The Preparation of Mixed Carbonato Complexes of Cobalt(III) with 2-Pyridinecarboxylic Acid

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Synopsis.   By the successive replacement of CO_3^{2-} ions in the $[Co(CO_3)_3]^{3-}$ complex with 2-pyridinecarboxylic acid (Hpicol), the $[Co(CO_3)_2(picol)]^{2-}$ complex and two geometrical isomers of the $[CoCO_3(picol)_2]^{-}$ complex have been prepared. By the reaction of the cis-$[Co(CO_3)_2(NH_3)_2]^{-}$ complex and picol, three geometrical isomers of the $[CoCO_3(picol)(NH_3)_2]$ have been prepared.

The most remarkable feature of the preparative method for cobalt(III) complexes starting from a potassium hydrogencarbonate aqueous solution of the tricarbonatocobaltate(III) is the successive replacement of the CO_3^{2-} ions with another ligand, and the first substitution step in the reaction with such a ligand as ammonia, ethylenediamine, pyridine, nitrite ion, or cyanide ion resulted in a dicarbonato complex.[1] However, the action of an α-amino acid (glycine, alanine or valine) on the $[Co(CO_3)_3]^{3-}$ complex resulted not in the dicarbonato complex, but in the carbonatobis (amino acidato) complex.[1] Thus, we adopted 2-pyridinecarboxylic acid (picolinic acid, abbreviated as Hpicol) in order to investigate successive substitution. In addition, the reaction of cis-$[Co(CO_3)_2(NH_3)_2]^{-}$ with 2-pyridinecarboxylic acid to give $[CoCO_3(picol)(NH_3)_2]$ was investigated.

Experimental

2-Pyridinecarboxylic acid was prepared from 2-methyl-pyridine in the form of hydrochloride by a familiar method.[2]

To a freshly prepared solution of tricarbonatocobaltate(III) ($Co(NO_3)_2 \cdot 6H_2O$, 29.1 g, 0.1 mol), we added a solution of Hpicol (0.1 mol); the mixture was stirred at $ca.$ 50 °C for 40 min, whereupon the solution turned blue-green. The resulting solution was allowed to cool in an ice bath. Ethanol was added, to the cold solution for the successive removal of the coexisting salts. Finally, an ethanol–ether (1:1) mixture was added to the solution, and the whole was kept in a refrigerator until blue-green crystals separated out. Recrystallization was performed by dissolving the crude product in a minimum amount of water, followed by the addition of an ethanol–ether (1:1) mixture when cold. Yield, $ca.$ 15 g. Found: C, 24.77; H, 1.44; N, 3.90%. Calcd for $K_2[Co(CO_3)_2(C_6H_4NO_2)] \cdot 1/2H_2O$: C, 24.75; H, 1.30; N, 3.61%.

A solution of Hpicol (0.05 mol) was added to a freshly prepared solution of $[Co(CO_3)_3]^{3-}$ (0.025 mol); when the mixture was then stirred at 60 °C for 4 h, it turned violet. The resulting solution was concentrated to a small volume with a rotary evaporator at $ca.$ 35 °C. To the concentrated solution we added an ethanol–ether mixture (1:1), and the whole was kept in a refrigerator overnight. The crude product thus obtained was filtered and recrystallized in the way described above. On the other hand, the filtrate was charged on a column containing Dowex 1 X-8 in the Cl-form (9×15 cm). By elution with a 0.3 M KCl aqueous

solution, a broad band consisting of univalent anionic species was descended; it was collected in a fraction. This was again chromatographed using a column (5×30 cm) and 0.3 M KCl; three violet bands were then separated. They were collected in fractions labeled A-1—A-3. The absorption spectra of these fractions indicated that the crystals obtained prior to the chromatographic separation were identical with the species in the A-2 fraction. Each fraction was evaporated almost to dryness, the residue being extracted with ethanol. After a small amount of water had been added to the extracted solution, the whole was kept in a refrigerator until crystals separated out. This was successful with the fractions A-2 and A-3, crystallization from the A-1 fraction being unsuccessful because of the poor yield and easy isomerization of the species. Yields, $ca.$ 3 g for the A-2 fraction plus the crystallized crop and $ca.$ 0.5 g for the A-3 fraction. Found for the A-2 complex: C, 35.82; H, 3.02; N, 6.60%. Calcd for $K[CoCO_3(C_6H_4NO_2)_2] \cdot 2H_2O$: C, 35.62; H, 2.76; N, 6.39%. Found for the A-3 complex: C, 36.44; H, 2.57; N, 6.17%. Calcd for $K[CoCO_3(C_6H_4NO_2)_2] \cdot 3/2H_2O$: C, 36.37; H, 2.58; N, 6.53%.

