Mixed Complexes with Bulky Ligands. I. Cobalt(II) Complexes Containing *N,N*-Bis[2-(dimethylamino)ethyl]methylamine

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Nine new cobalt(II) complexes were prepared which contained *N,N*-bis[2-(dimethylamino)ethyl]methylamine (dienMe) and some unidentate or bidentate ligands, such as acetonitrile, ammonia, ethylenediamine (en), trimethylenediamine (tn), the acetylacetonate ion (acac), or the oxalate ion. The solid-reflectance spectra revealed that six complexes of the $[Co(XX)dienMe](ClO_4)_n$ formula ($XX=2CH_3CN$, $2NH_3$, en, tn, acac, or $1/2C_2O_4$; $n=1$ or 2) are five-coordinated, whereas three complexes, $[Co(C_2O_4)(H_2O)dienMe]$ and $Co(C_2O_4)_{1/2}(solv)(dienMe)ClO_4$ ($solv=CH_3CN$ or CH_3OH), are six-coordinated. On the basis of their electronic spectra, most of the five-coordinated complexes were supposed to have a trigonal-bipyramidal structure in the solid state and in solution. The IR spectra of three hemioxalato complexes revealed the presence of quadridentate oxalate-ion bridging between two cobalt ions, regardless of their coordination number.

In recent years, five-coordinated complexes have been extensively studied. From this laboratory, it has been reported that the bulky ligand, 6-methyl-2-aminomethylpyridine (mepic), reacts with the bivalent metal salts to form five-coordinated complexes $[MX(mepic)_2]ClO_4$ (M=Cu, Ni, or Co; X=Cl, Br, or I).[1] However, six-coordinated complexes were also obtained when the halo-ligand was replaced with relatively small ligands, such as two isothiocyanate ions, a bidentate nitrate ion, or two molecules of water.

N,N-Bis[2-(dimethylamino)ethyl]methylamine (dienMe) is also a bulky ligand reported to form high-spin complexes with the bivalent transition metals from manganese to zinc, these complexes have the general formula of $[MX_2dienMe]$ (X=Cl, Br, or I).[2] We have attempted to study the preparation and the properties of a mixed complex containing a simple bidentate ligand or unidentate ones in place of the two halo-ligands. This paper will report a study of the mixed complexes with cobalt(II).

Experimental

Reagents. *N,N*-Bis[2-(dimethylamino)ethyl]methylamine was prepared by the method in the literature.[3] Cobalt(II) perchlorate was obtained from perchloric acid and cobalt(III) hydroxide, which had itself been prepared by the reaction of chloropentaamminecobalt(III) chloride and sodium hydroxide. Nitromethane was purified by the fractional distillation of the water azeotrope, followed by dehydration with calcium chloride and by distillation under a nitrogen atmosphere using a 50-cm column packed with glass helices. All the other reagents were reagent-grade chemicals.

Preparation of the Complexes. Because of the unstability of the complexes toward moisture and carbon dioxide, all the complexes were prepared in a dry box in the presence of solid potassium hydroxide and silica gel. The ethylenediamine and the trimethylenediamine complexes were prepared under nitrogen.

$[Co(CH_3CN)_2dienMe](ClO_4)_2$. An acetonitrile solution of cobalt(II) perchlorate hexahydrate (18.3 g : 50 mmol in 100 dm^3 of the solvent) was evaporated with stirring almost to dryness. An additional 100 dm^3 of acetonitrile was then added to the residue, and the mixture was evaporated repeatedly to a volume of about 30 dm^3. After the solution had cooled to room temperature, 8.67 g (50 mmol) of dienMe was added. The crystals thus formed were collected on a sintered glass filter and washed with ethanol. The crude product was recrystallized by the addition of ethanol to the acetonitrile solution. In the open air, the complex turned from purple to green in only a few minutes.

$[Co(XX)dienMe](ClO_4)_2$ ($XX=2NH_3$, en, or tn). Into a filtered solution of 2 mmol of $[Co(CH_3CN)_2dienMe](ClO_4)_2$ in 30 dm^3 of methanol, an equimolar quantity of ammonia or diamine in methanol was stirred. The complex thus precipitated was collected on a filter, washed with ethanol, and dried over phosphorus pentoxide. It was then recrystallized from hot methanol.

$[Co(acac)dienMe]ClO_4$. In to a solution of 2 mmol of bis(acetylacetonato)cobalt(II) in ethanol, a drop of acetylacetone, 4 mmol of dienMe and 2 mmol of cobalt(II) perchlorate hexahydrate were stirred successively. The resulting solution was evaporated to dryness under a reduced pressure at room temperature. The residue was treated with chloroform, filtered, and evaporated to dryness. It was then recrystallized from small amount of hot ethanol and washed with 1 : 1 ethanol and diethyl ether.

