

SHORT COMMUNICATIONS

New Cyano-Ammine Cobalt(III) Complexes

Nobufumi MAKI, Masaharu MOCHIZUKI and Shukichi SAKURABA

Department of Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu

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Shibata *et al.*¹⁾ reported the synthesis of $[\text{Co}(\text{CN})(\text{NH}_3)_5]\text{Cl}_2$ and $[\text{Co}(\text{CN})_3(\text{NH}_3)_3]$, while Siebert²⁾ independently published the preparation of the former-type of complex, $[\text{Co}(\text{CN})(\text{NH}_3)_5]\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}, \text{NO}_3, \text{ClO}_4$, or $1/2 \text{SO}_4$). Several years ago, Cambi *et al.*³⁾ reported the preparation of $\text{K}_2[\text{Co}(\text{CN})_5(\text{NH}_3)]$.

In the cyano-amine series, however, the complexes of *cis*- and *trans*-isomers described below are now still missing members: $[\text{Co}(\text{CN})_2(\text{NH}_3)_4]\text{X}$ and $\text{M}[\text{Co}(\text{CN})_4(\text{NH}_3)_2]$.

In the present communication, the preparation of complexes *cis*- $[\text{Co}(\text{CN})_2(\text{NH}_3)_4]\text{NO}_3 \cdot \text{H}_2\text{O}$, *cis*- $[\text{Co}(\text{CN})_2\text{en}(\text{NH}_3)_2]\text{NO}_3$ and $[\text{Co}(\text{CN})_3\text{en}(\text{NH}_3)] \cdot \text{H}_2\text{O}$ are reported.

Preparation of *cis*- $[\text{Co}(\text{CN})_2(\text{NH}_3)_4]\text{NO}_3 \cdot \text{H}_2\text{O}$.⁴⁾ Forty grams of *trans*- $[\text{Co}(\text{CN})\text{Cl}(\text{NH}_3)_4]\text{NO}_3$ ⁵⁾ were mixed with 29g of AgCN in 400 ml of water at room temperature and heated on a water bath (40–50°C) for three hours. Special care was taken to warm gently, because the complex solution tends to decompose above 50°C. No smell of ammonia should be present. The mixture was filtered and the residue repeatedly extracted with hot water (50°C).

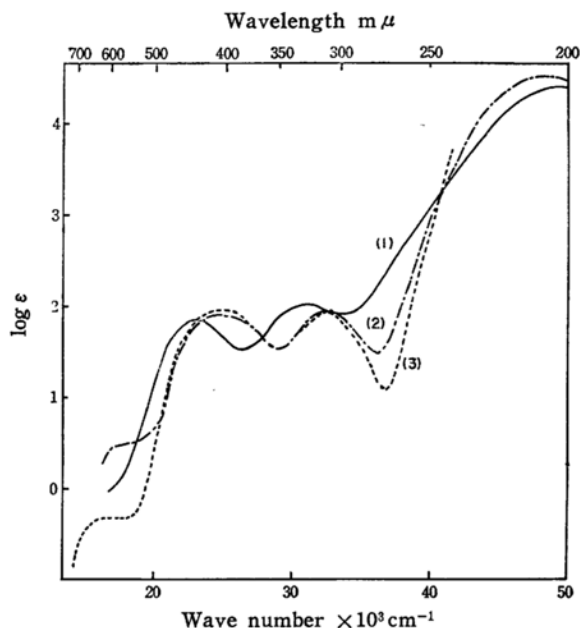


Fig. 1. The absorption spectra of dicyano cobalt (III) complexes: (1) — *cis*- $[\text{Co}(\text{CN})_2(\text{NH}_3)_4]\text{NO}_3 \cdot \text{H}_2\text{O}$; (2) --- *cis*- $[\text{Co}(\text{CN})_2\text{en}(\text{NH}_3)_2]\text{NO}_3$; (3) *cis*- $[\text{Co}(\text{CN})_2\text{en}_2]\text{NO}_3$.

TABLE 1. THE ABSORPTION MAXIMA OF DICYANO-COBALT(III) COMPLEXES

| Compound | | | | |
|---|---------------|--------------|--------------|--------------|
| <i>cis</i> - $[\text{Co}(\text{CN})_2(\text{NH}_3)_4]\text{NO}_3 \cdot \text{H}_2\text{O}$ | | 23.04 (1.86) | 31.28 (2.03) | 47.26 (4.31) |
| <i>trans</i> - $[\text{Co}(\text{CN})_2(\text{NH}_3)_4]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ | ca. 22 (1.81) | 24.02 (1.95) | 31.60 (2.05) | 47.80 (4.14) |
| <i>cis</i> - $[\text{Co}(\text{CN})_2\text{en}(\text{NH}_3)_2]\text{NO}_3$ | | 24.63 (1.91) | 32.46 (1.96) | 47.31 (4.41) |
| <i>cis</i> - $[\text{Co}(\text{CN})_2\text{en}_2]\text{NO}_3$ | | 24.73 (1.91) | 32.37 (1.93) | 47.37 (4.32) |
| <i>trans</i> - $[\text{Co}(\text{CN})_2\text{en}_2]\text{NO}_3$ | ca. 22 (1.38) | 24.33 (1.90) | 32.38 (1.93) | 47.62 (4.44) |
| $[\text{Co}(\text{CN})_3\text{en}(\text{NH}_3)] \cdot \text{H}_2\text{O}$ | | 25.51 (1.90) | 32.36 (1.92) | 48.31 (4.45) |
| $[\text{Co}(\text{CN})_3\text{dien}]$ | | 26.45 (2.45) | 33.33 (2.39) | 48.54 (4.11) |
| Unit: wave number $10^3/\text{cm}$ ($\log \epsilon$) dien=diethylenetriamine | | | | |

1) M. Shibata, M. Mori and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964).

2) H. Siebert, *Z. anorg. u. allgem. Chem.*, **327**, 63 (1964).

3) L. Cambi and E. Daglia, *Gazz. chim. ital.*, **88**, 691 (1964).

4) Independent of this work, the complex, *cis*- $[\text{Co}(\text{CN})_2(\text{NH}_3)_4]\text{Cl}$, has been reported by Nishikawa *et al.*; Proc. 21st Annual Meeting Chem. Soc. Japan, p. 1108 (1968).

5) K. Ohkawa, J. Hidaka and Y. Shimura, *This Bulletin*, **39**, 1715 (1966).