BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (9), 2741—2742 (1978)

The Preparation of 2,2′-Bipyridinedicarbonato and Dicarbonato-1,10-phenanthroline Complexes of Cobalt(III)

Yayoi Ida, Kiyoyuki Imai, and Muraji Shibata*

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920

(Received April 26, 1978)

Synopsis. Two new dicarbonato complexes, K[Co$(CO_3)_2$(bpy)]·$2H_2O$ and K[Co$(CO_3)_2$(phen)]·H_2O, have been prepared by the method starting from the [Co$(CO_3)_3$]$^{3-}$ complex and resolved by means of diastereoisomer formation.

The preparative method starting from a green solution of potassium tricarbonatocobaltate(III) has been characterized by the successive replacement of the CO_3^{2-} ion in the starting material with other ligands, and various dicarbonato complexes which are products of the first-step replacement have been reported; such complexes as *cis*-[Co$(CO_3)_2(NH_3)_2$]$^-$, [Co$(CO_3)_2$(en)]$^-$, *cis*-[Co$(CO_3)_2(NO_2)_2$]$^{3-}$, *cis*-[Co$(CO_3)_2(CN)_2$]$^{3-}$, and *cis*- and *trans*-[Co$(CO_3)_2$(py)$_2$]$^-$ are those examples,[1)] and have been used as convenient intermediates for further synthesis.[1,2)] The present work was undertaken in order to prepare dicarbonato complexes of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) by reactions of the green solution with these ligands. By the way, the preparation of (mono)carbonato complexes from the green solution has been reported by Kashiwabara *et al.*[3)]

Experimental

To a cold, green solution of tricarbonatocobaltate(III) (Co$(NO_3)_2$·$6H_2O$, 5.8 g, 0.02 mol scale), we added 2,2′-bipyridine (3.1 g, 0.02 mol) dissolved in 50 cm^3 of methanol, after which the mixture was stirred at room temperature for 1 h. To the resulting violet solution we added 100 cm^3 of ethanol, and the whole was cooled in an ice bath for 2 h. The solution was then filtered to remove the by-products, which contained a small amount of the bis(bipyridine)-carbonato complex. To the filtrate we added ether, and then the green, oily portion produced was removed by decantation. The supernatant was kept in a refrigerator overnight to deposit the crude product. Recrystallization of the product was performed from warm water (*ca.* 35 °C) by the addition of a small amount of ethanol. The yield was *ca.* 1.5 g. Found: C, 35.14; H, 2.96; N, 6.71%. Calcd for K[Co$(CO_3)_2(C_{10}H_8N_2)$]·$2H_2O$: C, 35.13; H, 2.95; N, 6.83%.

The corresponding dicarbonatophenanthroline complex was prepared in the manner described above except for the use of 1,10-phenanthroline instead of 2,2′-bipyridine. The yield was *ca.* 1.5 g. Found: C, 39.47; H, 2.30; N, 6.49%. Calcd for K[Co$(CO_3)_2(C_{12}H_8N_2)$]·H_2O: C, 39.54; H, 2.61; N, 6.59%.

The K[Co$(CO_3)_2$bpy]·$2H_2O$ compound (4.1 g, 0.01 mol) was dissolved in a warm solution of $(-)_{589}$[Co$(NO_2)_2$(en)$_2$]-$(C_2H_3O_2)$[4)] (0.005 mol in 20 cm^3 H_2O, *ca.* 40 °C), and then the mixture was cooled in an ice bath. After the side of the vessel had been scratched for a while, the whole was kept in an ice bath for 1 h. The crystals thus obtained were recrystallized from warm water (*ca.* 35 °C). The less soluble diastereoisomer was found to be $(-)_{589}$[Co$(NO_2)_2$(en)$_2$]·$(+)_{589}$[Co$(CO_3)_2$(bpy)]. The yield was *ca.* 1 g. Found: C, 28.87; H, 4.60; N, 17.43%. Calcd for [Co$(NO_2)_2(C_2H_8N_2)_2$]·[Co$(CO_3)_2(C_{10}H_8N_2)$]·$3H_2O$: C, 29.10; H, 4.58; N, 16.97%.

The resolution of the [Co$(CO_3)_2$(phen)]$^-$ complex was achieved with $(-)_{589}$[Co(ox)(en)$_2$]$(C_2H_3O_2)$[5)] in a manner similar to that used for the bipyridine complex. The less soluble diastereoisomer contained the $(-)_{589}$ form of the complex. The yield was *ca.* 1 g. Found: C, 38.12; H, 3.73; N, 13.22%. Calcd for [Co$(C_2O_4)(C_2H_8N_2)_2$]·[Co$(CO_3)_2$-$(C_{12}H_8N_2)$]: C, 38.35; H, 3.86; N, 13.42%.

By the way, two known carbonato complexes, [CoCO$_3$-(bpy)$_2$]$^+$ and [CoCO$_3$(phen)$_2$]$^+$, as well as two known tris complexes, [Co(bpy)$_3$]$^{3+}$ and [Co(phen)$_3$]$^{3+}$, could be prepared by the reactions of the [Co$(CO_3)_3$]$^{3+}$ complex and the ligands in stoichiometric amounts; in the case of the latter complexes, activated charcoal was used.

