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Synthesis and Absorption Spectra of the $[Co(O\text{-}O)_2(py)_2]^-$-type Complexes

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Five bis(dicarboxylato)bis(pyridine)-type complexes, *trans*-$[CoCO_3ox(py)_2]^-$, *trans*- and *cis*-$[Co(ox)_2(py)_2]^-$, and *trans*- and *cis*-$[Co(mal)_2(py)_2]^-$, have been isolated as crystals and characterized on the basis of the absorption spectra, the PMR spectra, *etc.* The *trans* isomers of the carbonatooxalato and bis(oxalato) complexes reveal spectra similar to that of the *trans*-$[Co(CO_3)_2(py)_2]^-$ complex synthesized previously; the splittings of the absorption bands are not observed in the I bands, but are observed in the II bands. On the other hand, the *trans* isomer of the bis(malonato) complex reveals no splittings in either the I band or the II band. The assignment of these absorption bands has been made from considerations based on the Angular Overlap Model.

In the studies previously carried out in our laboratory,[1-3] some dicarbonato complexes of the $[Co(CO_3)_2(a)_2]^{n-}$ type, where a represents unidentate ligands such as NH_3, NO_2^-, and CN^-, were synthesized by a method called the "tricarbonato method."[4] However, every complex isolated was of *cis* isomer. Under the circumstances, efforts were continued to find a *trans* isomer of this type of complex, and we finally succeeded in obtaining the isomer; the action of pyridine on an aqueous potassium bicarbonate solution of tricarbonatocobaltate(III) yielded not only the *cis* isomer, but also the *trans* one of the $[Co(CO_3)_2(py)_2]^-$ complex.[5] In addition to this success, it was found that the *trans* isomer revealed an unusual absorption spectrum; it showed a single maximum in the first absorption-band region (I band) and two maxima in the second absorption-band region (IIa and IIb bands).

Then, studies of the synthesis of the $[Co(O\text{–}O)_2(py)_2]^-$-type complexes were undertaken by using CO_3^{2-}, $C_2O_4^{2-}$, and $C_3H_2O_4^{2-}$ (malonate) ions as the bidentate O–O donor ligands. This paper will deal with the results of the studies; the synthesis gave a pair of *cis* and *trans* isomers for the $[CoCO_3ox(py)_2]^-$, $[Co(ox)_2(py)_2]^-$, and $[Co(mal)_2(py)_2]^-$ complexes. The *trans* isomers of the former two complexes revealed spectra similar to that of the *trans*-$[Co(CO_3)_2(py)_2]^-$ complex, while the *trans* isomer of the latter complex exhibited no splittings in either the first or the second absorption band.

Experimental

Synthesis. *1) Carbonatooxalatobis(pyridine)cobaltate(III). a) Potassium Salt of the* trans *Isomer,* trans-$K[CoCO_3ox(py)_2]\cdot 2.5H_2O$: To a green solution containing mainly the $[Co(CO_3)_2(ox)]^{3-}$ species, which had been prepared by the literature method[2] ($Co(NO_3)_2\cdot 6H_2O$, 15 g scale, 0.05 mol), we added pyridine (8 ml, 0.1 mol); the mixture was then stirred at 50 °C for 1.5 h. The resulting violet solution was kept in a refrigerator until red-violet crystals were deposited. The crystals were filtered and recrystallized from warm water (*ca.* 50 °C). The filtrate was preserved for the synthesis of the subsequent *cis* isomer. The yield was about 2.5 g. Found: C, 34.71; H, 3.66; N, 6.58%. Calcd for $K[CoCO_3(C_2O_4)(C_5H_5N)_2]\cdot 2.5H_2O$: C, 34.70; H, 3.36; N 6.23%.

b) cis *Isomer,* cis-$[CoCO_3ox(py)_2]^-$: A portion of the filtrate (*ca.* 1/5 volume) was charged on a column of Dowex 1-X8 resin (100—200 mesh) in the Cl-form (4.0×25.0 cm). After washing with water, the column was treated with a 0.1 M NaCl aqueous solution; three bands were thus separated. The first-descending band was of *cis*-$[Co(CO_3)_2(py)_2]^-$, and the last band, *cis*-$[Co(ox)_2(py)_2]^-$, while the middle band was the desired one. This was collected in a fraction and concentrated to a small volume, but no crystals were obtained because of its great solubility.

