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Synthesis and Magnetic, Spectral, and Electrochemical Properties of Strati-bis Cobalt(II) Complexes

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Synopsis. Strati-bis cobalt(II) complexes, [Co_2(sata)]·$2H_2O$ and [Co_2(sacta)] have been prepared, where H_4(sata) and H_4(sacta) denote 1,2,3,4-tetrakis(salicylideneamino)-2,3-dimethylbutane and 1,2-bis(salicylideneamino)-1,2-bis(salicylideneaminomethyl)cyclohexane, respectively. Since their magnetic moments are 4.89 and 4.73 BM at room temperature, respectively, the cobalt(II) ions in [Co_2(sata)] and [Co_2(sacta)] have a high spin d^7 configuration. From the temperature dependence of magnetic susceptibilities of these complexes the antiferromagnetic interaction exists between the two cobalt(II) ions. The oxidation potentials for $Co^{II} \rightarrow Co^{III}$ are observed at lower potentials compared with those of corresponding mononuclear cobalt(II) complexes.

Recently there is a growing interest in chemistry of strati-bis binuclear metal complexes in which two metal coordination planes are held in juxtaposition by flexible or nonflexible linkages. In the previous papers,[1-3] it was reported the synthesis and characterization of strati-bis copper(II)–copper(II) and copper(II)–nickel(II) complexes of 1,2,3,4-tetrakis(R-salicylideneamino)-2,3-dimethylburane (H_4(R-sata)) and 1,2-bis(R-salicylideneamino)-1,2-bis(R-salicylideneaminomethyl)cyclohexane (H_4(R-sacta)), where R are the substituents on salicylaldehyde. In these complexes, the following characteristics have been recognized: 1) an "en"-chelated structure (Fig. 1a) and the existence of an equilibrium between the stacked and non-stacked forms as in the face to face manner of the MN_2O_2-planes, 2) electron delocalization over the whole molecule through the ligand π-systems, 3) one electron transfer process, Cu^{II}–$Cu^{II} \rightarrow Cu^{II}$–$Cu^{I}$, occurring at a higher potential compared with the corresponding mononuclear copper(II) complexes.

In the present study the author has prepared the strati-bis complexes, [Co_2(sata)] and [Co_2(sacta)] and their corresponding mononuclear cobalt(II) complexes, [Co(salpn)] and [Co(sacda)], where H_2(salpn) and H_2(sacda) denote *N*,*N*′-disalicylidene-1,2-propanediamine and 1-(salicylideneamino)-1-(salicylideneaminomethyl)cyclohexane, respectively. Chemical structures of [Co_2(sata)], [Co_2(sacta)], [Co(salpn)], and [Co(sacda)] are shown in Fig. 2.

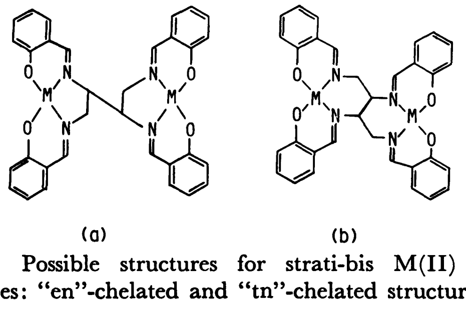

Fig. 1. Possible structures for strati-bis M(II) complexes: "en"-chelated and "tn"-chelated structures.

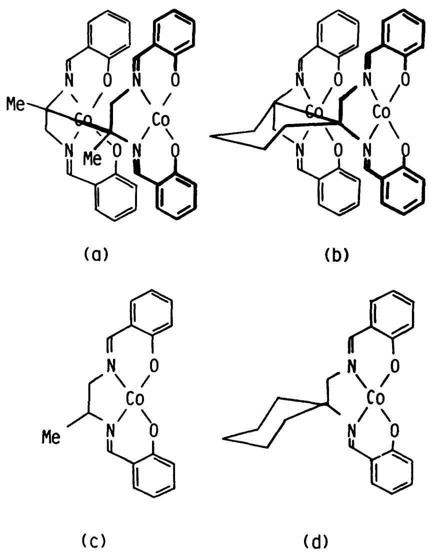

Fig. 2. Chemical structures of a) [Co_2(sata)], b) [Co_2(sacta)], c) [Co(salpn)], and d) [Co(sacda)].

Experimental

Syntheses. The ligands were synthesized by the method previously reported.[1-3]

[Co(salpn)] and [Co(sacda)]: These complexes were synthesized by the literature method.[4]

[Co_2(sata)]: Cobalt(II) acetate tetrahydrate (0.97 g), H_4(sata) (1.1 g), and NaOH (0.3 g) were dissolved in absolute methanol, and the solution was stirred for 6 h at room temperature under nitrogen. The orange-red fine crystals were obtained. Found: C, 57.30; H, 4.58; N, 7.55%. Calcd for $C_{34}H_{30}N_4O_4Co_2 \cdot 2H_2O$: C, 57.31; H, 4.81; N, 7.86%.

[Co_2(sacta)]: Cobalt(II) acetate tetrahydrate (0.25 g), H_4(sacta) (0.3 g), and NaOH (0.082 g) were dissolved in absolute methanol and the solution was stirred for 12 h at room temperature under nitrogen. The orange fine crystals were obtained. Found: C, 61.75; H, 4.85; N, 7.68%. Calcd for $C_{36}H_{32}N_4O_4Co_2$: C, 61.55; H, 4.59; N, 7.97%.

