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Synthesis and Magnetism of Cobalt(II)–Manganese(II)–Cobalt(II) Trinuclear Complexes with *N,N'*-Disalicylidenealkanediamines

Visit Kasempimolporn, Hisashi Okawa,* and Sigeo Kida

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

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Synopsis. Cobalt(II)–manganese(II)–cobalt(II) trinuclear complexes were synthesized by reacting *N,N'*-disalicylidenealkanediaminatocobalt(II) and manganese(II) halide in a 2:1 mole ratio. Cryomagnetic measurements indicated an antiferromagnetic spin-exchange interaction operating between the low-spin cobalt(II) and the high-spin manganese(II) ions, exchange integrals being estimated at −8—−12 cm^{-1}.

Recently we have reported the preparation and the characterization of the mixed-spin trinuclear cobalt(II) complexes with *N,N'*-disalicylideneethylenediamine and its homologues.[1] A considerably strong antiferromagnetic spin-exchange interaction (J=−10—−14 cm^{-1}) in these complexes prompted us to synthesize new trinuclear complexes of Co(II)(s=1/2)–Mn(II)(s=5/2)–Co(II)(s=1/2) system in order to obtain further informations of spin-exchange in polynuclear complexes containing low-spin cobalt(II) ion.

N,N'-Disalicylidenealkanediamines are abbreviated as $H_2(R_1,R_2\text{-L})$ (R_1,R_2=H, CH_3; L=en, pn), where R_1 and R_2 denote the substituents attached to the 5- and the α-positions of salicylaldehyde moiety, respectively, and L is the chain connecting two imino-nitrogens.

Experimental

Syntheses. Mononuclear cobalt(II) complexes were obtained by the method of Bailes and Calvin.[2] Syntheses of the trinuclear complexes are practically the same and exemplified by $[Co(H,H\text{-en})]_2MnBr_2$. A mixture of Co(H,H-en) (500 mg) and manganese(II) bromide tetrahydrate (287 mg) in ethanol (80 ml) was stirred for 3 h under reflux in an atmosphere of nitrogen and allowed to stand overnight. Orange crystals which separated were collected by suction, washed with ethanol and dried.

Elemental analyses of the complexes are given in Table 1.

Measurements. Electronic spectra of powder samples were measured with a Shimadzu multipurpose spectrophotometer Model MSP-5000. Infrared spectra were measured with a Hitachi grating infrared spectrophotometer Model 215 in the region 4000—650 cm^{-1} on a KBr disk. Magnetic susceptibilities were measured by the Faraday method over the range from liquid nitrogen temperature to room temperature. Effective magnetic moments were calculated from the equation, $\mu_{\text{eff}}=2.828(\chi_M \cdot T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for diamagnetisms using Pascal's constants.

Table 1. Elemental analyses of complexes

	Found (%)					Calcd (%)				
	C	H	N	Co	Mn	C	H	N	Co	Mn
$[Co(H,H\text{-en})]_2MnBr_2$	44.38	3.32	6.41	13.89	6.13	44.42	3.26	6.47	13.62	6.34
$[Co(H,Me\text{-en})]_2MnCl_2$	51.74	4.49	6.60	14.76	6.55	51.94	4.35	6.73	14.16	6.60
$[Co(Me,Me\text{-en})]_2MnCl_2$	53.50	4.96	6.17	12.82	6.23	54.07	4.99	6.30	13.26	6.18
$[Co(H,H\text{-pn})]_2MnBr_2$	45.43	3.53	6.19	13.70	6.40	45.71	3.61	6.27	13.19	6.15

Results and Discussion

Infrared spectra of the complexes display a skeletal vibration around 1530—1545 cm^{-1}, which is higher in frequency compared with that of the mononuclear cobalt(II) complexes. The high-frequency shift of this band has been utilized as a diagnosis of the bridging mode of the phenolic oxygen.[3] The similarity in infrared spectrum between $[Co(R_1,R_2\text{-L})]_2MnX_2$ and $[Co(R_1,R_2\text{-L})]_2CoX_2$[1] are indicative of the same structure between them. Since two molecules of $Co(R_1,R_2\text{-L})$ can not coordinate to a metal in a square plane because of the steric requirement of the molecule,[1,4,5] the most likely structure of the trinuclear complexes is *cis*-octahedral around the central manganese(II) ion (Fig. 1).

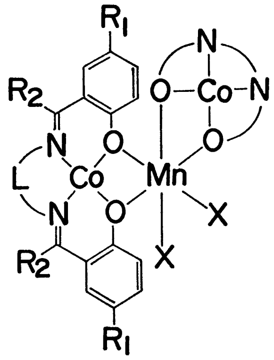

Fig. 1. Probable structure of $[Co(R_1,R_2\text{-L})]_2MnX_2$.

