

THE PREPARATION AND THE ABSORPTION SPECTRUM OF THE
cis-DICYANODICARBONATOCOBALTATE(III) COMPLEX

Shuhei FUJINAMI and Muraji SHIBATA
Department of Chemistry, Faculty of Science, Kanazawa University,
Marunouchi, Kanazawa

The dicyanodicarbonatocobaltate(III) anion has been isolated by the reaction of tricarbonatocobaltate(III) and cyanide as the tris(ethylenediamine)cobalt(III) salt. The geometrical structure of the complex has been determined as cis-form by comparing the absorption spectrum with that of the known related complex. The spectrum showed marked splitting of the first absorption band.

The preparation of a complex containing two kinds of ligands which are considerably separated in the spectrochemical series¹⁾ is generally difficult. The several complexes containing cyanide ion which occupies the highest position of the series and ammonia which is ranked in a middle position have been prepared by the particular methods with each device for the disproportionation reaction.^{2-a-i)} We have now succeeded in obtaining the mixed dicyano complex with carbonate ion which locates in a lower position of the series compared with ammonia. The complex obtained has been identified to be cis-form, and the absorption spectrum of the complex showed well-separated three bands due to the d-d transition. As other example for complexes of this type, only one, that is $K[Co(CN)_2(acac)_2]$, has so far been reported.^{2-f)}

Into a cold green solution of tricarbonatocobaltate(III)³⁾ ($CoCl_2 \cdot 6H_2O$, 10 g scale; 0.048 mol), potassium cyanide (7.7 g, 0.12 mol) was added in portion. The mixture had been carefully neutralized with an aqueous perchloric acid and then filtered, the filtrate was charged on a column of the Dowex 1x8 resin (100~200 mesh, Cl-form, 5 x 15 cm). When the adsorbed band was eluted with an aqueous solution of potassium chloride, a red band came out of the column, after a green one. This red effluent was concentrated to a small volume below 30°C. After that, a small amount of ethanol was added to the concentrate, and the whole was kept in a refrigerator to precipitate potassium chloride used for the elution. After the removal of this salt, an aqueous solution of $\Lambda-[Co(en)_3]Br_3 \cdot 2H_2O$ was added as the precipitant. On keeping the whole in a refrigerator, needle-like crystals colored in red-brown deposited. These were washed with cold water, ethanol and ether in turn, and finally dried in vacuo. Yield was about 1.5 g. This compound showed the same CD spectrum as the precipitant used. Attempt to obtain the complex as usual salt such as potassium or calcium salt ended in failure because of great solubility of the salt and of instability of the species in aqueous solution.

Found: C, 23.93; H, 5.68; N, 22.10%. Calcd for $[Co(C_2H_8N_2)_3][Co(CN)_2(CO_3)_2] \cdot 2H_2O$: C, 23.73; H, 5.58; N, 21.60%.

The IR absorption spectrum indicated the existence of the chelated carbonate ion⁴⁾ and of the coordinated cyanide ion.

The absorption spectrum of this complex was measured with an aqueous solution of the tris(ethylenediamine) salt (Fig. 1-a), and also with a solution of the potassium salt obtained by means of ion-exchange (b). On the basis of these spectra and known

spectrum of Λ -[Co(en)₃]³⁺ (c), the absorption maxima for the present complex were estimated. These are 18,300 (log ϵ , 1.96), 22,500 (2.03) and 27,500 cm⁻¹ (2.20). The first two maxima correspond to the maxima at 19,000 and ca. 23,000 cm⁻¹ (shoulder) for the known cis-[Co(CN)₂(acac)₂] complex. In addition, we have found that a related dicyanocarbonatooxalato complex could be resolved with the Λ -[Co(en)₃]³⁺ ion⁵⁾, although the same attempt was unsuccessful in the present complex. From these facts, the geometrical structure of the present complex could be determined as cis-form. Regarding the middle absorption maximum as one component of the so-called first absorption band, this complex is particularly interested in such a large splitting of the band. The extensive studies concerning complexes of this type will be reported elsewhere.

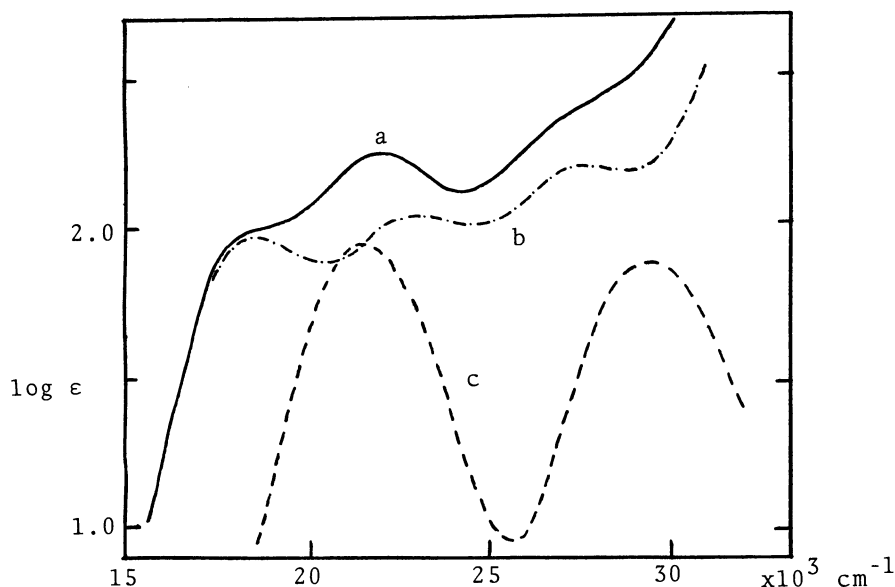


Fig.1 Absorption spectra of: (a) — [Co(en)₃][Co(CN)₂(CO₃)₂]·2H₂O
(b) —.— [Co(CN)₂(CO₃)₂]³⁻ (K-salt) (c) ---- Λ -[Co(en)₃]Br₃·2H₂O

References

- 1) Y. Shimura and R. Tsuchida, Bull. Chem. Soc. Japan, **29**, 311 (1956).
- 2) a) P. R. Rây and B. Sarma, J. Indian Chem. Soc., **28**, 59 (1951). b) H. Siebert, Z. anorg. allgem. Chem., **327**, 63 (1964). c) M. Shibata, E. Kyuno, and M. Mori, Inorg. Chem., **3**, 1573 (1964). d) K. Ohkawa, J. Fujita, and Y. Shimura, Bull. Chem. Soc. Japan, **38**, 66 (1965). e) K. Ohkawa, J. Hidaka, and Y. Shimura, *ibid.*, **39**, 1715 (1966). f) H. Nishikawa, K. Konya, and M. Shibata, *ibid.*, **41**, 1492 (1968). g) K. Konya, H. Nishikawa, and M. Shibata, Inorg. Chem., **7**, 1165 (1968). h) N. Maki, T. Hamazaki, and S. Sakuraba, Bull. Chem. Soc. Japan, **41**, 1735 (1968). i) M. Muto, T. Baba, and H. Yoneda, *ibid.*, **41**, 2918 (1968).
- 3) M. Shibata, Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.), **87**, 771 (1966).
- 4) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, J. Amer. Chem. Soc., **79**, 4900 (1957).
- 5) to be published.

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