2) Bis(oxalato)bis(pyridine)cobaltate(III). a) Potassium Salt of the trans *Isomer,* trans-$K[Co(ox)_2(py)_2]\cdot 3H_2O$: To an aqueous solution of $K_3[Co(ox)_3]\cdot 3H_2O$[6] (25 g, 0.05 mol in 60 ml H_2O), we added pyridine (8 ml, 0.1 mol) and activated charcoal (1 g); the mixture was then stirred at 60 °C for 2 h. The resulting solution was filtered once to remove the charcoal and any precipitated material, and then concentrated until pink crystals began to be deposited. After the whole had been cooled for a while, the crystals were collected by filtration and recrystallized from warm water (*ca.* 50 °C). The filtrate was preserved for the subsequent *cis* isomer. The yield was *ca.* 2 g. Found: C, 34.86; H, 3.55; N, 6.00%. Calcd for $K[Co(C_2O_4)_2(C_5H_5N)_2]\cdot 3H_2O$: C, 34.51; H, 3.31; N, 5.75%.

b) Lithium Salt of the cis *Isomer,* cis-$Li[Co(ox)_2(py)_2]\cdot H_2O$: The filtrate in *a*) was poured into a column of Dowex 50W-X8 resin (100—200 mesh) in the Li-form (5.0×10.0 cm) in order to obtain the lithium salt of the desired isomer. The effluent was collected and evaporated almost to dryness. The residue was then extracted with warm ethanol (*ca.* 50 °C), and the solution was kept in a refrigerator until violet crystals were deposited. The yield was about 1.5 g. Found: C, 40.23; H, 3.21; N, 6.75%. Calcd for $Li[Co(C_2O_4)_2(C_5H_5N)_2]\cdot H_2O$: C, 40.12; H. 2.89; N, 6.68%.

3) Bis(malonato)bis(pyridine)cobaltate(III). a) Potassium Salt of the trans *Isomer,* trans-$K[Co(mal)_2(py)_2]\cdot 2H_2O$: To a solution of potassium tris(malonato)cobaltate(III), which had been prepared by the literature method[7] ($Co(NO_3)_2\cdot 6H_2O$, 30 g scale, 0.1 mol), we added pyridine (16 ml, 0.2 mol); the mixture was then stirred at 50 °C for 40 min. After the insoluble material had been removed by filtration, the filtrate was concentrated to a small volume and then kept in a refrigerator until purple crystals separated out. The crystals were collected by filtration and recrystallized from warm water (*ca.* 50 °C). The filtrate was preserved for the subsequent *cis* isomer. The yield was about 2 g. Found: C, 38.73; H, 3.55; N, 5.68%. Calcd for $K[Co(C_3H_2O_4)_2(C_5H_5N)_2]\cdot 2H_2O$: C, 38.72; H, 3.66; N. 5.64%.

b) Bis(ethylenediamine)oxalatocobalt(III) Salt of the cis *Isomer,* $[Co(ox)(en)_2]\cdot$cis-$[Co(mal)_2(py)_2]\cdot 3H_2O$: The filtrate in *a*) was evaporated almost to dryness, after which the residue was extracted with methanol. The methanol solution was then dried, and the residue was again dissolved with a minimum amount of water. To this solution, we added an aqueous solution of bis(ethylenediamine)oxalatocobalt(III) acetate[6] (in excess). The whole was kept in a refrigerator until red-brown crystals were deposited. Recrystallization was performed from warm water (*ca.* 50 °C). The yield was about 3.5 g. Found: C, 35.73; H, 4.84; N, 11.03%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2]\cdot[Co(C_3H_2O_4)_2(C_5H_5N)_2]\cdot 3H_2O$: C, 35.59; H, 4.88; N, 11.32%.

An attempt to resolve this complex was successful; the racemate (3.5 g, 0.005 mol) was ground in a mortar with water (5 ml), and then NaI (0.83 g, 0.005 mol) was added. The mixture was filtered to remove precipitates of $[Coox(en)_2]I$. To an aqueous solution of $(-)_{589}[Coox(en)_2]^+$ (0.003 mol in 7 ml H_2O), which had been prepared in the acetate form according to the literature method,[8] we added the above filtrate; the mixture was then cooled in an ice bath, and a small amount of ethanol was added. After the sides of the vessel had been scratched with a glass rod for some time, the whole was kept for an hour in an ice bath. The crystals thus deposited were recrystallized several times from water (*ca.* 40 °C). The less soluble diastereoisomer was found to be $(-)_{589}[Coox(en)_2]\cdot(+)_{589}[Co(mal)_2(py)_2]\cdot 3H_2O$.

4) Dicarbonatobis(pyridine)cobaltate(III), trans- *and* cis-*K*$[Co(CO_3)_2(py)_2]\cdot 3H_2O$: The syntheses of these isomers have been described in a previous paper.[5]

The synthesis was attempted using 3- or 4-methylpyridine in place of pyridine; the *trans* isomers could be isolated, but no *cis* isomers were isolated because of their great solubility in ethanol. In the case of 2-methylpyridine, no substitution reaction proceeded.

