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Binuclear Metal Complexes. XXIV.[1] Synthesis and Magnetism of Binuclear Cobalt(II) Complexes in Mixed-spin State[2]

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Binuclear cobalt(II) complexes, $Co_2(fsaR)(py)_3$ and $Co_2(fsaR)MeOH \cdot 1/2H_2O$ with 3-formylsalicylic acid-diamine Schiff bases, H_4fsaR (R=en, pn, bn, ch, and ph), were prepared and characterized. Mixed-spin states of these complexes were demonstrated by the cryomagnetic measurements and no spin-exchange interaction was observed between high-spin and low-spin cobalt(II) ions. The absence of spin-exchange interaction in these complexes was discussed on the basis of the electronic configuration of the low-spin cobalt(II) ion and in comparison with the antiferromagnetic Cu(II)–Co(II) ($s=3/2$) complexes with the same ligands.

Binuclear metal complexes are classified into four types: homo-metal binuclear complexes (*e.g.*, Cu(II)–Cu(II)), mixed-spin binuclear complexes (*e.g.*, Ni(II)($s=0$)–Ni(II)($s=1$)), mixed-valence binuclear complexes (*e.g.*, Cu(I)–Cu(II)), and hetero-metal binuclear complexes (*e.g.*, Cu(II)–Ni(II)). Among these complexes homo-metal binuclear complexes have been most extensively studied because of the ease of preparation. Recently much attention has been denoted to the mixed-valence and the hetero-metal binuclear complexes in connection with metalloenzymes and homogeneous catalysis. On the other hand, there are very few characterized binuclear complexes in mixed-spin state.

Although there have been obtained some binuclear complexes with high-spin cobalt(II) ion,[3–8] no mixed-spin binuclear cobalt(II) complexes have yet been obtained. In the previous papers of this series,[9–13] the mixed-spin binuclear nickel(II) complexes[9] and the hetero-metal binuclear complexes[10–13] were obtained by use of 3-formylsalicylic acid-diamine Schiff bases (H_4fsaR). In $CuCo(fsaR)(H_2O)_{2-3}$ complexes with these ligands,[11,12,14] the high-spin cobalt(II) ion is bonded to the "outside" coordination site with two water molecules at the apical positions. On the other hand, the "inside" coordination site of these ligands quite resembles the coordination site of *N,N′*-disalicylideneethylenediamine and its homologues capable of forming low-spin cobalt(II) complexes. Thus, we aimed in this study to prepare mixed-spin binuclear cobalt(II) complexes with 3-formylsalicyclic acid-diamine Schiff bases and to investigate the spin-exchange interaction between high-spin and low-spin cobalt(II) ions.

The 2:1 condensation product of 3-formylsalicyclic acid with ethylenediamine, propylenediamine, 2,3-butanediamine, 1,2-cyclohexanediamine and *o*-phenylenediamine are abbreviated as H_4fsaen, H_4fsapn, H_4fsabn, H_4fsach, and H_4fsaph, respectively.

Experimental

Synthesis. 3-Formylsalicylic acid-diamine Schiff bases, H_4fsaR (R=en, pn, bn, ch, and ph), were obtained as yellow prisms by the reaction of 3-formylsalicylic acid and a diamine in ethanol in the 2:1 mole ratio. Syntheses of complexes were carried out in an atmosphere of nitrogen by means of a VAC Inert Atmosphere & Vacuum Deposition Equipment Model HE-43-2.

$Co_2(fsaen)(py)_3$. Cobalt(II) acetate tetrahydrate (500 mg) and H_4fsaen (350 mg) were dissolved in pyridine (20 ml) to form a deep red solution. When the solution was stirred at 60 °C for 30 min red prisms separated. Stirring was continued for additional two hours at 100 °C and the reaction mixture was allowed to stand overnight to give red-purple prisms. They were collected and dried at ordinary pressure.