$[Co(C_2O_4)(H_2O)dienMe]$. Freshly precipitated cobalt(II) oxalate was treated with equimolar quantities of dienMe in the presence of a small amount of water. The resulting solution was filtered and allowed to evaporate to dryness under a reduced pressure. The residue was dissolved in chloroform and was precipitated by the addition of diethyl ether to the filtrate.

$Co(C_2O_4)_{1/2}(dienMe)ClO_4$ and $Co(C_2O_4)_{1/2}(solv)(dienMe)ClO_4$ ($solv=CH_3CN$ or CH_3OH). To a slurry of 5.132 g (10 mmol) of $[Co(CH_3CN)_2dienMe](ClO_4)_2$ in 50 dm^3 of ethanol, 0.670 g (5 mmol) of sodium oxalate was added, after which the mixture was stirred overnight. The resulting crystals were collected on a glass filter and washed with hot ethanol. Recrystallization from hot methanol gave the methanol adduct, which yielded $Co(C_2O_4)_{1/2}(dienMe)ClO_4$ when washed with hot ethanol. The acetonitrile adduct was obtained by the addition of dry diethyl ether to the acetonitrile solution of the crude product.

Physical Measurements. The absorption spectra of the solutions were recorded at room temperature with a Shimadzu MPS-5000 recording spectrophotometer and silica cells with a path length of 1 cm. The reflectance spectra were obtained using the reflectance attachments and using potassium perchlorate as the reference. For the moisture-sensitive complexes, finely ground samples, prepared in a dry box, were covered with a glass plate. The IR spectra were measured over the range of 400—4000 cm^{-1} with a Hitachi EPI-G3 grating spectrophotometer. The samples were prepared as Nujol and hexachlorobutadiene mulls. The

magnetic moments were determined by the Gouy method at room temperature, using water as the standard. The molar susceptibility in each case was corrected for the diamagnetism of the ligands and perchlorate ions.

Analysis. The cobalt was determined volumetrically with an EDTA solution, using Xylenol Orange as the indicator. The sample solutions were prepared after decomposing the complexes with a mixture of sulfuric acid and perchloric acid. The organic elements were analyzed by Wako Pure Chemical Ind., Ltd., Osaka.

Results and Discussion

Table 1 shows the colors, the magnetic moments, and the analytical data for the complexes prepared. The analytical values of C, H, and N for $Co(C_2O_4)_{1/2}$(solv)-(dienMe)ClO_4 (solv=CH_3CN and CH_3OH) indicate that some of the solvent molecules were lost or displaced by water, however, the results of the metal analysis and the physical measurements, which were carried out in this laboratory with particular care taken to avoid moisture, show no signs of any loss of the solvent molecules or any adsorption of water.

The magnetic moments of $Co(C_2O_4)_{1/2}$(solv) (dienMe)ClO_4 (solv=CH_3CN and CH_3OH) and [$Co(C_2O_4)$(H_2O)dienMe] lie in the range of the six-coordinated cobalt(II) complexes (4.7—5.2 B.M.), whereas those of the others, which are identified from the electronic spectra as five-coordinated ones, are low, as Table 1 shows. The magnetic moments of most of the five-coordinated cobalt(II) complexes previously reported seem to lie in the range of the tetrahedral complexes (4.4—4.7 B.M.).[1b,2,4]

The IR spectra were measured for all the complexes studied. Because of their complex spectra, however, the assignment of each band was not possible. Thus, the configuration of the ligand was not determined. However, some information can be obtained from the characteristic bands due to anions or ligands: 1) The possibility of the coordination of a perchlorate ion can be rejected, because the bands at 1100 and 625 cm^{-1} are not appreciably split for any of the complexes containing the perchlorate ions. 2) As for the complexes with acetonitrile, *i.e.*, [$Co(CH_3CN)_2$dienMe]-$(ClO_4)_2$ and $Co(C_2O_4)_{1/2}(CH_3CN)$(dienMe)ClO_4, the sharp bands due to C≡N stretching were observed at 2280 and 2300 cm^{-1}, which are slightly higher than those of free acetonitrile, 2233 and 2282 cm^{-1}, in a neat solvent. No bands due to the presence of uncoordinated acetonitrile were observed in either complex. 3) In the 1600—1700 cm^{-1} region, the antisymmetric (O–C–O) stretching bands of the oxalato and the hemioxalato complexes are markedly different; *i.e.*, the former exhibits the splitted bands at 1614 and 1670 cm^{-1}, whereas the latter exhibit a sharp band at *ca.* 1660 cm^{-1}. The single peak found for the hemioxalato complexes seems to indicate that the four carbon-oxygen bonds of the oxalate ion are equivalent with each other. Thus, it may be inferred that the oxalate ion is bidentate in [$Co(C_2O_4)(H_2O)$-dienMe], whereas quadridentate in three hemioxalato complexes. It has been reported that an oxalate ion can bridge two metal ions, using all the oxygens as the ligand atoms.[5] This may also be the case for the present hemioxalato complexes.

