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# Antiferromagnetic Spin-exchange Interaction in Mixed-spin Trinuclear Cobalt(II) Complexes with Quadridentate Schiff Bases[1)]

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Trinuclear cobalt(II) complexes, $[Co(R_1,R_2\text{-}L)]_2CoX_2$ ($R_1$, $R_2$=H, Me; L=en, ch, ph; X=$Cl^-$, $Br^-$), have been synthesized, where $H_2(R_1,R_2\text{-}L)$ denotes the Schiff bases obtained by condensing a 5($R_1$), α($R_2$)-substituted salicylaldehyde with a diamine ($H_2N\text{-}L\text{-}NH_2$) in a 2:1 mole ratio. From IR spectra and cryomagnetic properties, it was concluded that these complexes are in mixed-spin state of a Co(II)($s$=1/2)–Co(II)($s$=3/2)–Co(II)($s$=1/2) system, strong antiferromagnetic spin-exchange interaction operating between low-spin and high-spin cobalt(II) ion *via* $d_\pi$(low-spin Co)-$p_\pi$(O)-$d_\pi$(high-spin Co) super pathway.

Low-spin cobalt(II) complexes have an electronic configuration of either $(d_{x^2-y^2})^2(d_{z^2})^1$ or $(d_{x^2-y^2})^2(d_{yz})^1$. In mixed-spin polynuclear cobalt(II) complexes in which high-spin and low-spin cobalt(II) ions are kept in close distance, spin-exchange interaction between the cobalt(II) ions would markedly depend upon the electronic structure of the low-spin cobalt(II) ion. We obtained mixed-spin binuclear cobalt(II) complexes, $Co_2(fsaR)(py)_3$, with *N,N'*-bis(3-carboxysalicylidene)alkanediamine($H_4$fsaR) and demonstrated that no spin-exchange interaction operates between the metal ions.[2)] In these complexes low-spin cobalt(II) has an unpaired electron on the $d_{z^2}$ orbital. Thus, it is worth while to examine spin-exchange interaction in mixed-spin polynuclear cobalt(II) complexes in which low-spin cobalt(II) has an unpaired electron on the $d_{yz}$ orbital. However, no such mixed-spin polynuclear cobalt(II) complexes have yet been obtained.

Sinn and Harris[3)] synthesized mixed-metal trinuclear complexes of Cu(II)–M(II)–Cu(II) (M(II)=Cu(II), Ni(II), Co(II), Fe(II), Mn(II)) system by reacting copper(II) complexes of *N,N'*-disalicylideneethylenediamine or its homologues with an M(II) ion in a 2 : 1 mole ratio. Since the electronic structure of Co(salen) and its homologues was recently demonstrated to be $(d_{x^2-y^2})^2(d_{yz})^1$[1,4,5)] we have attempted to prepare Co(II)($s$=1/2)–Co(II)($s$=3/2)–Co(II)($s$=1/2) complexes with the quadridentate Schiff bases in order to investigate their magnetic property in connection with the electronic configuration of the low-spin cobalt(II) ion.

*N,N'*-Disalicylidenealkanediamines are abbreviated to $H_2(R_1, R_2\text{-}L)$ ($R_1$, $R_2$=H, Me; L=en, ch, ph), where $R_1$ and $R_2$ denote the substituents attached to the 5- and α-positions of salicylaldehyde moiety, respectively, and L denotes the chain combining the two nitrogen atoms.

## Experimental

*Preparation of Complexes.* Co(H,H-en) was synthesized by the method of Bailes and Calvin.[6)] Other mononuclear cobalt(II) complexes were obtained in a similar way. The syntheses of all the trinuclear complexes, $[Co(R_1,R_2\text{-}L)]_2CoX_2$, were nearly the same and are exemplified by that of $[Co(H,H\text{-}en)]_2CoCl_2$ as follows.

Co(H,H-en) (500 mg) and $CoCl_2\cdot6H_2O$ (219 mg) were dissolved in ethanol (100 ml) and the mixture was refluxed for *ca.* 2 h to give red-brown crystals. After the reaction mixture had been allowed to stand overnight, crystals were collected by filtration, washed with a small amount of ethanol and dried under reduced pressure. All operations were carried out in a nitrogen atmosphere by means of a VAC inert atmosphere & vacuum deposition equipment Model HE-43-2. Elemental analyses of $[Co(R_1,R_2\text{-}L)]_2CoX_2$ are given in Table 1.

