CHEMISTRY LETTERS, pp. 517-520, 1973. Published by the Chemical Society of Japan

# THE SYNTHESES OF BIS(ETHYLENEDIAMINE)-TETRAMETHYLENEDIAMINE AND -DODECAMETHYLENEDIAMINE COBALT(III) COMPLEXES

Hiroshi OGINO and Junnosuke FUJITA
Department of Chemistry, Faculty of Science, Tohoku University,
Aoba, Aramaki, Sendai

Dimethylsulfoxide(DMSO) was found to be useful solvent for synthesizing various novel complexes. The reactions between cis- or trans-$[CoCl_2(en)_2]^+$ and tetramethylenediamine or dodecamethylenediamine in DMSO produce new complexes, $[Co(en)_2(tmd)]_n^{3n+}$ (n = 1 and 2), $[Co(en)_2(tmdH)_2]^{5+}$, $[Co(en)_2(don)]_n^{3n+}$ (n = 1 or 2) and $[Co(en)_2(donH)(H_2O)]^{4+}$, where en, tmd, don, $tmdH^+$ and $donH^+$ denote ethylenediamine, tetramethylenediamine, dodecamethylenediamine, mono-protonated tetramethylenediamine and mono-protonated dodecamethylenediamine, respectively.

A number of metal complexes with alkylenediamines such as ethylenediamine (en) or trimethylenediamine (tn) which form five- or six-membered chelate ring are well known. However, attempts to prepare cobalt(III) complexes with diamines having more methylene groups than three between the two nitrogen atoms have not been successful(1). In the course of preparative work on cobalt(III) complexes containing large chelate ring, the use of DMSO as solvent was found to be very useful for preparing such complexes. This letter reports the syntheses of cobalt(III) complexes containing tetramethylenediamine (tmd) or dodecamethylenediamine (don) and some features found in this work.

To a DMSO (500 ml) solution of tmd (1.4 g) was added cis- or trans-$[CoCl_2(en)_2]Cl$ (4.4 g) with stirring. The solution was kept at 50°C for 20 hr and then cooled to room temperature. The reddish orange solution resulted was diluted with water to 3 ℓ and then neutralized with conc. HCl. This was poured on a Sephadex SP C-25 ion-exchange column (ø 5 x 40 cm). At this stage the column gave four bands, pink (very small amount), red (small amount), yellow and yellowish orange colors from the bottom to top of the column. After washing the column with water, the first pink band was eluted off with 0.1 M KBr solution and then the second red and the third yellow bands were eluted with 0.2 M KBr solution. The pink and the red eluates were not characterized in this experiment, but the former seemed to correspond to Co(II) species produced during the reaction. The third yellow eluate was concentrated by a rotary evaporator until yellowish orange crystals appeared. The product was recrystallized from water. Yield: about 70 %. Anal. Calcd for $[Co(en)_2tmd]Br_3$: C, 18.95; H, 5.57; N, 16.58 %. Found: C, 18.71; H, 5.76; N, 16.58 %. This formulation is supported by the following: The complex gives two absorption bands at 479 nm ($\varepsilon$ = 90) and 345 nm ($\varepsilon$ = 88), indicating that the complex is of $[Co^{III}N_6]$ type (Fig. 1). Two enantiomers, $\Delta$ and $\Lambda$ isomers are obtained by the Sephadex SP C-25 column chromatographic resolution with 0.15 M sodium$(+)_{589}$-tartratoantimonate(III) solution, as shown in Fig. 1 ($\varepsilon_l - \varepsilon_r$ = + 0.96 at 505 nm, and - 0.32 at 450 nm for $\Lambda$ isomer). Furthermore, the complex on the Sephadex column can easily be eluted with 0.2 M KBr solution. This suggests that the complex is not a polymeric high changed species, but monomeric tripositive one.

The last band which was adsorbed strongly on the column was eluted with 1 M KBr solution. Yellowish orange crystals were obtained by evaporating the eluate and recrystallized from water.