The electronic spectra of these complexes were measured both in the solid state and in solution. Table 2 shows the positions and the molar absorptivities of the observed maxima.

The solid-reflectance spectra reveal that [$Co(C_2O_4)$-(H_2O)dienMe] and $Co(C_2O_4)_{1/2}$(solv) (dineMe)ClO_4 (solv=CH_3CN and CH_3OH) are six-coordinated, whereas the others are five-coordinated. The spectra of these five-coordinated complexes resemble that of [CoCl(trenMe)]Cl (trenMe=tris[2-(dimethylamino)-ethyl]amine) rather than that of [$CoCl_2$(dienMe)].[2,6] It has been reported that the former has essentially a trigonal-bipyramidal structure,[6,7] whereas the latter has a structure intermediate between a trigonal-bipyramidal one and a tetragonal-pyramidal one.[8] The similarlity of the spectra is the most remarkable in the acetylacetonato complex, the most probable structure of which is shown in Fig. 1. It may be supposed that the en, tn, and diammine complexes also take this structure.

In solution, most of the complex ions seem to maintain their structure in the solid state, because the absorption spectrum of the solution is essentially the same as the reflectance spectrum of the solid. An exception is the hemioxalato complex, $Co(C_2O_4)_{1/2}$-(dienMe)ClO_4. As Fig. 2 shows, the absorption spectra of this complex in nitromethane, in acetonitrile, and in methanol are different from each other,

Table 1. Color, magnetic moments, and chemical analyses of the dienMe complexes

Complex[a]	Color	μ_{eff} (B.M.)	Temp. (°C)	Found (%)				Calcd (%)			
				Co	C	H	N	Co	C	H	N
$2CH_3CN$, $2ClO_4$	purple	4.43	15.1	11.56	30.38	5.76	13.12	11.48	30.42	5.70	13.65
$2NH_3$, $2ClO_4$	purple	4.51	13.7	12.41	23.40	6.34	14.47	12.67	23.24	6.28	15.05
en, $2ClO_4$	violet	4.42	17.3	12.07	26.61	6.14	14.27	12.00	26.90	6.36	14.26
tn, $2ClO_4$	violet	4.50	19.8	11.54	28.31	6.51	13.81	11.66	28.53	6.58	13.86
acac, ClO_4	olive	4.45	15.7	13.45	39.17	7.14	9.92	13.68	39.03	7.02	9.75
C_2O_4, H_2O	red	4.96	15.7	17.08	40.13	7.14	12.56	17.42	39.06	7.45	12.42
$½C_2O_4$, ClO_4	violet	4.41	15.7	15.53	31.50	6.12	11.07	15.69	31.97	6.17	11.18
$½C_2O_4$, CH_3OH, ClO_4	purple	4.94	22.2	14.44	31.66	6.42	10.39	14.45	32.40	6.67	10.31
$½C_2O_4$, CH_3CN, ClO_4	purple	4.78	21.8	14.08	33.35	6.08	12.81	14.14	34.58	6.29	13.44

a) All the species contained in the complex per one cobalt ion are indicated but a dienMe molecule.

Table 2. Absorption maxima of the dienMe complexes

Complex[a]	State	ν_{max}, 10^3 cm^{-1} (ε_{max} for the solution)
$2CH_3CN$, $2ClO_4$	solid	*ca.* 5.6, 15.2, 18.1, 20 sh., 21.5
	CH_3CN soln.	6.0(10.0), 15.0(15.2), 17 sh., 17.9(47.1), 20 sh., 21.6(35.2)
$2NH_3$, $2ClO_4$	solid	*ca.* 5.6, 13.7, 17.5, 19.5 sh., 20.0, 21 sh.
	CH_3CN soln.	*ca.* 5.5(10.0), 14.0(14.5), 17.9(27.6), 19.2 sh., 20.2(31.8), 21 sh.
en, $2ClO_4$	solid	*ca.* 5.6, 14.3, 17.1, 20.2, 20 sh.
	CH_3CN soln.	*ca.* 5.0(10.0), 14.0(15.5), 17.3(16.6), 20.1(41.5), 21 sh.
tn, $2ClO_4$	solid	*ca.* 5.6, 13.9, 17.2, 20.2, 21 sh.
	CH_3CN soln.	5.0(10.1), 13.9(15.2), 17.5(20.5), 20.0(45.2), 21 sh.
acac, ClO_4	solid	5.9, 14.3, 17.0, 20.5, 21.3 sh.
	soln.[b]	5.8(12.4), 14.5(21.0), 17.1(29.0), 20.5(47.6), 21.5 sh.
C_2O_4, H_2O	solid	8.6, 19 sh., 19.5, 20 sh., 21 sh.
	soln.[b]	8.8(6.1), 19.0 sh., 19.8(26.7)
$\frac{1}{2}C_2O_4$, ClO_4	solid	*ca.* 4.5, 13.3, 17.3, 18.7, 19.5, 21.5 sh.
	CH_3NO_2 soln.	*ca.* 5.2(8.9), 13.7(11.2), 17.3(17.6), 18.9 sh., 19.5(23.3). 23 sh.
	CH_3CN soln.	8.8(5.9), *ca.* 14(2.0), 17 sh., 18.5 sh., 19.4(25.2), 20.3(24.2)
	CH_3OH soln.	8.5(4.6), *ca.* 14(2.5), 17 sh., 18.5 sh., 19.7(22.5), 21 sh.