Three isomers of the diamminecarbonatopicolinatocobalt-(III) complex were obtained analogously to those of the $[CoCO_3(gly)(NH_3)_2]$ complex.[3] To a solution of $K[Co(CO_3)_2(NH_3)_2] \cdot H_2O$[1] (10 g, 0.037 mol in $ca.$ 20 ml H_2O) we added a solution of the Hpicol ligand (0.05 mol); the mixture was then stirred at room temperature for 3 h. During the reaction, a considerable amount of red-violet crystals separated out as the first crop. The crystals were collected by filtration, and the filtrate was concentrated to a small volume. Ethanol was added to the concentrate, and then the whole was cooled in an ice bath, the second crop of the crystals being thus obtained. The combined first and second crops of crystals were recrystallized from a large quantity of hot water (50 °C).

On the other hand, the filtrate from the second crop of crystals was chromatographed on a column containing 100—200 mesh Dowex 50W-X 8 resin in the Na-form (4.5×25 cm). By washing the column with water, the band of unreacted $[Co(CO_3)_2(NH_3)_2]^{-}$ was descended first, followed by the three bands of the desired isomers. Since the first-descended band was very poor in yield and was found to be identical with the crystals separated during the reaction, this portion of the eluate was discarded. The second and third bands were collected in fractions. Each fraction was concentrated to a small volume. After the addition of ethanol, the concentrate was kept in a refrigerator overnight. Red needle-like crystals separated out from the fraction of the second band, while pink plates were obtained from the fraction of the third band. Yields, $ca.$ 1 g (red-violet crystals), $ca.$ 0.5 g (red crystals), and $ca.$ 0.5 g (pink crystals). Found for the red-violet crystals: C, 30.53; H, 4.03; N, 14.86%. Calcd for $[CoCO_3(C_6H_4NO_2)(NH_3)_2]$: C, 30.56; H, 3.66 N, 15.07%. Found for the red crystals: C, 27.00; H, 4.87; N, 13.18%. Calcd for $[CoCO_3(C_6H_4NO_2)(NH_3)_2] \cdot 2H_2O$: C, 27.02; H, 4.54; N, 13.51%. Found for the pink crystals: C, 28.79; H, 4.42; N, 14.43%. Calcd for $[CoCO_3(C_6H_4NO_2)(NH_3)_2] \cdot$

H_2O: C, 28.68; H, 4.13; N, 14.34%.

The absorption spectra were measured with a Hitachi Model 323 spectrophotometer. The proton magnetic resonance (PMR) spectra were recorded on a JEOL JNM-PS-100 NMR spectrometer at *ca.* 25 °C, using D_2O as the solvent. The values of the chemical shifts were referred to internal sodium d_4-trimethylsilylpropionate (TMSP).

Results and Discussion

The absorption spectra in solution for the present three kinds of complexes are shown in Figs. 1 and 2. The numerical data are summarized in Table 1, the data[4] on related complexes being included for comparison. When the spectral data of the $[Co(CO_3)_2$-(picol)]$^{2-}$ complex are compared with those of the $[Co(ox)_2(gly)]^{2-}$ complex. a bathochromic shift is observed in the spectrum of the dicarbonato complex. This shift can reasonably be explained by the facts that the CO_3^{2-} is ranked in a position of the spectrochemical series lower than the $C_2O_4^{2-}$ ion, and that the picol lies close to the gly ligand in the series.[5]