Measurements. For the measurement of the absorption spectra in solution, a Hitachi 323 recording spectrophotometer was used. The spectra of the *trans-* and *cis*-$[Co(CO_3)_2(py)_2]^-$ complexes were measured with aqueous solutions containing a small amount of $KHCO_3$ in order to prevent the decomposition of the complex species. For the $[Coox(en)_2]\cdot$*cis*-$[Co(mal)_2(py)_2]$ complex, the spectrum was measured with the effluent obtained by passing its aqueous solution through a column of Dowex 50W-X8 resin in the Na-form. The absorption spectrum of the *trans*-$[Coox(H_2O)_2(py)_2]^+$ species was measured with an acidified solution of the *trans*-$[CoCO_3ox(py)_2]^-$ complex with 10% $HClO_4$; the acid-hydrolyzed species was chromatographically pure, and its absorption spectrum was reformed into the original spectrum of the parent carbonato complex when $KHCO_3$ was added to the acidified solution. This fact was evidence for the complete retention of the configuration during the acid-hydrolysis. The crystal absorption spectra were measured with a microspectrophotometer constructed in our laboratory.[9]

The proton magnetic resonance (PMR) spectra were recorded on a JEOL JNM PS-100 NMR spectrometer at 25 °C, using TMSP as the internal reference. The infrared absorption (IR) spectra in the 700—4000 cm^{-1} region were measured by means of a KBr disc method using a JASCO IRA-2 grating infrared spectrophotometer. The far-infrared spectra were taken by the Nujol method using a JASCO IR-F far-infrared spectrophotometer.

The isomerization of the *trans*-$[Co(CO_3)_2(py)_2]^-$ species was monitored spectrophotometrically at 400 and 560 nm at 25 °C under the following conditions: $[Co^{III}\text{ complex}]=(4.30-4.72)\times10^{-3}$ M, $[HCO_3^-]=0.25$ M, $[H^+]=3.98\times10^{-9}$ M and $[py]=6.18\times10^{-6}$ M. The ionic strength was made up to 1.0 M with KCl. The pH measurement was carried out with a Hitachi-Horiba M-7E pH-meter.

The calculations for curve analysis were carried out at Data Processing Center, Kanazawa University.

Results and Discussion

Characterization. In a previous work,[5] we characterized two isomers of the $[Co(CO_3)_2(py)_2]^-$ complex on the basis of the electronic absorption and the far-infrared spectra; the isomer which exhibits a distinct splitting in the second absorption band and a very simple pattern of the far-infrared spectrum was determined to be the *trans* isomer. Figure 1 shows the solution spectra for the isomers obtained at the earlier stage in each synthesis of the $[CoCO_3ox(py)_2]^-$ and $[Co(ox)_2(py)_2]^-$ complexes, the spectrum of the *trans*-$[Co(CO_3)_2(py)_2]^-$ being included for comparison. Both the isomers exhibit splittings of the second absorption bands (IIa and IIb), although the extents of the splittings are considerably reduced compared with that for *trans*-$[Co(CO_3)_2(py)_2]^-$. The absorption spectrum of the isomer obtained at the later stage in the synthesis of the $[Co(ox)_2(py)_2]^-$ complex and the spectrum of the *cis*-$[Co(CO_3)_2(py)_2]^-$ complex are compared in Fig. 2.

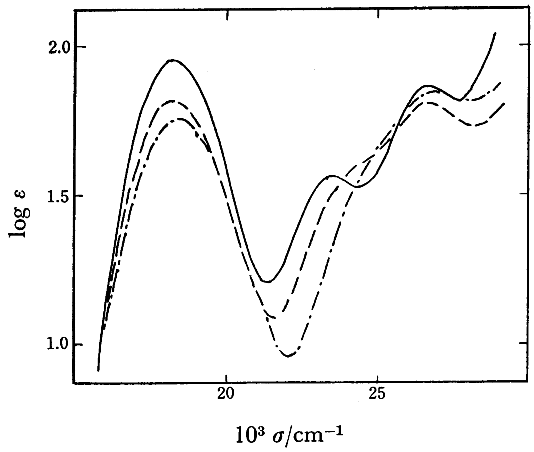


Fig. 1. Absorption spectra of *trans* isomers of; --- $[CoCO_3ox(py)_2]^-$, —·—$[Co(ox)_2(py)_2]^-$, and —— $[Co(CO_3)_2(py)_2]^-$.