Measurements. Infrared spectra were measured with a Hitachi Infrared Spectrometer Model 215 on a KBr disk. Electronic spectra were recorded on a Shimadzu spectrophotometer MPS-5000 in dichloromethane. Magnetic susceptibilities were measured by Faraday method in the range from liquid nitrogen temperature to room temperature. Diamagnetic correction was made using Pascal's constants.[5] Effective magnetic moments were calculated by the equation, $\mu_{eff} = 2.828(\chi_A \times T)^{1/2}$, where χ_A is the susceptibility per cobalt(II) ion. Differential pulse polarograms and cyclic voltammograms were recorded on a Yanagimoto Voltammetric Analyzer Model P-1000 in dichloromethane containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. A three electrode cell was used for measurements, in which the working electrode is a glassy carbon and the auxiliary electrode a platinum coil. A saturated calomel electrode (SCE) was used as the reference electrode. In practice, instead of the reference electrode an internal standard, the ferrocene/ferricinium(1+) couple was utilized.[6]

Results and Discussion

The IR spectra of [Co_2(sata)] and [Co_2(sacta)] resemble those[1,2] of previously reported [Ni_2(sata)], [Cu_2(sata)], and [Cu_2(sacta)], and also that of mononuclear [Co(salpn)],[7] all of which have the "en" chelated structures. However, the IR spectra of the cobalt complexes do not resemble that of [Co(saltn)][8] (H_2(saltn) = *N*, *N'*-disalicylidene-1,3-propanediamine), which is the mononuclear complex of the "tn"-chelated structure. Based on these resemblance between the IR spectra, [Co_2(sata)] and [Co_2(sacta)] seem to have the "en"-chelated structure (Fig. 2).

The effective magnetic moments per cobalt(II) ions of [Co_2(sata)] and [Co_2(sacta)] are 4.89 and 4.73 BM at room temperature, respectively, and 4.48 and 4.09 BM at liquid nitrogen temperature, respectively. These results suggest that the cobalt(II) ions in [Co_2(sata)] and [Co_2(sacta)] have a high spin d^7 configuration. On the other hand, the related mononuclear cobalt(II) complex, [Co(salpn)],[9,10] has a low spin d^7 configuration. Thus, the spin states of cobalt(II) ions change to high spin on forming binuclear complexes. This may be caused by the stacking of two CoN_2O_2 moieties in the face to face manner. The magnetic moments of [Co_2(sata)] and [Co_2(sacta)] decrease with lowering of temperature. The χ_A *vs.* T^{-1} plots reveal that they obey the Curie-Weiss law $\chi_A = C/(T-\theta)$. The negative Weiss constants obtained for [Co_2(sata)] and [Co_2(sacta)], $\theta = -24$ and -42 K, respectively, imply the existence of an antiferromagnetic spin-exchange interaction.

Electronic spectra of [Co_2(sata)], [Co_2(sacta)], [Co(salpn)], and [Co(sacda)] measured in dichloromethane are shown in Fig. 3. Absorption bands in the near-infrared region of [Co(salpn)] and [Co(sacda)] are characteristic of the low spin square-planer cobalt(II) complexes,[10,11] whereas the same spectra of [Co_2(sata)] and [Co_2(sacta)] do not show sharp peaks. This difference implies that the binuclear cobalt(II) complexes have different spin states from those of mononuclear cobalt(II) complexes in solution as well.

Electrochemical properties of the cobalt(II) complexes studied by means of differential pulse polarography (D.P.P.) and cyclic voltammetry (C.V.) are given in Table 1. For mononuclear cobalt(II) complexes, [Co(salpn)] and [Co(sacda)], the one-electron oxidation from Co^{II} to Co^{III} was observed at +0.01 and +0.11 V, respectively, positive to the internal reference standard, the ferrocene/ferricinium(1+) couple.[6] In contrast, for the binuclear complexes, [Co_2(sata)] and [Co_2(sacta)] the two oxidation waves were observed at more cathodic region. These two oxidation waves may also be assigned to the oxidation from Co^{II} to Co^{III}. These electrochemical behaviors seem to reflect the presence of intramolecular spin-delocalization in the strati-bis cobalt(II) complexes.

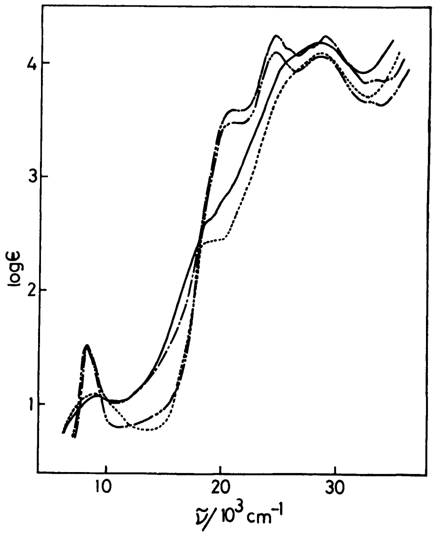

Fig. 3. Electronic absorption spectra of (——) [Co_2(sata)], (······) [Co_2(sacta)], (·—·—·) [Co(salpn)], and (—··—) [Co(sacda)] in dichloromethane.

Table 1. ELECTROCHEMICAL DATA OF THE Co(II) COMPLEXES

Complex	E_{pc} a) / V	E_{pa} a) / V	ΔE_p / mV	$E_{1/2}$ a) / V (D.P.P.)
Co(salpn)	−0.08	0.02	100	0.01
Co(sacda)·3/4 H_2O	0.02	0.10	80	0.11
Co_2(sata)·2H_2O		−0.14		−0.18
		0.03		0.00
Co_2(sacta)		−0.18		−0.22
		−0.01		−0.06

a) V *vs.* E_{Fc/Fc^+} (E_{Fc/Fc^+}; The oxidation potential of the ferrocen/ferricinium (1+) couple as an internal reference.)

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