In the same way as the above $Co_2(fsapn)(py)_3$, $Co_2(fsabn)(py)_3$, $Co_2(fsach)(py)_3$, and $Co_2(fsaph)(py)_3$ were obtained.

$Co_2(fsaen)MeOH \cdot 1/2H_2O$. To a solution of H_4fsaen (700 mg) in methanol (50 ml) was added cobalt(II) acetate tetrahydrate (1.0 g) and the mixture was stirred under reflux for 24 h. After the reaction mixture was left standing overnight, red fine-crystals which separated were collected and dried.

$Co_2(fsach)MeOH \cdot 1/2H_2O$ and $Co_2(fsaph)MeOH \cdot 1/2H_2O$ were obtained by the procedures similar to that for $Co_2(fsaen)MeOH \cdot 1/2H_2O$. Syntheses of metal complexes with H_4fsach and H_4fsabn were also carried out. Red prisms obtained became black on exposure to air. Composition of black product was assumed to be $Co_2(fsaR)(MeOH)_2 \cdot O_2 \cdot 1/2H_2O$ (R=pn, bn).

Elemental analyses of the complexes are tabulated in Table 1.

Measurements. Infrared spectra of the complexes were measured with a Hitachi Infrared Spectrophotometer Model 215 on a KBr disk. Electronic spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MSP-5000 by the reflection on a powder sample. ESR spectra were measured with a JES-ME-3 Spectrometer by the X-band. Magnetic susceptibility was measured by the Faraday method in the temperature range from liquid nitrogen temperature to room temperature. The apparatus was calibrated by use of $HgCo(NCS)_4$. Magnetic moments were calculated by the expression, $\mu_{eff}=2.828(\chi_M \times T)^{1/2}$, where χ_M is the magnetic susceptibility per molecule corrected for diamagnetism by use of Pascal's constants.

Results and Discussion

Reaction of H_4fsaR with cobalt(II) acetate in pyridine always resulted in the formation of $Co_2(fsaR)(py)_3$. Since in $CuCo(fsaR)(H_2O)_{2-3}$ the cobalt(II) ion is in the "outside" coordination site and has a pseudo-octahedral configuration with water molecules at the apical positions[14], it is likely that the "outside" cobalt(II) in $Co_2(fsaR)(py)_3$ also has a pseudo-octahedral structure coordinated by pyridine at the apical positions. It is known[15] that *N,N′*-disalicylidene-ethylenediaminatocobalt(II) (Co(salen)) reacts with pyridine

Table 1. Elemental analyses of complexes

	Found (%)				Calcd (%)			
	C	H	N	Co	C	H	N	Co
Co_2(fsaen)$(py)_3$	56.24	3.98	10.01	16.88	56.03	3.85	9.90	16.66
Co_2(fsapn)$(py)_3$	56.13	4.03	9.55	16.11	56.60	4.05	9.71	16.34
Co_2(fsabn)$(py)_3$	57.15	4.31	9.66	16.23	57.16	4.25	9.52	16.03
Co_2(fsach)$(py)_3$	58.59	4.59	9.65	15.58	58.36	4.37	9.20	15.48
Co_2(fsaph)$(py)_3$	58.82	3.71	9.36	15.29	58.82	3.71	9.27	15.60
Co_2(fsaen)MeOH$\cdot 1/2H_2O$	44.29	3.19	5.29	23.30	44.64	3.35	5.42	23.06
Co_2(fsapn)$(MeOH)_2\cdot O_2\cdot 1/2H_2O$	48.39	3.93	4.90	19.70	48.87	4.10	4.96	20.00
Co_2(fsabn)$(MeOH)_2\cdot O_2\cdot 1/2H_2O$	49.17	3.02	5.02	19.60	49.40	3.06	5.01	19.28
Co_2(fsach)MeOH$\cdot 1/2H_2O$	42.36	3.68	4.53	21.00	42.75	3.93	4.75	20.85
Co_2(fsaph)MeOH$\cdot 1/2H_2O$	43.59	3.95	4.35	20.75	43.22	4.12	4.58	21.08

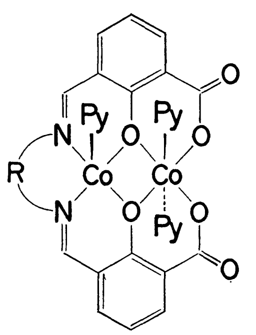

Fig. 1.

