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Trimethylenediamine Complexes. I. Some Trimethylenediamine Complexes Derived from *trans*-[$CoCl_2tn_2$]Cl in Methanol

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Several diacidobis(trimethylenediamine)cobalt(III) complexes including nitrate, nitrite and thiocyanate ions as ligands have been prepared by ligand substitution reactions of *trans*-dichlorobis(trimethylenediamine)cobalt(III) chloride in methanol. All these compounds were assumed to have the trans configuration according to the Baldwin's criterion based on the CH_2 rocking vibration. Isomeric pairs of chloronitro and chloronitrito complexes were also characterized by means of infrared data.

The metal complexes of ethylenediamine have been extensively studied in various aspects, but the investigations on the corresponding trimethylenediamine complexes have been quite limited. The X-ray analysis of *trans*-[$CoCl_2tn_2$]$Cl\cdot HCl\cdot 2H_2O$ has been performed by Matsumoto, Ooi and

Kuroya. It was reported[1] that the six-membered chelate ring has a chair form and the bond angles around cobalt and nitrogen atoms are all larger than those in the corresponding ethylenediamine complex. The difference in stabilities of five- and six-membered chelate rings may be reflected in the labilities of ethylenediamine and trimethylenediamine complexes.

The preliminary data by Pearson, Boston and Basolo[2] show that *trans*-$CoCl_2tn_2^+$ hydrolyzes rapidly although the rate of hydrolysis of the mixed complex *trans*-$CoCl_2entn^+$ is only ten times as large as that of *trans*-$CoCl_2en_2^+$. However the rate of carbonate exchange of $CoCO_3tn_2^+$ was reported to be much smaller than that of $CoCO_3en_2^+$ ion.[3] Thus it seems quite necessary to compare the chemistry of trimethylenediamine complexes with that of the corresponding ethylenediamine complexes in more detailed fashion. This paper reports several compounds derived from *trans*-dichlorobis(trimethylenediamine)cobalt(III) chloride by the ligand substitution reactions in methanol.

Experimental

The starting material *trans*-[$CoCl_2tn_2$]Cl was synthesized according to the methods by Bailar and Work,[4] and Werner.[5] The latter method *via* [$Co(NO_2)_2tn_2$]NO_2 is preferable.

Found: C, 23.11; H, 6.59; N, 17.42; Cl, 34.44; Co, 18.97%. Calcd for $C_6H_{20}N_4Cl_3Co$=[$CoCl_2tn_2$]Cl: C, 23.00; H, 6.38; N, 17.87; Cl, 33.94; Co, 18.83%.

1) **Nitrato Complexes.** A methanol solution of silver nitrate (0.65 g, 3.8 mmol) in 15 m*l* was added to a methanol solution of *trans*-[$CoCl_2tn_2$]Cl (1.2 g, 3.8 mmol) in 120 m*l*. Silver chloride produced was warmed and filtered off during hot. The filtrate was evaporated up to about 50 m*l* and kept standing overnight at room temperature. Bright green leaflet crystals deposited, which were filtered, washed with methanol and dried in air. Yield: 1.1 g. The same compound was also produced by the reaction between *trans*-[$CoCl_2tn_2$]Cl and potassium nitrate in hot methanol.

Found: C, 21.45; H, 6.02; N, 21.14%. Calcd for $C_6H_{20}N_5O_3Cl_2Co$=[$CoCl_2tn_2$]NO_3: C, 21.19; H, 5.93; N, 20.59%.

When 1.3 g (7.6 mmol) or more than 2.0 g (11.8 mmol) of silver nitrate was employed in the above reaction, dark green crystals of [$CoCl(NO_3)tn_2$]NO_3 or russety plates of [$Co(NO_3)_2tn_2$]NO_3 were obtained, respectively.

Found: C, 19.87; H, 5.75; N, 22.68%. Calcd for $C_6H_{20}N_6O_6ClCo$=[$CoCl(NO_3)tn_2$]NO_3: C, 19.66; H, 5.50; N, 22.92%.

Found: C, 18.70; H, 5.11; N, 25.14; Co, 14.96%. Calcd for $C_6H_{20}N_7O_9Co$=[$Co(NO_3)_2tn_2$]NO_3: C, 18.33; H, 5.13; N, 24.94; Co, 14.99%.