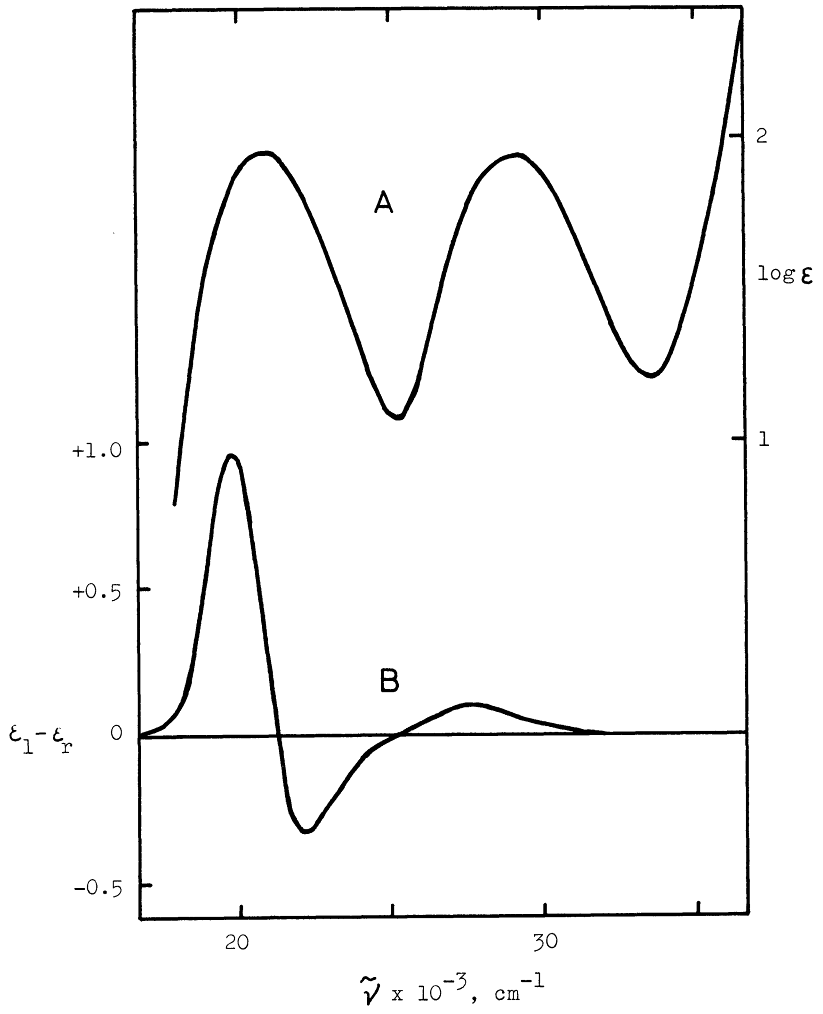


Fig. 1 Absorption spectrum (A) and circular dichroism curve (B) of $(-)_{589}$-$[Co(en)_2(tmd)]^{3+}$ ion in water.

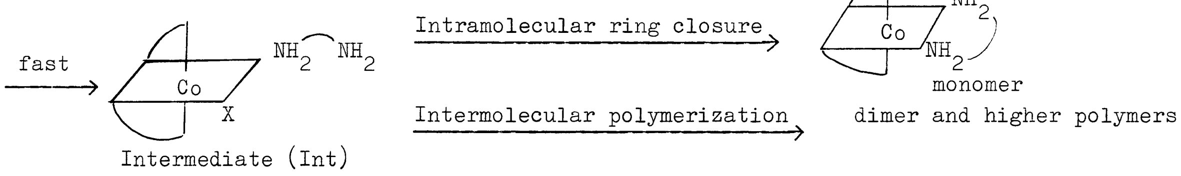
Anal. Calcd for $[Co_2(en)_4(tmd)_2]Br_6 \cdot 6H_2O$: C, 17.13; H, 6.11; N, 14.98 %. Found: C, 17.01; H, 6.16; N, 15.09 %. Elemental analysis does not distinguish whether the complex is dimeric or monomeric. The dimeric formula given above was determined on the bases of the chromatographic behavior and the measurement of electrical conductivity. The slope of the equivalent conductivity ($\Lambda e$) vs. the square root of gram-equivalent per liter is much steeper than that for the monomer, and a large deviation from the Onsager's equation (2) is observed. This result can be attributed to an appreciable ion association between the dimer and the bromide ions. The complex shows two absorption bands at 482 nm ($\varepsilon$ = 97) and 346 nm ($\varepsilon$ = 92). These wavelenghts are slightly longer than those of the $[Co(en)_2(tmd)]^{3+}$ given previously.