a) All the species contained in the complex per one cobalt ion are indicated but a dienMe molecule. b) The chloroform, nitromethane, and the acetonitrile solutions give rise to practically the same spectra with each other.

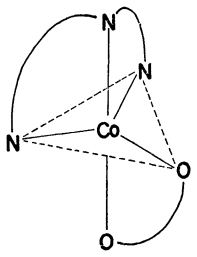

Fig. 1. The plausible coordination in $[Co(acac)dienMe]ClO_4$.

but are quite similar to the reflectance spectra of $Co(C_2O_4)_{1/2}(dienMe)ClO_4$, $Co(C_2O_4)_{1/2}(CH_3CN)(dienMe)ClO_4$, and $Co(C_2O_4)_{1/2}(CH_3OH)(dienMe)ClO_4$ respectively. The fact implies that solvolysis occurs both in acetonitrile and in methanol to form six-coordinated complexes. The coordination structure of this complex in a solid appears not to change only in nitromethane. No signs of the formation of six-coordinated complex were found in the nitromethane solution in the range of 9000—11000 cm^{-1}.

Both in the solid state and in solution, the ν_{max} values of the acac complex are slightly higher than those of the complexes containing en, tn, or ammonia. This is curious because the spectrochemical series of these ligands are generally in this order: en>tn>NH_3≫acac. This fact may be ascribed to the stereochemical nature of the dienMe ligand, which has bulky methyl groups at the terminal nitrogen atoms. The steric repulsion between the methyl groups and the amine or ammine hydrogens may make the field around the cobalt(II) ion weaker than that in the acac complex.

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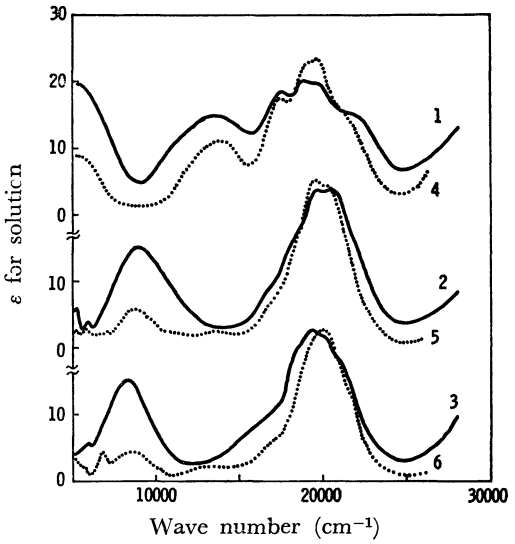

Fig. 2. The electronic spectra of the hemioxalato complexes in the solid state (——) and in solution (·····): the reflectance spectra of 1) $Co(C_2O_4)_{1/2}(dienMe)ClO_4$, 2) $Co(C_2O_4)_{1/2}(CH_3CN)(dienMe)ClO_4$, and 3) $Co(C_2O_4)_{1/2}(CH_3OH)(dienMe)ClO_4$; and the absorption spectra of $Co(C_2O_4)_{1/2}(dienMe)ClO_4$ in 4) nitromethane, 5) acetonitrile, and 6) methanol.

References

1) S. Ustuno, *J. Inorg. Nucl. Chem.*, **32**, 1631 (1970); b) S. Ustuno, *ibid.*, **32**, 183 (1970); c) S. Ustuno and K. Sone, *ibid.*, **28**, 2647 (1966).
2) M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, **5**, 45 (1966).
3) A. Marxer and K. Miesher, *Helv. Chim. Acta*, **34**, 924 (1951).
4) R. L. Carlin, "Transition Metal Chemistry," Vol. 1, ed. by R. L. Carlin, Marcel Dekker, New York (1965), p. 20.
5) N. F. Curtis, *J. Chem. Soc.*, **1963**, 4109.
6) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).
7) M. Di Vaira and P. L. Orioli, *ibid.*, **6**, 955 (1967).
8) M. Di Vaira and P. L. Orioli, *Chem. Commun.*, **1965**, 590.