*Measurements.* Elemental analyses of carbon, hydrogen, and nitrogen were carried out at the Elemental Analysis Service Center, Kyushu University. Cobalt analyses were carried out with a Shimadzu atomic absorption-flame spectrophotometer Model 610S. The standard solution was prepared by decomposing Co(H,H-en) with nitric acid and diluting the decomposed mixture with water in a volumetric flask. Solutions of samples were also prepared by the same method. IR spectra were measured in the range 4000—650 $cm^{-1}$ with a Hitachi infrared spectrophotometer Model 215 on a KBr disk. Magnetic susceptibilities were measured by the Faraday method in the temperature range 78—300 K, the apparatus being calibrated with $HgCo(NCS)_4$.[7)] Effective magnetic moments were calculated by the equation, $\mu_{eff}=2.828(\chi_M\times T)^{1/2}$, in which $\chi_M$

Table 1. Elemental analyses of complexes

| | Found (%) | | | | Calcd (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | Co | C | H | N | Co |
| $[Co(H,H\text{-}en)]_2CoCl_2$ | 49.04 | 3.54 | 7.08 | 22.65 | 49.25 | 3.61 | 7.15 | 22.65 |
| $[Co(H,H\text{-}en)]_2CoBr_2$ | 44.02 | 3.26 | 6.37 | 20.33 | 44.21 | 3.24 | 6.44 | 20.34 |
| $[Co(Me,Me\text{-}en)]_2CoCl_2$ | 53.77 | 4.94 | 6.24 | 19.96 | 53.83 | 4.96 | 6.27 | 19.81 |
| $[Co(Me,Me\text{-}en)]_2CoBr_2$ | 48.72 | 4.50 | 5.61 | 17.89 | 48.95 | 4.51 | 5.70 | 18.01 |
| $[Co(H,Me\text{-}en)]_2CoBr_2$ | 46.66 | 4.18 | 6.11 | 19.11 | 46.73 | 3.92 | 6.05 | 19.10 |
| $[Co(H,H\text{-}ph)]_2CoBr_2$ | 49.96 | 2.92 | 5.88 | 18.30 | 49.77 | 2.92 | 5.80 | 18.31 |
| $[Co(H,H\text{-}ch)]_2CoBr_2$ | 49.17 | 4.22 | 5.61 | 17.91 | 49.15 | 4.12 | 5.73 | 18.09 |

TABLE 2. COLOR AND IR SKELETAL BAND ($\mathrm{cm}^{-1}$) OF COMPLEXES

| | Color | Skeletal[a] |
|---|---|---|
| $[\mathrm{Co(H,H\text{-}en)}]_2\mathrm{CoCl}_2$ | reddish brown | 1550 (1530) |
| $[\mathrm{Co(H,H\text{-}en)}]_2\mathrm{CoBr}_2$ | orange | 1548 (1530) |
| $[\mathrm{Co(Me,Me\text{-}en)}]_2\mathrm{CoCl}_2$ | deep-orange | 1540 (1515) |
| $[\mathrm{Co(Me,Me\text{-}en)}]_2\mathrm{CoBr}_2$ | orange | 1540 (1515) |
| $[\mathrm{Co(H,Me\text{-}en)}]_2\mathrm{CoBr}_2$ | deep-orange | 1540 (1515) |
| $[\mathrm{Co(H,H\text{-}ph)}]_2\mathrm{CoBr}_2$ | black | 1520 (1520) |
| $[\mathrm{Co(H,H\text{-}ch)}]_2\mathrm{CoBr}_2$ | orange | 1540 (1530) |

a) Value in parentheses is the skeletal vibration for $\mathrm{Co(R_1,R_2\text{-}L)}$.

is molar magnetic susceptibility corrected for diamagnetism for all the constituent atoms by the use of Pascal's constants.[8]