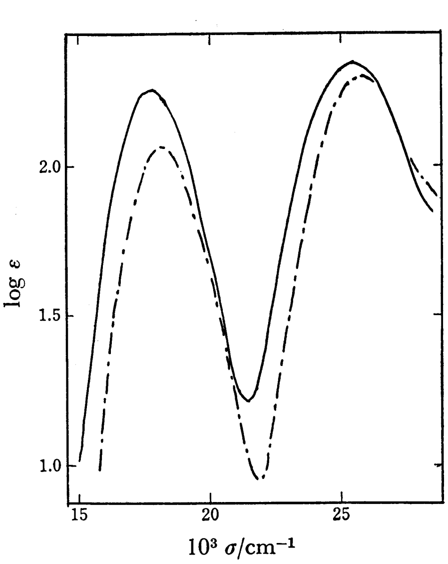


Fig. 2. Absorption spectra of *cis* isomers of; —·— $[Co(ox)_2(py)_2]^-$ and —— $[Co(CO_3)_2(py)_2]^-$.

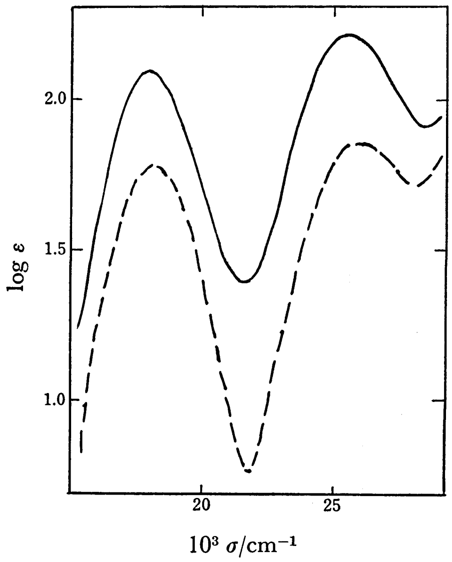


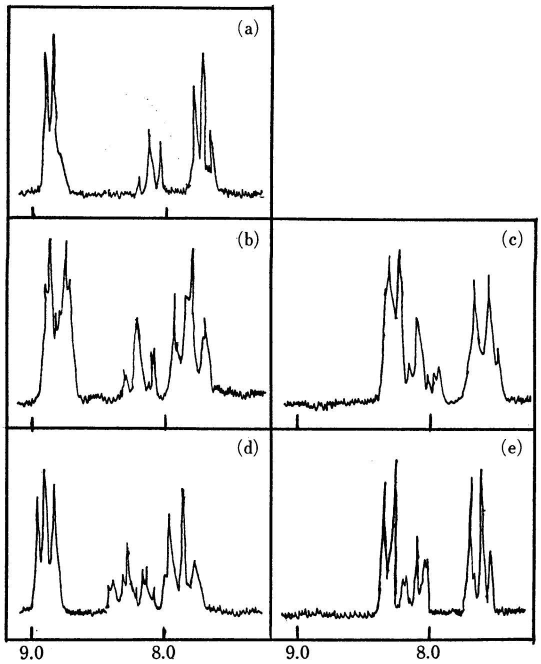
Fig. 3. Absorption spectra of;
---- *trans*-$[Co(mal)_2(py)_2]^-$ and
—— *cis*-$[Co(mal)_2(py)_2]^-$.

The spectra in the two figures are quite similar to each other. From a comparison of the spectra, the present isomers can be characterized.

The absorption spectra of the two isomers of the $[Co(mal)_2(py)_2]^-$ complex are shown in Fig. 3. The spectra are similar to each other except that there is a considerable difference in ε value between the isomers. However, as a successful resolution was effected with the isomer obtained at a later stage in the synthesis, the *cis* configuration is assigned to that isomer. Consequently, the remainder is regarded as the *trans* isomer. In this connection, the optical resolution was performed with one isomer of the $[Co(CO_3)_2(py)_2]^-$ complex and one of the $[Co(ox)_2(py)_2]^-$ complex. Our CD spectral studies of these *cis*-$[Co(O\text{-}O)_2(N)_2]^-$-type complexes[10] will be reported in a subsequent paper.

The PMR spectra of the present bis(pyridine) complexes are shown in Fig. 4. It is well known that, in free pyridine, the α-, γ-, and β-protons resonate at 8.50, 7.36, and 6.98 ppm (*vs.* TMSP) respectively. In the present complexes, these protons resonate at lower fields; for the *trans* isomers, at 8.9—8.7 ppm (α), 8.2—8.0 ppm (γ), and 8.0—7.6 ppm (β), while for the *cis* isomers, at 8.4—8.2 (α), 8.2—7.9 (γ), and 7.7—7.4 (β). A marked difference in chemical shift is observed between the α-protons of a *trans* isomer and those of the corresponding *cis* isomer. This phenomenon can be understood by the empirical rule of Watabe *et al.*[11] found from the studies of α-amino carboxylato complexes of cobalt(III): "The methine proton adjacent to the coordinated N atom resonates at a higher magnetic field when the O atom occupies the site *trans* to the N atom than when the N atom occupies the same site." The former case applies to the present *cis* isomer, which exhibits the resonance due to the α-protons at a higher magnetic field, the latter case, to the *trans* isomer.