The yield of $[Co(en)_2tmd]^{3+}$ decreases remarkably, while that of $[Co_2(en)_4(tmd)_2]^{6+}$ increases, when the amount of DMSO is reduced. In the synthesis with a small amount of DMSO, several complexes of the luteo type with various positive charges other than tri- and hexa-positive complexes given above are formed. One of the products is $[Co(en)_2(tmdH)_2]Br_5 \cdot 4H_2O$. Anal. Calcd for $[Co(en)_2(tmdH)_2]Br_5 \cdot 4H_2O$: C, 17.39; H, 6.08; N, 13.52 %. Found: C, 17.22; H, 6.49; N, 13.56 %.

In a similar way, two don complexes were obtained. A solution of cis- or trans-$[CoCl_2(en)_2]Cl$ (1.4 g) and don (1.0 g) in 800 ml of DMSO was kept at 70°C for 30 hr. The reddish orange solution was treated similarly with Sephadex column. By elution with 0.1 - 0.4 M KBr solutions, the column gave seven bands with different colors. Four products have been identified so far; Co(II), $[Co(en)_3]Br_3$, $[Co(en)_2(don)]_nBr_{3n}$, and $[Co(en)_2(donH)(H_2O)]Br_4$. Anal. Calcd for $[Co(en)_2(don)]_nBr_{3n}$: C, 31.04; H, 7.16; N, 13.57 %. Found: C, 31.27; H, 7.94; N, 13.58 %. Calcd for $[Co(en)_2(donH)(H_2O)]Br_4$: C, 26.76; H, 6.60; N, 11.70 %. Found: C, 26.91; H, 6.78; N, 12.16 %. The value of n for the $[Co(en)_2(don)]_nBr_{3n}$ is not determined yet, but may be 1 or 2 since the complex can be eluted with 0.4 M KBr solution.

For the present reactions between $[CoCl_2(en)_2]^+$ and diamines, the following mechanism is proposed:

cis- or trans-$[CoCl_2(en)_2]^+$ + diamine ($NH_2 \frown NH_2$)



where ⌒ denotes en.

The ligand X in the intermediate (Int) would be chloride ion or DMSO. A unimolecular ring closure of the Int leads to the formation of monomer and intermolecular reactions result in the formation of dimer and higher polymers. As stated previously, the yields of monomer and polymer depend markedly on the amount of DMSO used for the solvent. This result will be interpreted by the proposed mechanism. The rate of ring closure should be independent of the concentration of Int, whereas that of intermolecular reaction should be dependent on the concentration of Int. Therefore, the reaction in a dilute solution favors the formation of monomer. The formation of $[Co(en)_2(donH)(H_2O)]^{4+}$ will also support this mechanism.

A partial reduction of Co(III) to Co(II) seems to occur during the reaction. The formation of a small amount of $[Co(en)_3]^{3+}$ may be related to this reduction reaction.

The present synthetic method can be applied to the reactions between various Co(III) complexes and diamines. For example, a DMSO solution containing $[Co(H_2O)(NH_3)_5]^{3+}$ and en changes its color from red to yellow which indicates the formation of a $[Co^{III}N_6]$ type complex. The use of DMSO as solvent will provide new synthetic routes for various novel complexes.

## References

1) J. C. Bailar, Jr. and J. B. Work, J. Amer. Chem. Soc., 68, 232 (1946), and references cited therein.

2) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", p.171, Butterworths Scientific Publications, London (1959).

( Received March 28, 1973)