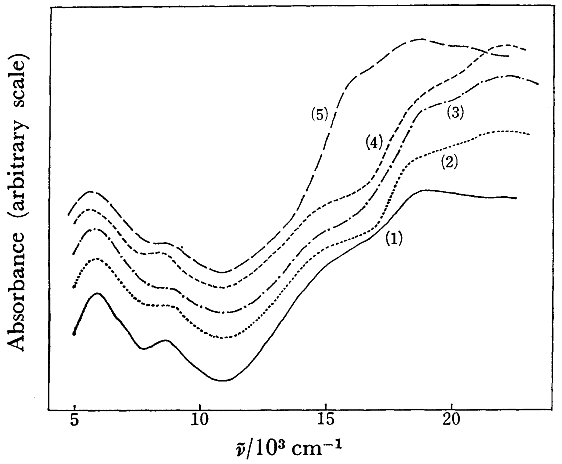

Fig. 2. Reflectance spectra of (1) Co_2(fasen)$(py)_3$, (2) Co_2(fsapn)$(py)_3$. (3) Co_2(fsabn)$(py)_3$, (4) Co_2(fsach)$(py)_3$, and (5) Co_2(fsaph)$(py)_3$.

to form Co(salen)py, where the cobalt(II) is in the low-spin state and has a tetragonal-pyramidal geometry with pyridine at the apex. Therefore, it is likely that Co_2(fsaR)$(py)_3$ has a binuclear structure composed of a low-spin tetragonal-pyramidal and a spin-free pseudo-octahedral cobalt(II) ions (Fig. 1). Coordination of pyridine was demostrated by the infrared absorption band around 700 cm^{-1}.

Reflectance spectra of Co(fsaR)$(py)_3$ are shown in Fig. 2. Each spectrum possesses several absorption bands in the region 5000—25000 cm^{-1}. The spectrum must be the superposition of the spectra of the "inside" and the "outside" cobalt(II) chromophores. Despite the difference in the apical ligands, the "outside" cobalt(II) in Co_2(fsaR)$(py)_3$ should display a spectrum similar to that of the "outside" cobalt(II) in CuCo(fsaR)$(H_2O)_{2-3}$, because pyridine does not differ much from water in the ligand field strength. In CuCo(fsaR)$(H_2O)_{2-3}$ d-d bands due to the "outside" cobalt(II) were found at 8300, 11000, and 19200 cm^{-1}.[12] On the other hand, the spectrum of the "inside" cobalt(II) in Co_2(fsaR)$(py)_3$ should be similar to that of Co(salen)py, which has d-d bands at 6000, 9000, 13500, and 16000 cm^{-1}.[16,17] Accordingly the spectra shown in Fig. 2 can be interpreted in terms of the superposition of the spectra of the five-coordinate "inside" cobalt(II) and the six-coordinate "outside" cobalt(II) ions.

Two types of complexes, Co_2(fsaR)MeOH$\cdot 1/2H_2O$ (R=en, ch, ph) and Co_2(fsaR)$(MeOH)_2\cdot O_2\cdot 1/2H_2O$ (R=pn, bn), were obtained by the reaction in methanol. The latter is tentatively assumed to be an oxygen-carrying complex, since its color turned black from red when exposed to air and its elemental analysis quite agrees with the formula shown above. It is to be noted that the oxygen-carrying complexes contain two molecules of methanol, while the complexes lacking oxygen-carrying ability contain one molecule of methanol. Since low-spin cobalt(II) complexes with the quadridentate Schiff bases usually exhibit the oxygen-carrying ability when coordinated by a base at the fifth position,[18] it is supposed that one of the methanol molecules in Co_2(fsaR)$(MeOH)_2\cdot O_2\cdot 1/2H_2O$ coordinates to the "inside" cobalt(II) ion.