## Results and Discussion

Color and IR skeletal band near 1550 $\mathrm{cm}^{-1}$ are given in Table 2. A skeletal band at 1515—1530 $\mathrm{cm}^{-1}$ found for $\mathrm{Co(R_1,R_2\text{-}L)}$ shifts to higher frequency (1540—1550 $\mathrm{cm}^{-1}$) in $[\mathrm{Co(R_1,R_2\text{-}L)}]_2\mathrm{CoX}_2$, except for the complex with $\mathrm{H_2(H,H\text{-}ph)}$. The shift of the skeletal vibration to higher frequency was elucidated by Sinn *et al.*[9–12] for binuclear copper(II) complexes and is used for diagnosis of a bridging mode of phenolic oxygen in homometal polynuclear complexes,[13–18] mixed-metal polynuclear complexes[19] and Cu(II)–Cu(I) mixed-spin complexes.[20] It is likely that in the present complexes metal ions are bridged by the phenolic oxygens. Except for this skeletal band, each IR spectrum of $[\mathrm{Co(R_1,R_2\text{-}L)}]_2\mathrm{CoX}_2$ resembles that of the corresponding $\mathrm{Co(R_1,R_2\text{-}L)}$.

The complexes are insoluble in most nonpolar organic solvents. They are soluble in polar solvents such as pyridine and dimethyl sulfoxide, but they decompose in these solvents. Reflectance spectra of the complexes were not well resolved. No information was available on the structure of the complexes from the electronic spectra.

As pointed out by Gruber *et al.*,[21] steric requirement of $\mathrm{Co(R_1,R_2\text{-}L)}$ as a bidentate ligand is nearly the same as that of 2,2′-biquinolyl (biq). Because of the steric hindrance between hydrogens attached to the 8-position, two 2,2′-biquinolyl molecules can not coordinate to a metal ion in a plane; *e.g.*, the coordination geometry of $[\mathrm{Cu(biq)_2}](\mathrm{ClO_4})_2$ is pseudo-tetrahedral.[22] For the same reason, two molecules of $\mathrm{M(R_1,R_2\text{-}L)}$ should assume a pseudo-tetrahedral or cis-octahedral coordination because of the steric repulsion between the hydrogens attached to the 3-position of salicylaldehyde moiety. In fact, the configurations of $\mathrm{Na^+}$ in $[\mathrm{Cu(H,H\text{-}en)}]_2\mathrm{NaClO_4}$[23] and the central copper(II) in $[\mathrm{Cu(R_1,R_2\text{-}L)}]_2\mathrm{Cu(H_2O)_2(ClO_4)_2}$[24] are cis-octahedral. Thus, we assume that the present complexes have the structure shown in Fig. 1.

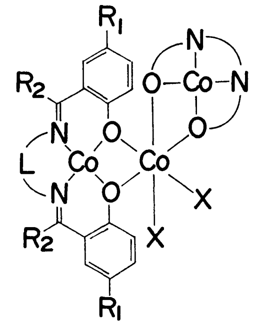

Fig. 1. Probable structure of $[\mathrm{Co(R_1,R_2\text{-}L)}]_2\mathrm{CoX}_2$.

Magnetic susceptibilities of the complexes were measured in the range from liquid nitrogen temperature to room temperature. Magnetic susceptibilities and magnetic moments at various temperatures are given in Table 3. Magnetic moments per molecule at room temperature fall in the range 5.83—6.02 BM, the moments decreasing with lowering of temperature. Since magnetic moments for mononuclear high-spin cobalt(II) (octahedral) and for mononuclear low-spin cobalt(II) complexes are known to be 4.5—5.2 and 2.0—2.8 BM, respectively,[25] the magnetic moment for a magnetically non-interacting Co(II)($s$=1/2)–Co(II)($s$=3/2)–Co(II)($s$=1/2) mixed-spin system is estimated at 5.33—6.54 BM by the equation $\mu_M{}^2=\sum\mu_i{}^2$. The observed magnetic moments of $[\mathrm{Co(R_1,\ R_2\text{-}L)}]_2\mathrm{CoX}_2$ at room temperature fall in this range. On the other hand, moments near liquid nitrogen temperature are close to or less than the lowest limit 5.33 BM. Thus it is likely that $[\mathrm{Co(R_1,R_2\text{-}L)}]_2\mathrm{CoX}_2$ are mixed-spin trinuclear complexes, in which an antiferromagnetic spin-exchange interaction operates between the low-spin and high-spin cobalt(II) ions.