2) **Isothiocyanato Complexes.** A methanol solution of potassium thiocyanate (1.5 g, 15.4 mmol) in 50 m*l* was added gradually into a methanol solution of *trans*-[$CoCl_2tn_2$]Cl (1.0 g) in 140 m*l*. The mixture was cooled with ice and salt for several hours. Deposited green needles were separated, washed with methanol and dried in air. Yield: 0.9 g.

Found: C, 25.28; H, 6.65; N, 20.15%. Calcd for $C_7H_{20}N_5SCl_2Co$=[$CoCl_2tn_2$]SCN: C, 25.16; H, 6.03; N, 20.95%.

To a hot solution of *trans*-[$CoCl_2tn_2$]Cl (1.0 g, 3.1 mmol) in 200 m*l* of methanol was added 0.3 g (3.1 mmol) of solid potassium thiocyanate. The solution was heated for about 5 min and then kept standing overnight at room temperature. Purple crystals of [CoCl(NCS)tn_2]Cl were obtained. Yield: 0.8 g. The same compound was also produced when 1.0 g of *trans*-[$CoCl_2tn_2$]SCN was dissolved in about 200 m*l* of hot methanol, and the solution was heated for about 5 min, concentrated to about 50 m*l* under reduced pressure and cooled in ice overnight. Yield: 0.6 g. In this experiment a prolonged heating should be avoided since a disproportionation to dichloro- and dithiocyanato-complexes occurs.

Found: C, 25.03; H, 6.26; N, 20.36%.

When twice as many moles or large excess of potassium thiocyanate was employed against the starting dichloro-complex in the above experiment, purple crystals of [$Co(NCS)_2tn_2$]Cl (yield 0.85 g) or dark purple crystals of [$Co(NCS)_2tn_2$]SCN (yield 0.7 g) were obtained, respectively.

Found: C, 27.17; H, 5.79; N, 23.30%. Calcd for $C_8H_{20}N_6S_2ClCo$=[$Co(NCS)_2tn_2$]Cl: C, 26.78; H, 5.62; N, 23.42%.

Found: C, 28.50; H, 5.42; N, 25.66%. Calcd for $C_9H_{20}N_7S_3Co$=[$Co(NCS)_2tn_2$]SCN: C, 28.34; H, 5.28; N, 25.71%.

If solid potassium thiocyanate is added in excess to a methanol solution of [CoCl(NCS)tn_2]Cl or [$Co(NCS)_2tn_2$]Cl, and the solution is cooled, the respective thiocyanate is obtained, [CoCl(NCS)tn_2]SCN appearing as grayish blue needles.

Found: C, 27.43; H, 6.04; N, 22.68%.

3) **Nitro Complexes.** A cold methanol solution of sodium nitrite (0.30 g, 4.37 mmol) was added gradually to a cold solution of *trans*-[$CoCl_2tn_2$]Cl (1.37 g, 4.37 mmol) in 200 m*l* methanol under vigorous agitation. The solution was evaporated up to about 150 m*l* under reduced pressure at room temperature and then cooled for a few hours with ice and salt. Orange red powder was obtained. Yield: 0.35 g.

Found: C, 22.27; H, 6.29; N, 20.20%. Calcd for $C_6H_{20}N_5O_2Cl_2Co$=[$CoCl(NO_2)tn_2$]Cl: C, 22.23; H, 6.22; N, 21.61%.

If the above reaction mixture is heated for a while, evaporated on a hot water bath, and then cooled in ice, brown crystals were obtained. Yield: 0.97 g. Results of the elemental analysis are quite the same with the above compound.

Found: C, 21.90; H, 6.28; N, 19.85%.

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[1] K. Matsumoto, S. Ooi and H. Kuroya, Preprints for the 17th Annual Meeting of the Chemical Society of Japan (1964), 31W08.

[2] R. G. Pearson, C. R. Boston and F. Basolo, *J. Am. Chem. Soc.*, **75**, 3089 (1953).

[3] J. E. Boyle and G. M. Harris, *ibid.*, **80**, 782 (1958).

[4] J. C. Bailar, Jr., and J. B. Work, *ibid.*, **88**, 232 (1946).

[5] A. Werner, *Ann.*, **386**, 265 (1912).

Solid sodium nitrite (1.5 g, 21.7 mmol) was added to a hot solution of *trans*-[$CoCl_2tn_2$]Cl (1.0 g) in about 100 m*l* of methanol, and heated for a while. The solution changed from green to yellow, and was kept standing overnight at room temperature. Lustrous yellow crystals were separated. The filtrate was evaporated to about half the volume, and further quantity of crystals were obtained. All crystals were joined, washed with methanol and dried in air.