Properties. The present compounds are all soluble in water, methanol, and ethanol. No *cis* isomer could be isolated as potassium or sodium salt because of their great solubilities in either an aqueous or an alcoholic medium. The use of the $[Coox(en)_2]^+$ ion as a counter ion was effective for the isolation of the *cis*-$[Co(mal)_2(py)_2]^-$ complex. The *cis*-$[Co(ox)_2(py)_2]^-$ complex was isolated as the lithium salt. The isolation of the *cis*-$[CoCO_3ox(py)_2]^-$ complex was unsuccessful in spite of various attempts. With respect to the corresponding *trans* isomers, all of the complexes were isolated as potassium salts.



ppm *vs.* TMSP

Fig. 4. PMR spectra of;
a) *trans*-$[CoCO_3ox(py_2)]^-$, b) *trans*-$[Co(ox)_2(py)_2]^-$, c) *cis*-$[Co(ox)_2(py)_2]^-$, d) *trans*-$[Co(mal)_2(py)_2]^-$ and e) *cis*-$[Co(mal)_2(py)_2]^-$.

Davies and Hung[12] investigated the kinetics of the reaction between the $[Co(CO_3)_3]^{3-}$ species and excess pyridine in an aqueous sodium hydrogencarbonate medium and reported that the reaction produced only the *cis*-$[Co(CO_3)_2(py)_2]^-$ species. Contrary to their statement, we found an isomerization of the *trans*-$[Co(CO_3)_2(py)_2]^-$ species; under the conditions mentioned in Experimental, *ca.* 40% of the initial amount of the *trans* species isomerized to the *cis* species after 12 h, and *ca.* 70% after 22 h, while the reaction was completed after 3 days.

The *trans*-$[CoCO_3ox(py)_2]^-$ species was acid-hydrolyzed in aqueous perchloric acid to give the *trans*-$[Coox(H_2O)_2(py)_2]^+$ species; the hydrolysis proceeded slowly. In a 10% perchloric acid medium, it took about an hour to complete the reaction. The absorption spectrum of the diaqua complex species thus produced is shown in Fig. 5.

The *trans*- and *cis*-$[Co(CO_3)_2(py)_2]^-$ species are also hydrolyzed in the same acid medium to give diaquacarbonato species. However, the species produced are not pure chromatographically because of the rather unstable nature of the parent dicarbonato species in an aqueous medium.

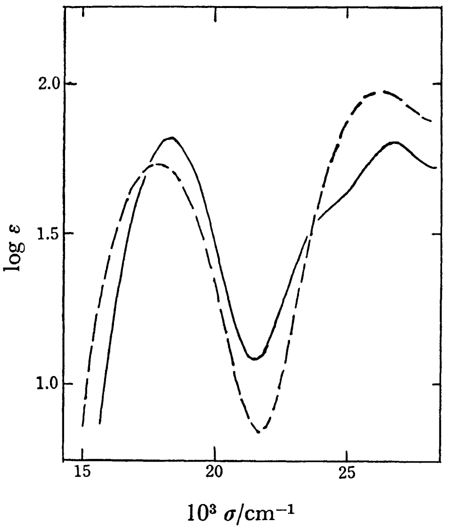


Fig. 5. Absorption spectra of; ---- *trans*-$[Coox(H_2O)_2(py)_2]^+$ and —— *trans*-$[CoCO_3ox(py)_2]^-$.

When excess ammonia reacts on the $[Co(CO_3)_3]^{3-}$ complex, the reaction proceeds successively, yielding *cis*-$[Co(CO_3)_2(NH_3)_2]^-$ and then $[CoCO_3(NH_3)_4]^+$.[1)] In contrast, the action of excess pyridine on the $[Co(CO_3)_3]^{3-}$ complex gives only the *trans*- and *cis*-$[Co(CO_3)_2(py)_2]^-$ complexes, no further reaction to give the tetrakis(pyridine) complex occurring. Springborg and Schäffer[13)] reported that the action of excess pyridine on an aqueous potaasium bicarbonate solution of the $[Co(CO_3)_3]^{3-}$ complex, which had been prepared using $CoCl_2\cdot 6H_2O$, at room temperature, yielded the $[CoClCO_3(py)_3]$ complex after 2—3 days. Further, the action of pyridine on this tris(pyridine) complex in the presence of bis(pyridine)mercury(II) perchlorate gave the tetrakis(pyridine) complex $[CoCO_3(py)_4]^+$. The acid decomposition of this carbonato complex to give carbon dioxide is unusually slow and results in the formation of the *trans*-$[Co(H_2O)_2(py)_4]^{3+}$ species.[13)]