Molar magnetic susceptibility for Co(II)($s$=1/2)–Co(II)($s$=3/2)–Co(II)($s$=1/2) system is given by

$$\chi_M = \frac{Ng^2\beta^2}{4kT}\cdot\frac{35+10\exp(-3J/kT)+10\exp(-5J/kT)+\exp(-8J/kT)}{3+2\exp(-3J/kT)+2\exp(-5J/kT)+\exp(-8J/kT)}+N\alpha,$$

which was first derived Gruber *et al.* for Cu(II)–Co(II) ($s$=3/2)–Cu(II) system.[26] In this equation $J$ is the exchange integral between the low-spin and high-spin cobalt(II) ions and other symbols have their usual meanings, spin-exchange interaction between the terminal low-spin cobalt(II) ions being neglected. Magnetic susceptibilities for $[\mathrm{Co(R_1,R_2\text{-}L)}]_2\mathrm{CoX}_2$ can be explained by means of this equation. In Fig. 2 the best fit between empirical and theoretical inverse magnetic susceptibilities for $[\mathrm{Co(H,H\text{-}en)}]_2\mathrm{CoCl}_2$ is shown as an example. Magnetic parameters, $J$ and $g$, obtained for $[\mathrm{Co(R_1,R_2\text{-}L)}]_2\mathrm{CoX}_2$ are given in Table 4; temperature independent paramagnetism, $N\alpha$, being estimated at $500\times10^{-6}$ c.g.s./mol. It is evident that an antiferromagnetic spin-exchange interaction operates between low-spin and high-spin cobalt(II) ions. The exchange integrals (−10— −14 $\mathrm{cm}^{-1}$) are appreciably large and comparable to the value ($J$=−16— −24 $\mathrm{cm}^{-1}$) found for the Cu(II)–Co(II)($s$=3/2)–Cu(II) complexes.[3,26]