Found: C, 20.33; H, 5.91; N, 27.22%. Calcd for $C_6H_{20}N_7O_6Co$=[$Co(NO_2)_2tn_2$]NO_2: C, 20.88; H, 5.84; N, 28.40%.

Results and Discussion

The infrared absorption spectrum of dinitrobis(trimethylenediamine)cobalt (III) nitrite derived from *trans*-[$CoCl_2tn_2$]Cl in methanol completely coincides with that of *trans*-[$Cc(NO_2)_2tn_2$]NO_2 which was synthesized by the reaction between potassium hexanitrocobaltate(III) and trimethylenediamine in water according to the Werner's direction.[5] The other compounds now obtained are all new compounds and their structures are very interesting.

Several attempts have been made to distinguish between geometrical isomers of cobalt (III) bis(ethylenediamine) complexes by means of the infrared absorption data.[6] Baldwin[7] suggested that the most consistent variation between the spectra of cis and trans isomers is found in the CH_2 rocking region (900—870 cm^{-1}), cis isomers showing two peaks while trans isomers only one, and that these bands are insensitive to natures of A, B and X in complexes of the type [$CoABen_2$]X.

TABLE 1. THE CH_2 ROCKING FREQUENCIES OF [$CoABtn_2$]X COMPLEXES DERIVED FROM *trans*-[$CoCl_2tn_2$]Cl IN METHANOL

Compound	Frequency, cm^{-1}
trans-[$CoCl_2tn_2$]Cl*	889
[$CoCl_2tn_2$]NO_3	887
[$CoCl(NO_3)tn_2$]NO_3	891
[$Co(NO_3)_2tn_2$]NO_3	895
[$CoCl_2tn_2$]SCN	886
[$CoCl(NCS)tn_2$]Cl	885
[$CoCl(NCS)tn_2$]SCN	885
[$Co(NCS)_2tn_2$]Cl	889, 895
[$Co(NCS)_2tn_2$]SCN	890
[$CoCl(NO_2)tn_2$]Cl (red)	896
[$CoCl(NO_2)tn_2$]Cl (brown)	895
trans-[$Co(NO_2)_2tn_2$]NO_2	899

* Starting material

As shown in Table 1 these diacidobis(trimethylenediamine)cobalt(III) complexes, except [$Co(NCS)_2tn_2$]Cl, show a single peak respectively in the CH_2 rocking region. If Baldwin's empirical rule can be applied to these trimethylenediamine complexes, all these compounds are considered to be trans isomers. Diisothiocyanatobis(trimethylenediamine)cobalt(III) chloride shows two distinct peaks at 889 and 895 cm^{-1}. Therefore it should be assigned the cis configuration according to this criterion. It is not conceivable, however, that only this compound is a cis isomer while the corresponding thiocyanate [$Co(NCS)_2tn_2$]SCN assumes the trans configuration. Baldwin's rule must be concluded not to hold in this case. The X-ray analysis of [$Co(NO_3)_2tn_2$]NO_3 is now being performed by Komiyama and his coworkers. According to their preliminary report[8] crystals are monoclinic and the cobalt atom lies at the center of symmetry, certifying the trans configuration of this complex ion.

It is well known that methanol is much more favorable than water for the trans form of dichlorobis(ethylenediamine)cobalt(III) complex.[9] Such a solvent effect is considered to be due to the lesser power than water of stabilizing the cis form by solvation, and will also apply to the diacidobis(trimethylenediamine)cobalt(III) complexes. On the contrary water will be suitable in synthesizing the corresponding cis compounds.

Two compounds, orange red and brown crystals, were obtained whose analytical data both correspond to the formula [$CoCl(NO_2)tn_2$]Cl, suggesting that they are isomeric. The red form is unstable and easily transformed by heat to the brown form. The frequencies of CH_2 rocking vibration of these compounds indicate that both of them have the trans configuration. The other possibility to be considered is the linkage isomerism. It has been reported[10] that nitropentaamminecobalt(III) shows the NO_2 symmetric stretching peak at 1310 cm^{-1} but nitritopentaamminecobalt(III) at 1065 cm^{-1}. In the present case the less stable red form of this compound shows a very strong peak at 1170 cm^{-1}, but the brown form does not have such a peak. Thus the red isomer can safely be concluded to be a nitrito complex, [$CoCl(ONO)tn_2$]Cl.