The absorption spectra of the two isomers of the $[CoCO_3(picol)_2]^-$ complex are quite similar to each other (Fig. 1); hence, the geometrical configurations have not been determined from the spectral data. Although another isomer had not been isolated as crystals from the eluate, the spectrum of the eluate exhibited the first band at 18200 cm^{-1} which is rather broader than those for the isolated two isomers and the second band at 25200 cm^{-1}. Concerning the [Coox-(gly)$_2$]$^-$ complex, Matsuoka *et al.*[4] reported that one somer, whose structure is determined to be *trans*(N)i from the splitting of the first absorption band, corresponds to the first-eluated band in chromatographic separation, and that other two isomers, determined to be C_1-*cis*(N) and C_2-*cis*(N) on the basis of the PMR spectra, correspond to the second band and the third
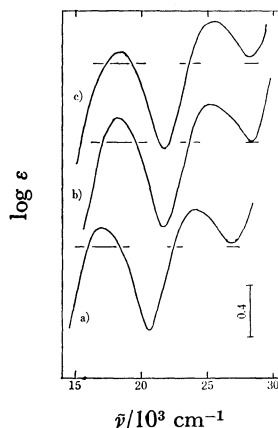

Fig. 1. Absorption spectra of;
a) $[Co(CO_3)_2(picol)]^{2-}$, b) C_1-*cis*(N)-$[CoCO_3(picol)_2]^-$ and c) C_2-*cis*(N)-$[CoCO_3$ (picol)$_2$]$^-$.
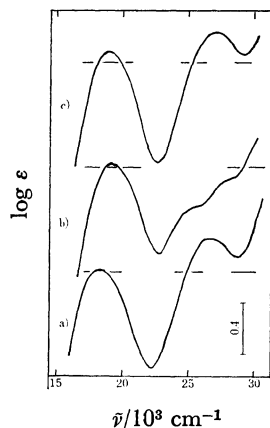Short horizontal lines show the levels of log ε=2.00 for each the complexes.

Fig. 2. Absorption spectra of three isomers of $[CoCO_3$-(picol)(NH$_3$)$_2$];
a) *mer-cis*(N)-isomer, b) *mer-trans*(N)-isomer and c) *fac*-isomer.

Table 1. Absorption spectral data ($\bar{\nu}$ in 10^3 cm^{-1})

Complex	I Band		II Band	
	$\bar{\nu}_{max}$	log ε	$\bar{\nu}_{max}$	log ε
$[Co(CO_3)_2(picol)]^{2-}$	17.0	2.16	24.1	2.28
$[Co(ox)_2(gly)]^{2-}$ [4]	17.9	2.20	25.0	2.26
$[CoCO_3(picol)_2]^-$				
trans(N) (1)[a]	18.2	—	25.2	—
C_1-*cis*(N) (2)	18.2	2.19	25.3	2.27
C_2-*cis*(N) (3)	18.4	2.06	25.2	2.30
$[Coox(gly)_2]^-$ [4]				
trans(N) (1)	16.7 / 18.9	1.70 / 2.00	25.8	2.23
C_1-*cis*(N) (2)	18.3	2.15	25.8	2.24
C_2-*cis*(N) (3)	17.8	2.08	25.9	2.20
$[CoCO_3(picol)(NH_3)_2]$				
mer-cis(NH$_3$) (1)	18.3	2.02	26.8	2.26
mer-trans(NH$_3$) (2)	19.2	2.04	25.0(sh) / 28.4(sh)	
fac (3)	18.9	2.07	26.9	2.23
$[CoCO_3(gly)(NH_3)_2]$[3]				
mer-cis(NH$_3$) (1)	18.1	2.03	26.5	2.25
mer-trans(NH$_3$) (2)	18.7	2.07	24.9(sh) / 27.3	1.85
fac (3)	18.7	2.02	26.7	2.13

a) Numbers in parentheses indicate the elution order.

band respectively. The two isomers isolated in the present work exhibit the proton signals due to the pyridine rings of picol in the region of δ 7.4—9.2 ppm. The patterns were so complicated that the assignments of the peaks have not been performed, but the spectrum of the isomer from the second eluate exhibited a more complex pattern than that from the third eluate. Considering these differences in the absorption spectrum, in the elution order, and in the PMR spectrum, the three isomers are assumed to adopt *trans*(N), C_1-*cis*(N), and C_2-*cis*(N) configurations respectively, according to the order of elution.

The characterization of the three isomers of the $[CoCO_3(picol)(NH_3)_2]$ complex can be made in the same way as that used for the isomers of the $[CoCO_3$-(gly)(NH$_3$)$_2$] complex;[3] the isomer, exhibiting splitting of the second absorption band is identified as that of *mer-trans*(NH$_3$); the isomer exhibiting the first absorption band with the largest half-width, as that of the *mer-cis*-(NH$_3$) isomer, and the remainder, which was obtained from the last eluate, as the *fac* one.

References

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