TABLE 3. TEMPERATURE VARIATIONS OF MAGNETIC SUSCEPTIBILITY AND MAGNETIC MOMENT

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $[Co(H,H\text{-}en)]_2CoCl_2$ | | | | | | | | | | | | |
| $T$ (K) | 78.8 | 98.3 | 120.2 | 141.5 | 162.7 | 185.3 | 207.7 | 229.9 | 250.7 | 274.3 | 296.6 | |
| $\chi_M \times 10^6$ | 39045 | 33566 | 29383 | 26176 | 23380 | 21629 | 19698 | 18184 | 16882 | 15636 | 14476 | |
| $\mu_{eff}$ | 4.96 | 5.14 | 5.31 | 5.44 | 5.52 | 5.66 | 5.72 | 5.78 | 5.82 | 5.86 | 5.86 | |
| $[Co(H,H\text{-}en)]_2CoBr_2$ | | | | | | | | | | | | |
| $T$ (K) | 81.2 | 101.5 | 119.8 | 139.9 | 159.7 | 178.9 | 199.6 | 219.6 | 238.7 | 259.2 | 279.1 | 298.3 |
| $\chi_M \times 10^6$ | 36829 | 31339 | 28023 | 25551 | 23416 | 22076 | 20504 | 18956 | 17616 | 16407 | 15357 | 14461 |
| $\mu_{eff}$ | 4.89 | 5.04 | 5.18 | 5.35 | 5.47 | 5.62 | 5.72 | 5.77 | 5.80 | 5.83 | 5.85 | 5.87 |
| $[Co(Me,Me\text{-}en)]_2CoCl_2$ | | | | | | | | | | | | |
| $T$ (K) | 82.9 | 103.5 | 129.1 | 149.4 | 169.9 | 190.3 | 213.7 | 235.6 | 257.4 | 275.5 | 297.1 | |
| $\chi_M \times 10^6$ | 44703 | 37226 | 30460 | 26962 | 24218 | 21908 | 19961 | 18355 | 16948 | 15969 | 14868 | |
| $\mu_{eff}$ | 5.44 | 5.55 | 5.61 | 5.68 | 5.74 | 5.77 | 5.84 | 5.88 | 5.91 | 5.93 | 5.94 | |
| $[Co(Me,Me\text{-}en)]_2CoBr_2$ | | | | | | | | | | | | |
| $T$ (K) | 83.4 | 103.0 | 122.5 | 142.0 | 161.6 | 180.2 | 199.9 | 219.3 | 238.7 | 258.4 | 278.1 | 297.4 |
| $\chi_M \times 10^6$ | 43780 | 37598 | 32536 | 29103 | 25922 | 23706 | 21771 | 20202 | 18735 | 17281 | 16253 | 15229 |
| $\mu_{eff}$ | 5.40 | 5.57 | 5.65 | 5.75 | 5.79 | 5.85 | 5.90 | 5.93 | 5.98 | 5.98 | 6.01 | 6.02 |
| $[Co(H,Me\text{-}en)]_2CoBr_2$ | | | | | | | | | | | | |
| $T$ (K) | 81.1 | 100.9 | 120.2 | 139.5 | 159.7 | 179.5 | 199.2 | 219.0 | 238.4 | 258.7 | 278.1 | 297.8 |
| $\chi_M \times 10^6$ | 42937 | 36726 | 32319 | 28634 | 25587 | 23299 | 21233 | 19512 | 18135 | 16887 | 15811 | 14864 |
| $\mu_{eff}$ | 5.28 | 5.44 | 5.57 | 5.65 | 5.72 | 5.78 | 5.82 | 5.85 | 5.88 | 5.91 | 5.93 | 5.95 |
| $[Co(H,H\text{-}ph)]_2CoBr_2$ | | | | | | | | | | | | |
| $T$ (K) | 84.6 | 103.3 | 123.3 | 142.8 | 162.7 | 181.9 | 201.4 | 221.1 | 240.4 | 259.5 | 278.1 | 298.0 |
| $\chi_M \times 10^6$ | 40159 | 34940 | 30377 | 27201 | 24540 | 22172 | 20342 | 18750 | 17357 | 16204 | 15209 | 14254 |
| $\mu_{eff}$ | 5.21 | 5.36 | 5.47 | 5.57 | 5.65 | 5.68 | 5.72 | 5.76 | 5.78 | 5.80 | 5.82 | 5.83 |
| $[Co(H,H\text{-}ch)]_2CoBr_2$ | | | | | | | | | | | | |
| $T$ (K) | 82.3 | 102.0 | 127.8 | 147.5 | 166.3 | 186.9 | 210.7 | 232.7 | 256.0 | 274.3 | 296.1 | |
| $\chi_M \times 10^6$ | 44780 | 36999 | 30281 | 26574 | 23960 | 21754 | 19607 | 17978 | 16539 | 15611 | 14658 | |
| $\mu_{eff}$ | 5.43 | 5.49 | 5.56 | 5.60 | 5.65 | 5.70 | 5.75 | 5.78 | 5.82 | 5.85 | 5.89 | |

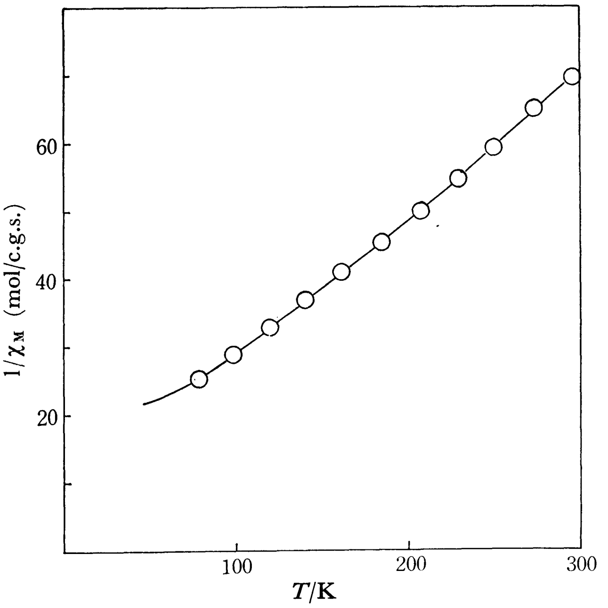

Fig. 2. Temperature variation of inverse molar magnetic susceptibility of $[Co(H,H\text{-}en)]_2CoCl_2$. The solid line represents the theoretical susceptibility with $J=-14\ cm^{-1}$, $g=2.68$ and $N\alpha=500\times10^{-6}$ c.g.s./mol.