Formation of nitritopentaamminecobalt(III) complex by the reaction between aquopentaamminecobalt(III) and nitrous acid in water is believed to

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6) M. N. Hughes and W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **28**, 1659 (1966).

7) M. E. Baldwin, *J. Chem. Soc.*, **1960**, 4369.

8) H. Yazaki, I. Onishi and Y. Komiyama, Reported at the 17th Symposium on the Chemistry of Metal Coordination Compounds of the Chemical Society of Japan, Hiroshima, December, 1967.

9) D. D. Brown and R. S. Nyholm, *J. Chem. Soc.*, **1953**, 2696; W. R. Fitzgerald and D. W. Watts, *J. Am. Chem. Soc.*, **89**, 821 (1967).

10) R. B. Penland, T. J. Lane and J. V. Quagliano, *J. Am. Chem. Soc.*, **78**, 887 (1956); K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y. (1963), p. 155.

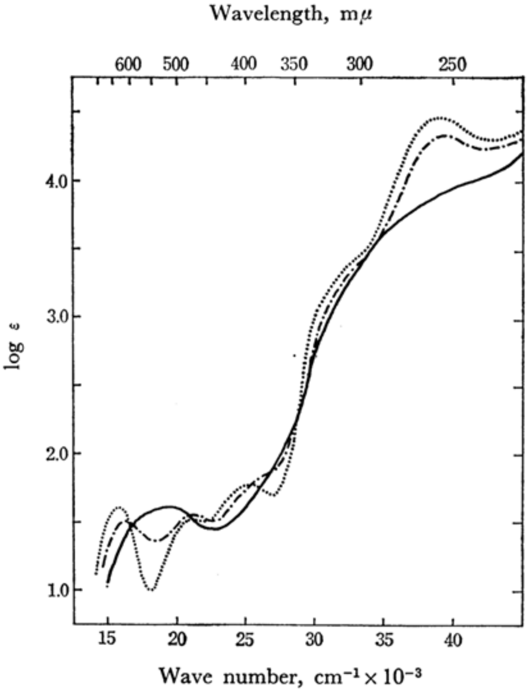

Fig. 1. Absorption spectra in methanol.
—— *trans*-[$Co(NO_3)_2tn_2$]NO_3
—·— *trans*-[$CoCl(NO_3)tn_2$]NO_3
······ *trans*-[$CoCl_2tn_2$]NO_3

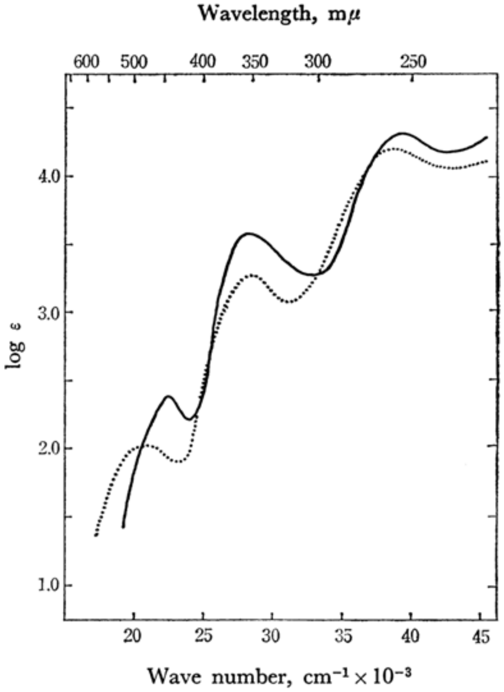

Fig. 3. Absorption spectra in methanol.
—— *trans*-[$Co(NO_2)_2tn_2$]NO_2
······ *trans*-[$CoCl(NO_2)tn_2$]Cl