The coordination of the O–O donor ligands was ascertained from the IR spectral data according to the literature.[14,15)] As to the IR spectra of pyridine complexes, Gill *et al.*[16)] pointed out that coordinated pyridine is usually distinguished from the free base by the presence of a weak band between 1235 and 1250 cm^{-1}, by a shift of the strong 1578 cm^{-1} band to 1600 cm^{-1}, and by shifts of the 601 and 403 cm^{-1} bands to 625 and

TABLE 1. ABSORPTION SPECTRAL DATA OF *trans*(N) COMPLEXES ($\tilde{\nu}$ in 10^3 cm^{-1})

Complex		I		IIa		IIb	
		$\tilde{\nu}_{max}$ (log ε)	Half-width	$\tilde{\nu}_{max}$ (log ε)	Half-width	$\tilde{\nu}_{max}$ (log ε)	Half-width
trans-$[Co(CO_3)_2(py)_2]^-$	obsd	18.2 (1.95)	3.00	23.5 (1.56)		26.7 (1.86)	
	calcd[a)]	18.2 (1.95)	2.93	23.3 (1.55)	3.42	26.5 (1.76)	2.48
trans-$[CoCO_3ox(py)_2]^-$	obsd	18.2 (1.82)	3.12	*ca.* 23.8		26.7 (1.80)	
	calcd[a)]	18.2 (1.82)	3.06	23.8 (1.47)	2.92	26.6 (1.75)	3.02
trans-$[Co(ox)_2(py)_2]^-$	obsd	18.4 (1.76)	3.25	*ca.* 24.2		26.7 (1.84)	
	calcd[a)]	18.4 (1.76)	3.12	24.0 (1.25)	2.57	26.7 (1.79)	3.53
		I		II			
trans-$[Co(mal)_2(py)_2]^-$		18.1 (1.78)	3.31	26.0 (1.85)	4.05		
trans-$[Co\ ox(H_2O)_2(py)_2]^+$		17.9 (1.73)	3.70	26.5 (1.95)	4.12		
		Ia		Ib		II	
trans(N)-$[Co\ ox(gly)_2]^-$ [b)]		16.7 (1.70)		18.9 (2.00)		25.8 (2.23)	
trans(N)-$[Co(ida)_2]^-$ [b)]		16.7 (1.05)		20.4 (1.72)		27.8 (1.75)	
trans(N)-$[Co(L\text{-}asp)_2]^-$ [b)]		15.9 (1.16)		19.5 (1.90)		26.5 (1.90)	

a) Results from Gaussian Analysis. b) Ref. 17.

TABLE 2. ABSORPTION SPECTRAL DATA OF THE *cis* COMPLEXES ($\tilde{\nu}$ in 10^3 cm^{-1})

Complex	I		II	
	$\tilde{\nu}_{max}$ (log ε)	Half-width	$\tilde{\nu}_{max}$ (log ε)	Half-width
cis-$[Co(CO_3)_2(py)_2]^-$	17.7 (2.24)	2.94	25.5 (2.34)	3.77
cis-$[Co(Cx)_2(py)_2]^-$	18.2 (2.06)	2.89	25.8 (2.29)	3.58
cis-$[Co(mal)_2(py)_2]^-$	18.0 (2.07)	3.23	25.4 (2.20)	3.72
C_2-*cis*(N)-$[Coox(gly)_2]^-$ [a)]	17.8 (2.08)	—	25.9 (2.20)	—
C_1-*cis*(N)-$[Coox(gly)_2]^-$ [a)]	18.3 (2.15)	—	25.8 (2.24)	—
cis(N)-$[Co(ida)_2]^-$ [a)]	17.8 (2.18)	—	26.3 (2.13)	—
cis(N)*trans*(O_6)-$[Co(L\text{-}asp)_2]^-$ [a)]	*ca.* 16.7 (1.90) 19.2 (2.25)	—	26.2 (1.87)	—
cis(N)*trans*(O_5)-$[Co(L\text{-}asp)_2]^-$ [a)]	17.2 (2.09) *ca.* 20.0 (1.88)	—	26.5 (1.80)	—

a) Ref. 17.

420 cm^{-1} respectively. In our spectra, a similar trend was observed; a weak 1250 cm^{-1} band was observed in the spectrum of each of the dicarbonato and carbonato-oxalato complexes (in the spectra of the other complexes, this absorption region was hidden by other bands). The strong band at *ca.* 1580 cm^{-1} in the free base shifted to 1600—1610 cm^{-1}. The shifts in the *ca.* 600 and 400 cm^{-1} bands could not be identified, because other bands due to the coordinated O-O ligands occurred. There was little difference in the spectrum of the 700—4000 cm^{-1} region between any isomeric pair of the complexes. In the far-infrared region, however, a marked difference was observed between the *trans* and *cis* isomers of the $[Co(CO_3)_2(py)_2]^-$ complex,[5] while the spectra of the other isomeric complexes were weak and broad.