Powder reflectance spectra of the trinuclear complexes are nearly the same as those of the mononuclear cobalt(II) complexes except for Co(H,H-en), showing d-d bands at 8000 and 19000 cm^{-1}. Monomeric square-planar[6] and dimeric square-pyramidal[7] modifications are known for Co(H,H-en), and the electronic spectra of the present complexes are substantially the same as that of monomeric Co(H,H-en).[8] Since high-spin manganese(II) complexes show no spin-allowed d-d bands, the electronic spectra indicate that the electronic configuration of the low-spin cobalt(II) in $[Co(R_1,R_2\text{-L})]_2MnX_2$ is identical with that of Co(H,H-en), whose $(d_{x^2-y^2})^2(d_{yz})^1$ ground state electronic configuration was already demonstrated.[9,10]

Magnetic moments of the trinuclear complexes depend upon temperature (Table 2). This fact can be attributed to an antiferromagnetic spin-exchange interaction between the cobalt(II) and the manganese(II) ions. Molar magnetic susceptibility for the Co(II)(s=1/2)–Mn(II)(s=5/2)–Co(II)(s=1/2) system is given by

TABLE 2. TEMPERATURE VARIATION OF MOLAR MAGNETIC SUSCEPTIBILITY (c.g.s./mol) AND MOLAR MAGNETIC MOMENT(B.M.)

$[Co(H,H\text{-}en)]_2MnBr_2$												
T/K	81.1	95.1	115.6	135.4	155.6	176.2	196.1	216.7	236.5	256.3	276.6	296.6
$\chi_M \times 10^6$	53664	46543	40131	35006	31399	28307	25993	23814	22180	20721	19379	18212
μ_{eff}	5.90	5.97	6.09	6.16	6.25	6.32	6.38	6.42	6.48	6.52	6.55	6.57
$[Co(H,Me\text{-}en)]_2MnCl_2$												
T/K	82.8	102.5	122.5	141.9	161.3	180.9	200.5	219.6	239.5	258.4	278.3	297.6
$\chi_M \times 10^6$	46261	38907	34559	30764	28380	25808	23943	22308	20707	19492	18250	17223
μ_{eff}	5.53	5.65	5.82	5.91	6.05	6.11	6.20	6.26	6.30	6.35	6.37	6.40
$[Co(Me,Me\text{-}en)]_2MnCl_2$												
T/K	81.7	93.0	113.2	134.5	154.4	175.1	195.1	215.5	236.1	256.8	277.3	297.1
$\chi_M \times 10^6$	54620	50750	43996	38064	34415	30841	27750	25375	23262	21468	19973	18776
μ_{eff}	5.97	6.14	6.31	6.40	6.52	6.57	6.58	6.61	6.63	6.64	6.66	6.68
$[Co(H,H\text{-}pn)]_2MnBr_2$												
T/K	83.4	102.0	121.1	140.7	160.0	179.2	198.3	217.3	237.6	256.5	276.3	296.1
$\chi_M \times 10^6$	50857	42979	37638	33150	29946	27335	25193	23312	21693	20230	19133	17984
μ_{eff}	5.82	5.92	6.04	6.11	6.19	6.26	6.32	6.37	6.42	6.44	6.50	6.53

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \times \frac{35+10\exp(-7J/kT)+35\exp(-2J/kT)+84\exp(5J/kT)}{3+2\exp(-7J/kT)+3\exp(-2J/kT)+4\exp(5J/kT)} + N\alpha,$$[11)]

where J is the exchange integral between the low-spin cobalt(II) and the high-spin manganese(II) ions and other symbols have their usual meanings. This expression is applicable to the present complexes. Agreement between the theoretical and the experimental χ_M *versus* T curves is satisfactory. An example of this is shown in Fig. 2. The magnetic parameters, g and J, were determined by the best fit technique on estimating the temperature-independent paramagnetism, $N\alpha$, at 120×10^{-6} c.g.s./mol. The results are as follows. $[Co(H,H\text{-}en)]_2MnBr_2$: g=2.13, J=−10; $[Co(H,Me\text{-}en)]_2MnCl_2$: g=2.12, J=−12; $[Co(Me,Me\text{-}en)]_2MnCl_2$: g=2.14, J=−8; $[Co(H,H\text{-}pn)]_2MnBr_2$: g=2.13, J=−11 cm^{-1}.

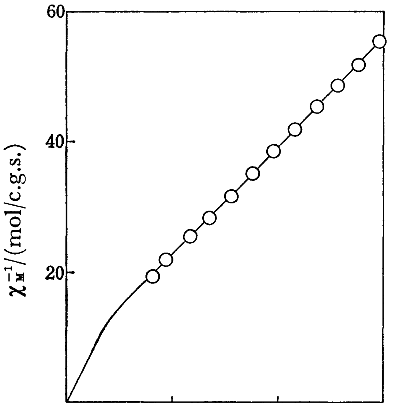

Fig. 2. Temperature variation of inverse molar magnetic susceptibility of $[Co(H,H\text{-}en)]_2MnBr_2$. The solid line represents the theoretical inverse susceptibility with $J=-10\ cm^{-1}$, g=2.13 and $N\alpha = 120 \times 10^{-6}$ c.g.s./mol.

The present complexes quite differ from the cobalt(II)–manganese(II) complexes, $CoMn(fsaR)(py)_3$,[12)] in magnetic property (where H_4fsaR represents N,N'-bis(3-carboxysalicylidene)alkanediamines). In CoMn(fsaR)$(py)_3$ the low-spin cobalt(II) ion possesses an unpaired electron in its d_{z^2} orbital and no spin-exchange interaction is operating between the metal ions. Thus, we may conclude that an antiferromagnetic spin-exchange interaction in the present complexes results from the π-superpathway of $d_\pi(Co)$-$p_\pi(O)$-$d_\pi(Mn)$ overlapping.

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