The absorption spectra were measured with a Hitachi 323 recording spectrophotometer. The CD spectra were recorded with a JASCO J-40CS automatic recording spectropolarimeter equipped with a JASCO Model J-DPZ data processor for CD, and with the samples converted into potassium salts by means of the ion-exchange technique. For the measurement of the optical rotation, a JASCO Model DIP-SL automatic polarimeter was used.

Results and Discussion

The absorption and CD spectra are shown in Fig. 1. The maximum of the first absorption band is observed

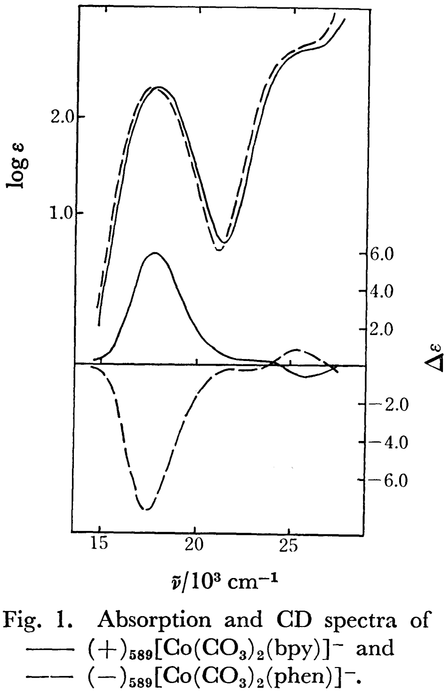

Fig. 1. Absorption and CD spectra of
—— $(+)_{589}$[Co$(CO_3)_2$(bpy)]$^-$ and
– – – $(-)_{589}$[Co$(CO_3)_2$(phen)]$^-$.

at 17800 cm^{-1} (logε=2.18) for the bpy complex and at 17600 cm^{-1} (log ε=2.18) for the phen complex. The second absorption band is observed as a shoulder at *ca.* 25600 cm^{-1} (log ε, *ca.* 2.38) for the bpy complex and as one at *ca.* 25400 cm^{-1} (log ε, *ca.* 2.40) for the phen complex.

Recently, we studied the CD spectra of the [Co(O,O)$_2$(N)$_2$]$^-$-type complexes (O,O=CO_3^{2-}, ox^{2-} and mal^{2-}; (N)$_2$=en, 2NH$_3$ and 2py) and found that the related $(+)_{589}$[Co(CO$_3$)$_2$(en)]$^-$, $(-)_{589}$[Co(CO$_3$)$_2$(NH$_3$)$_2$]$^-$ and $(+)_{589}$[Co(CO$_3$)$_2$(py)$_2$]$^-$ complexes exhibit only one CD peak in the first absorption band region; 17600 cm^{-1} ($\Delta\varepsilon=-1.91$) for the en complex, 17800 cm^{-1} ($\Delta\varepsilon=-2.32$) for the NH$_3$ complex, and 18400 cm^{-1} ($\Delta\varepsilon=+2.94$) for the py complex.⁶⁾ The absolute configurations of these complexes were assigned on the basis of the (+) sign of the CD peak referring to Λ, and the (−) sign, to Δ.⁶⁾ The CD spectra of the present dicarbonato complexes also exhibit only one CD peak in the first band region; 17700 cm^{-1} ($\Delta\varepsilon=+5.93$) for the bpy complex and 17500 cm^{-1} ($\Delta\varepsilon=-7.72$) for the phen complex. From these CD signs, the Λ configuration is given to the $(+)_{589}$[Co(CO$_3$)$_2$(bpy)]$^-$ complex and the Δ configuration to the $(-)_{589}$[Co(CO$_3$)$_2$(phen)]$^-$ complex. The large $\Delta\varepsilon$ values observed for the present complexes may be attributed to the chelating bpy or phenligand. In an aqueous solution, the $(-)_{589}$[Co(CO$_3$)$_2$(phen)]$^-$ complex racemized with a half-life of *ca.* 7 h at room temperature. In this connection, the $(-)_{589}$[Co(CO$_3$)$_2$(NH$_3$)$_2$]$^-$ complex racemized with a half-life of *ca.* 3 min.⁷⁾

References

1) M. Shibata, *Proc. Jpn. Acad.*, **50**, 779 (1974), and the references cited therein.

2) T. Ito and M. Shibata, *Inorg. Chem.*, **16**, 108 (1977).

3) K. Kashiwabara, K. Igi, and B. E. Douglas, *Bull. Chem. Soc. Jpn.*, **49**, 1573 (1976).

4) *Inorg. Synth.*, Vol. 4, 195 (1953).

5) F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Am. Chem. Soc.*, **83**, 1285 (1961).

6) S. Muramoto, K. Kawase, and M. Shibata, *Bull. Chem. Soc. Jpn.*, submitted for publication.

7) S. Muramoto and M. Shibata, *Chem. Lett.*, **1977**, 1499.