Absorption Spectra. In order to discuss this subject in some detail, we summarize the numerical data on the absorption spectra in Tables 1 and 2, also including the spectral data[17] on some related complexes. As to all the *trans* isomers except for the *trans*-bis(malonato) complex, the observed spectra were divided into three Gaussians (I, IIa, and IIb);[18] the calculations were repeated until the corrections became sufficiently small. The calculated data are included in Table 1 and are illustrated in Fig. 6.

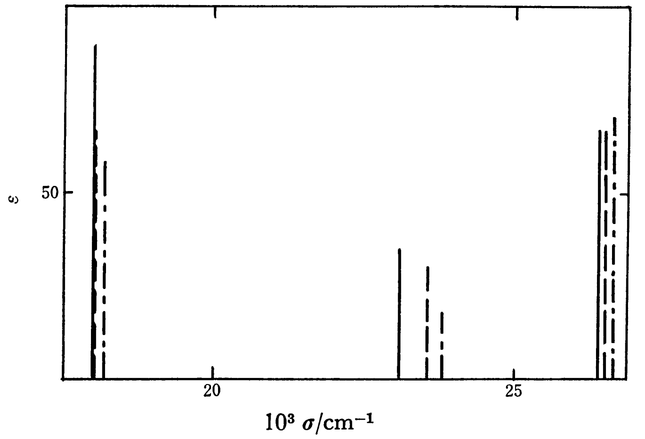


Fig. 6. Calculated positions and intensities for absorption maxima;
---- $[CoCO_3ox(py)_2]^-$, —·— $[Co(ox)_2(py)_2]^-$ and —— $[Co(CO_3)_2(py)_2]^-$.

Most of the $[CoN_2O_4]^-$-type complexes thus far prepared contain the N-donor in the form of an amino acidate, iminodiacetate, or nitrilotriacetate ion, and their *trans*(*N*) isomers exhibit explicit splittings of their first absorption bands (Table 1).[17,19–21] The situation differs in the present complexes, which contain unidentate pyridine molecules; the *trans*-$[Co(CO_3)_2(py)_2]^-$, *trans*-$[CoCO_3ox(py)_2]^-$ and *trans*-$[Co(ox)_2(py)_2]^-$ complexes exhibit the first bands which can be expressed by only one Gaussian and the second bands which can be divided into two Gaussians, while the *trans*-$[Co(mal)_2(py)_2]^-$ complex shows no splittings in either the first or the second absorption band. As far as the *cis* isomers are concerned, their spectra are typical of the *cis*-$[CoN_2O_4]^-$-type (Table 2).

When the spectral data of the above-mentioned three *trans* isomers are compared with each other, the following tendencies can be found:

1) The maximum positions of the I bands are similar to each other. This was a rather unexpected fact in view of the ligand-field-strengths of the two ligands (the $\varDelta$ values for octahedral $[Co(O\text{-}O)_3]^{3-}$ complexes are 17300 cm^{-1} (CO_3^{2-}) and 18000 cm^{-1} ($C_2O_4^{2-}$)).[22] The ε_{max} values decrease in the order of the dicarbonato, carbonatooxalato, and bis(oxalato) isomers.

2) The half-widths of the I bands are all narrow, but they tend to broaden progressively from the dicarbonato to the bis(oxalato) isomer.

3) The maximum positions of the IIa bands shift to shorter wavelengths in the order of the dicarbonato, carbonatooxalato, and bis(oxalato) isomers, and the ε_{max} values decrease in the same order. The half-widths also decrease in this order.

4) The IIb maxima are located at almost the same positions, and the ε_{max} values are nearly identical. The half-widths increase from the dicarbonato to the bis(oxalato) isomer.

Let us first discuss the assignment of the absorption bands for the three *trans* isomers besides the bis(malonato) isomer. It is well known that, under the D_{4h} symmetry, the $^1T_{1g}$ component in the O_h parentage splits into the $^1E_g{}^a$ and $^1A_{2g}$ components and the $^1T_{2g}$ into the $^1E_g{}^b$ and $^1B_{2g}$. From a comparison of our spectral data on the $^1T_{1g}$ region with those of the related *trans*(*N*)-$[CoN_2O_4]^-$-type complexes, it can be said that the observed I bands (18200—18400 cm^{-1}) are mainly due to the $^1A_{1g}\rightarrow{}^1E_g{}^a$ transition; the transitions to the $^1A_{2g}$ component are perhaps hidden by the feet of the I bands.

For the assignment of the IIa and IIb bands, the π contributions from the N and O donors must be considered. Schäffer *et al.*[23] have recently reported π-back bonding due to the N ligators with respect to the *trans*-$[Cr(py)_4AB]^{n+}$-type complexes. On the other hand, we previously reported that the positions of the IIa and IIb bands for the *trans*-$[Co(CO_3)_2(py)_2]^-$ complex calculated by means of Yamatera's prediction[24] roughly agreed with the observed positions, although any π contribution was ignored in the calculation. We shall discuss this subject in more detail below.

