA). Hatfield and Inman [14] derived the exact susceptibility equation for the system, which includes a 4×4 matrix to be solved in terms of choices of the exchange integrals. If one (or two) of the exchange integrals is negligibly small compared with the others, the magnetic susceptibility equation becomes much simpler and the magnetic parameters determined with this simplified equation must be much reliable. It is expected that this is the case for the present complexes, because the integral J is associated with the spin-exchange through the phenolic oxygen bridge, while J' and J'' are the exchange integrals between the paramagnetic centers without bridging atoms.

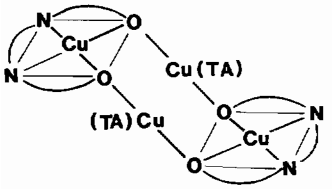


Fig. 6. A possible tetranuclear structure for Cu(SB)Cu-(TA)$(ClO_4)_2$.

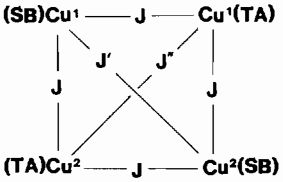


Fig. 7. Exchange integrals for the tetranuclear system.

In order to obtain an evidence for the above assumption, we prepared Ni(salen)Cu(dien)$(ClO_4)_2$ by the use of diamagnetic Ni(salen) instead of Cu(salen). The Ni-substituted complex was demonstrated to be isostructural with Cu(salen)Cu(dien)$(ClO_4)_2$, based on their essentially identical X-ray powder spectra. The effective magnetic moment of Ni(salen)Cu-(dien)$(ClO_4)_2$ per molecule was practically independent of temperature (1.83 BM at room temperature and 1.81 BM near liquid nitrogen temperature). This clearly indicates that the exchange integral J'' between Cu^1(TA) and Cu^2(TA) is negligibly small. Though the evaluation of the exchange integral J' is impossible at present because of the difficulty in synthesizing Cu(SB)M(TA)$(ClO_4)_2$ with a diamagnetic M(II) ion, it seems reasonable to presume that the integral is very small relative to J in analogy with the case of J''. Thus, the magnetisms of the present complexes were analyzed by the susceptibility equation derived by considering only the exchange integral J.

Based on the Heisenberg model and by the use of the Van Vleck equation, the magnetic susceptibility equation per metal for the tetranuclear system is given by:

$$\chi_A = (Ng^2\beta^2/2kT) \times \{\exp(-4J/kT) + 2\exp(-2J/kT) + 5/\exp(-6J/kT) + 3\exp(-4J/kT) + 7\exp(-2J/kT) + 5\} + N\alpha$$

where J is the exchange integral mentioned above, N the Avogadro number, g the Landé g factor,

β the Bohr magneton, k the Boltzmann constant, and T the absolute temperature. As is seen in Fig. 2, the magnetism of Cu(salen)Cu(dien)(ClO$_4$)$_2$ can be simulated by this equation with the magnetic parameters $g = 2.07$, $J = -34$ cm^{-1}, and $N\alpha = 60 \times 10^{-6}$ c.g.s./mol. Similarly, the other complexes are also magnetically characterized by this equation. Thus, the magnetical investigations add a support to the tetranuclear structure for the present complexes. Magnetic parameters thus determined are given in Table II.

TABLE II. Magnetic Parameters of the Complexes[a].

	g	$-J$/cm^{-1}
Cu(salen)Cu(tpy)(ClO$_4$)$_2$	2.08	33
Cu(salpn)Cu(tpy)(ClO$_4$)$_2$	2.08	28
Cu(salen)Cu(dien)(ClO$_4$)$_2$	2.07	34
Cu(salpn)Cu(dien)(ClO$_4$)$_2$	2.07	64
Cu(salen)Cu(ditn)(ClO$_4$)$_2$·H$_2$O	2.07	28
Cu(salpn)Cu(ditn)(ClO$_4$)$_2$	2.08	32

[a] The temperature independent paramagnetism is assumed to be 60×10^{-6} c.g.s./mol.

It should be emphasized that the exchange integrals J are relatively small compared with the integrals of other binuclear [3, 15] and trinuclear [16] copper(II) complexes with Cu(SB) as bidentate chelates. The exchange integrals of bi- and oligonuclear copper(II) complexes with oxygen bridges have been variously discussed from a structural point of view. McGreger *et al.* [17] have shown a correlation between the exchange integral and the Cu–O–Cu angle. Countryman *et al.* [5] suggested the importance of the co-planarity of the binuclear skeleton. Mikuriya and others [18–20] have pointed out the importance of planarity around the bridging oxygen. As mentioned above, the configuration around the phenolic oxygen must be distorted from plane to tetrahedron in the present complexes. Hence, the relatively weak antiferromagnetic spin-exchange interaction through the phenolic oxygen bridge may be best rationalized in terms of the distortion from the plane of the bonding system around the bridging oxygen.

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