Reflectance spectra of Co_2(fsaR)MeOH$\cdot 1/2H_2O$ are not well resolved and exhibit broad bands around 6000, 12000—14000, and 18000 cm^{-1}. Because of the complexity in the composition and in the visible spectra, we could not deduce a difinite structure to Co_2(fsaR)MeOH$\cdot 1/2H_2O$.

Magnetic moments of Co_2(fsaR)$(py)_3$ and Co_2(fsaR)MeOH$\cdot 1/2H_2O$ at room temperature are in the range 4.9—5.6 B.M. Since low-spin cobalt(II) and high-spin cobalt(II) (octahedral) have magnetic moments of 1.9—2.8 and 4.3—5.2 B.M.,[19] respectively, the magnetic moments expected for high-spin binuclear cobalt(II), mixed-spin binuclear cobalt(II) and low-spin binuclear cobalt(II) complexes are 6.1—7.4, 4.7—5.9, and 2.7—4.0 B.M. respectively, provided that no

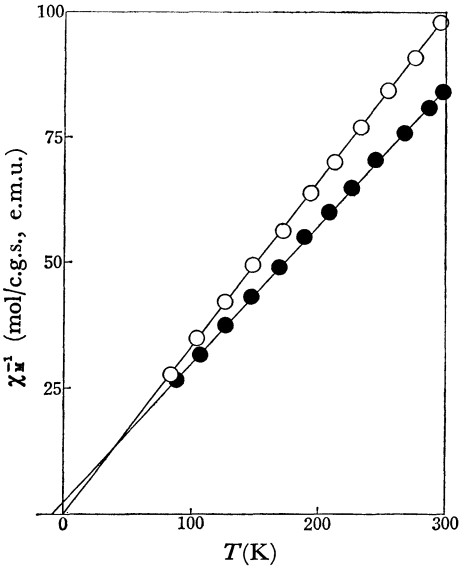

Fig. 3. Temperature variations of inverse magnetic susceptibilities of (○) Co$_2$(fsaen)(py)$_3$ and (●) Co$_2$-(fsaen)MeOH·1/2H$_2$O.

Table 2. Effective magnetic moments near liquid nitrogen temperature and at room temperature, and Weiss constant of complexes

	μ_{eff}(T) (BM)		θ (K)
Co$_2$(fsaen)(py)$_3$	4.91(82.9)	4.92(297.4)	≈0
Co$_2$(fsapn)(py)$_3$	5.32(81.2)	5.34(297.4)	≈0
Co(fsabn)(py)$_3$	5.31(90.3)	5.29(296.8)	≈0
Co$_2$(fsach)(py)$_3$	5.44(82.8)	5.58(298.3)	−8
Co$_2$(fsaph)(py)$_3$	5.24(81.7)	5.31(296.8)	−4
Co$_2$(fsaen)MeOH·1/2H$_2$O	5.18(87.4)	5.34(297.8)	−10
Co$_2$(fsach)MeOH·1/2H$_2$O	5.09(81.7)	5.15(289.3)	−3
Co$_2$(fsaph)MeOH·1/2H$_2$O	5.23(84.6)	5.34(296.6)	−4