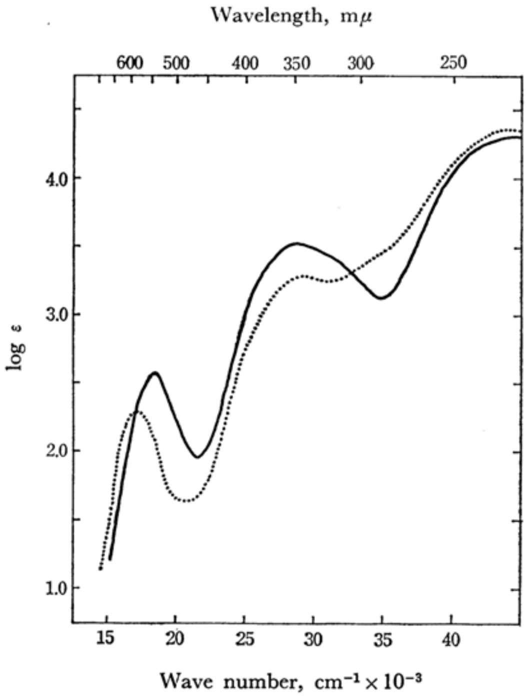

Fig. 2. Absorption spectra in methanol.
—— *trans*-[$Co(NCS)_2tn_2$]SCN
······ *trans*-[$CoCl(NCS)tn_2$]Cl

proceed as a nitrosation reaction keeping the Co–O bond intact.[11] In the present case, however, the chloronitrito complex was obtained by the reaction between the dichloro complex and sodium nitrite in methanol. It is not certain whether the overall reaction proceeds *via* the solvolysis process or not, but some novel reaction pathway might be passed through. Kinetic and tracer studies will soon be undertaken to clarify the reaction mechanism.

Absorption spectra of several trimethylenediamine complexes are shown in Figs. 1—3. The first band of $CoClXtn_2^+$ shifts to the shorter wavelength side progressively as the acido group X is substituted from Cl^- to NO_3^-, NCS^- and NO_2^- in accordance with the widely accepted order in the spectrochemical series.[12] Comparison of absorption data of these *trans*-diacidobis(trimethylenediamine)cobalt(III) complexes with corresponding bis(ethylenediamine) complexes as shown in Table 2 clearly indicates that trimethylenediamine is a weaker field ligand than ethylenediamine.

Aquation reactions were examined preliminarily. Dichloro complexes hydrolyze quickly, and the

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[11] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y. (1967), p. 230.

[12] T. M. Dunn, "Modern Coordination Chemistry," ed. by J. Lewis and R. G. Wilkins, Interscience Publishers, New York, N. Y. (1960), p. 266.

Table 2. Absorption bands of some *trans*-diacidobis(diamine)cobalt (III) complexes

Compound	Solvent	λ_{max}, mμ (ε)			
$[CoCl_2tn_2]Cl$	MeOH	650 (38.3)	475 (29.0)	398 (54.8)	259 (21330)
$[CoCl_2en_2]Cl$*	MeOH-Water	625 (34.7)	450 (25.2)	385 (43.7)	252 (20500)
$[CoCl(NO_3)tn_2]NO_3$	MeOH	610 (32.0)	470 (36.4)	380sh (69.4)	255 (21200)
$[Co(NO_3)_2tn_2]NO_3$	MeOH	510 (40.5)	310sh	250—260sh	
$[Co(NO_3)_2en_2]NO_3$**	60% $HClO_4$ aq	517 (63)	455 (40)	353 (80)	
$[CoCl(NCS)tn_2]Cl$	MeOH	580 (203)	350 (1796)	227 (22300)	
$[CoCl(NCS)en_2]SCN$*	MeOH-Water	520 (175)	335 (2500)		
$[Co(NCS)_2tn_2]SCN$	MeOH	550 (331)	348 (3292)	223 (20000)	
$[Co(NCS)_2en_2]SCN$*	MeOH-Water	515 (365)	335 (3250)		
$[CoCl(NO_2)tn_2]Cl$	MeOH	500 (87)	353 (1475)	259 (21900)	
$[CoCl(NO_2)en_2]NO_3$*	MeOH-Water	466 (81)	340 (1380)	245 (15500)	
$[Co(NO_2)_2tn_2]NO_2$	MeOH	450 (222)	358 (3900)	255 (21500)	
$[Co(NO_2)_2en_2]NO_2$*	MeOH-Water	433 (220)	347 (4200)	250 (12400)	

* F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

** Y. Shimura, R. Tsuchida, *Nippon Kagaku Zassi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **77**, 734 (1956).

half time of about 6 min was observed at 0°C in either case. Chloronitrato and dinitrato complexes react more rapidly and the half time was about 1 min. On the other hand diisothiocyanato and dinitro complexes are quite inert, whose absorption spectra in aqueous solutions do not change even after 24 hr at room temperature. Detailed features of these reactions must await further investigations.

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