TABLE 4. MAGNETIC PARAMETERS FOR COMPLEXES

| | $-J$ ($cm^{-1}$) | $g$ |
|---|---|---|
| $[Co(H,H\text{-}en)]_2CoCl_2$ | 14 | 2.68 |
| $[Co(H,H\text{-}en)]_2CoBr_2$ | 14 | 2.65 |
| $[Co(Me,Me\text{-}en)]_2CoCl_2$ | 12 | 2.78 |
| $[Co(Me\text{-}en)]_2CoBr_2$ | 12 | 2.78 |
| $[Co(H,Me\text{-}en)]_2CoBr_2$ | 12 | 2.71 |
| $[Co(H,H\text{-}ph)]_2CoBr_2$ | 12 | 2.66 |
| $[Co(H,H\text{-}ch)]_2CoBr_2$ | 10 | 2.65 |

$N\alpha$ is estimated at $500\times10^{-6}$ c.g.s./mol.

We showed that no spin-exchange interaction operates between low-spin and high-spin cobalt(II) ions in $Co_2(fsaR)(py)_3$.[2] In these complexes low-spin cobalt(II) ion has an unpaired electron on its $d_{z^2}$ orbital. The absence of magnetic interaction may be attributed to a negligibly small overlapping between the cobalt $d_{z^2}$ orbital and the oxygen orbital. Thus, it is important to determine the ground-state electronic configuration of the low-spin cobalt(II) in antiferromagnetic $[Co(R_1,R_2\text{-}L)]_2CoX_2$. Since $[Co(R_1,R_2\text{-}L)]_2CoX_2$ shows no well-defined ESR signal owing to high-spin cobalt(II) ion, it is desirable to prepare a complex of Co(II)($s=1/2$)–M(II)–Co(II)($s=1/2$) system, in which the central cobalt(II) is replaced by a diamagnetic M(II) ion. However, we were unsuccessful in obtaining $[Co(R_1,R_2\text{-}L)]_2MX_2$. Thus, the electronic structure of the low-spin cobalt(II) was surmised by considering binuclear complexes related to the present complexes. It was shown[20] that Cu($R_1$,$R_2$-L) and [$Cu_2$($R_1$,$R_2$-L)$CH_3$CN]$ClO_4$ (Cu(II)–Cu(I) complex bridged by the phenolic oxygen) show ESR spectra displaying substantially identical $g_\parallel$, $g_\perp$, and $A_\parallel$ values. This indicates that the electronic property of Schiff base complexes coordinated to another metal as a bidentate ligand is almost the same as that of the original mononuclear complexes, M($R_1$,$R_2$-L). This is in line with the fact that in binuclear complexes of this type the distance between the phenolic oxygen and the metal bound to the $N_2O_2$-donating site is nearly the same as that for the original Schiff base complex M($R_1$,$R_2$-L), while the distance between the phenolic oxygen and the second metal is much elongated.[27,28] A similar trend in bond distance is observed for the binuclear complexes with 1,3,5-triketone-diamine Schiff bases.[29–31] Recently we have found that the electronic spectrum of [Co($R_1$,$R_2$-L)]$_2$Mn$X_2$ is almost the same as that of Co($R_1$,$R_2$-L).[32] Thus, it is concluded that the electronic property of the low-spin cobalt(II) in [Co($R_1$,$R_2$-L)]$_2$Co$X_2$ is the same as that of Co($R_1$,$R_2$-L), where an unpaired electron occupies $d_{yz}$ orbital. Since high-spin cobalt(II) has unpaired electrons in $d_{x^2-y^2}$, $d_{z^2}$ and one of the $d_\pi$ orbitals, we may conclude that in the present complexes $d_\pi$(low-spin Co)-$p_\pi$(O)-$d_\pi$(high-spin Co) super pathway plays an important role in antiferromagnetic spin-exchange interaction.

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