spin-exchange interaction is operating between the cobalt(II) ions. Thus, the present complexes may be mixed-spin binuclear complexes or magnetically coupled high-spin binuclear complexes. As already mentioned above electronic spectra of Co$_2$(fsaR)(py)$_3$ are in favor of a mixed-spin binuclear structure. Mixed-spin state for Co$_2$(fsaR)(py)$_3$ as well as Co$_2$(fsaR)-MeOH·1/2H$_2$O was further demonstrated by the magnetic susceptibility measurements down to liquid nitrogen temperature. Plots of inverse magnetic susceptibility *versus* temperature obey the Curie law or the Curie-Weiss law with a very small negative Weiss constant; some representatives of the $1/\chi_M$ *vs.* T plot being shown in Fig. 3. In Table 2 the magnetic moments at room temperature and near liquid nitrogen temperature and the Weiss constants determined by the Curie-Weiss plot are given. It is evident that the magnetic moments of the present complexes are almost independent on the temperature. Thus, it is concluded that Co$_2$(fsaR)(py)$_3$ and Co$_2$(fsaR)MeOH·1/2H$_2$O are mixed-spin binuclear complexes and no spin-exchange interaction is operating between the low-spin and the high-spin cobalt(II) ions.

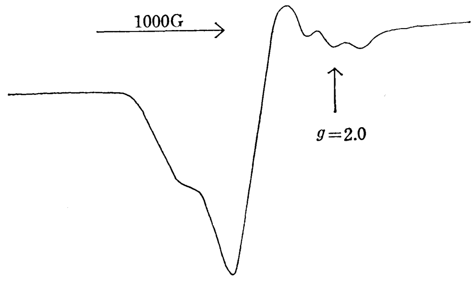

Fig. 4. ESR spectrum of CoMg(fsaen)(py)$_3$ (in DMF at liq. nitrogen temperature).

Since a considerably strong antiferromagnetic spin-exchange interaction was observed for CuCo(fsaR)-(H$_2$O)$_{2-3}$,$^{11,12)}$ the difference in magnetic exchange interaction between the Cu(II) (s=1/2)-Co(II) (s=3/2) and the Co(II) (s=1/2)-Co(II) (s=3/2) systems may be attributed to the difference in the ground-state electronic configuration between copper(II) and low-spin cobalt(II) ions. In general copper(II) has an unpaired electron on $d_{x^2-y^2}$ orbital (x and y axes are taken on the donating atoms in the tetragonal plane). On the other hand, in low-spin cobalt(II) complexes an unpaired electron is in either a d_{yz} or d_{z^2} orbital. It is known that in Co(salen) an unpaired electron occupies d_{yz} orbital, while Co(salen)py has the ground-state electron configuration in which an unpaired electron occupies d_{z^2} orbital.$^{17,20-22)}$ The main difference between the "inside" cobalt(II) of Co$_2$(fsaR)(py)$_3$ and Co(salen)py is in the donating phenolic oxygen; a bridging oxygen in the former while a simply donating oxygen in the latter. It is unlikely that a considerable change in the electronic configuration is brought about when the phenolic oxygen acts as a bridge.

In order to determine precisely the electronic configuration of the "inside" cobalt(II) ion, we measured ESR spectra of Co$_2$(fsaR)(py)$_3$ and their related complex, CoMg(fsaen)(py)$_3$. Although no ESR signal was detected for Co$_2$(fsaR)(py)$_3$ owing to the "outside" high-spin cobalt(II) ion, an *N,N*-dimethylformamide solution of CoMg(fsaen)(py)$_3$ displayed a well defined ESR spectrum, in which g_x, g_y, and g_z are found to be *ca.* 2.40, 2.25, and 2.00, respectively (Fig. 4). Three-lined hyperfine structure with hyperfine splitting constant of *ca.* 90 G around g=2.00 clearly indicates that pyridine is coordinated to the "inside" cobalt(II) ion. This ESR spectrum is quite similar to the spectrum of Co(salen)py$^{17)}$ and can be interpreted in terms of a d_{z^2} ground-state electronic configuration. Based on these facts we may conclude that the "inside" cobalt(II) ion in Co$_2$(fsaR)(py)$_3$ has an unpaired electron in d_{z^2} orbital. Thus, it is presumed that no spin-exchange interaction in Co$_2$(fsaR)(py)$_3$ and Co$_2$(fsaR)MeOH·1/2H$_2$O is attributed to a negligibly small overlapping between the metal d_{z^2} orbital and the bridging oxygen orbital.$^{23)}$

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