According to the Angular Overlap Model,[25] the energies of the $(t_{2g})^6\rightarrow(t_{2g})^5(e_g)$ transition in a complex whose holohedrized symmetry is D_{4h} are expressed as follows:

$$\mathbf{E}(A_{2g}) = \langle x^2-y^2|\mathbf{A}|x^2-y^2\rangle - \langle xy|\mathbf{A}|xy\rangle - C \tag{1}$$

$$\mathbf{E}(B_{2g}) = \langle z^2|\mathbf{A}|z^2\rangle - \langle xy|\mathbf{A}|xy\rangle + 16B - C \tag{2}$$

$$\begin{array}{c} E_g{}^a \\ \\ E_g{}^b \end{array}\begin{vmatrix} \begin{array}{l} 3/4\langle z^2|\mathbf{A}|z^2\rangle \\ \quad +1/4\langle x^2-y^2|\mathbf{A}|x^2-y^2\rangle \\ \quad -\langle yz|\mathbf{A}|yz\rangle - C - \mathbf{E} \end{array} & \begin{array}{l} \sqrt{3}/4\{\langle z^2|\mathbf{A}|z^2\rangle \\ \quad -\langle x^2-y^2|\mathbf{A}|x^2-y^2\rangle\} \end{array} \\ \\ \begin{array}{l} \sqrt{3}/4\{\langle z^2|\mathbf{A}|z^2\rangle \\ \quad -\langle x^2-y^2|\mathbf{A}|x^2-y^2\rangle\} \end{array} & \begin{array}{l} 1/4\langle z^2|\mathbf{A}|z^2\rangle \\ \quad +3/4\langle x^2-y^2|\mathbf{A}|x^2-y^2\rangle \\ \quad -\langle yz|\mathbf{A}|yz\rangle + 16B \\ \quad -C - \mathbf{E} \end{array} \end{vmatrix} = 0 \tag{3}$$

where **A** represents a one-electron potential operator, and where B and C denote Racah parameters. From these relations, the energies of the degenerate E_g states can be expressed by the parameters B and C, and the energies $\mathbf{E}(A_{2g})$ and $\mathbf{E}(B_{2g})$ and the energy difference between d_{yz} antibonding energy and d_{xy} antibonding energy, $\langle yz|\mathbf{A}|yz\rangle - \langle xy|\mathbf{A}|xy\rangle$ ($\equiv \Delta\mathbf{E}(\pi)$). Actually the $\mathbf{E}(B_{2g})$ value as well as the $\mathbf{E}(E_g{}^b)$ value can be estimated from the observed IIa maximum and the IIb maximum, and the $\mathbf{E}(A_{2g})$ value from the related complexes which exhibit remarkable splittings in their I band region. Thus, assuming C=4B,[26] the variation in the $\mathbf{E}(E_g{}^a)$ or the $\Delta\mathbf{E}(\pi)$ with varying B values is found.

Let us take the *trans*-$[\text{Co(ox)}_2(\text{py})_2]^-$ complex as a representative example; we assume two cases, one of which is that the IIb band is assumed to be the ${}^1A_{1g} \rightarrow {}^1B_{2g}$ transition (Case a), and the other is that the IIb band is assumed to be the ${}^1A_{1g} \rightarrow {}^1E_g{}^b$ transition (Case b). For the $\mathbf{E}(A_{2g})$ value, various values are adopted in the 16000—17000 cm^{-1} region. The B parameter varies in the 400—520 cm^{-1} range. The results are illustrated in Figs. 7 and 8.

In Case a, the calculated $\mathbf{E}(E_g{}^a)$ values are almost independent of the varying $\mathbf{E}(A_{2g})$ values, and the estimated $\Delta\mathbf{E}(\pi)$ has positive values. On the other hand, in Case b the $\mathbf{E}(E_g{}^a)$ values are sensitive to the variation in the $\mathbf{E}(A_{2g})$, and the $\Delta\mathbf{E}(\pi)$ has negative values, which are evidence for a net π back-bonding from metal(III) to ligand. In this connection, for the other *trans* bis(pyridine) complexes similar situations were obtained.

The most suitable B value can be evaluated by fitting a calculated $\mathbf{E}(E_g{}^a)$ value to the observed I maximum; the value is estimated to be less than 400 cm^{-1} in Case a, while in Case b it is *ca.* 480 cm^{-1}. In view of the separation between the I maximum and the II maximum for the *cis*-$[\text{Co(ox)}_2(\text{py})_2]^-$ complex, the value in Case a ($\approx$400 cm^{-1}) seems to lose its physical meaning.

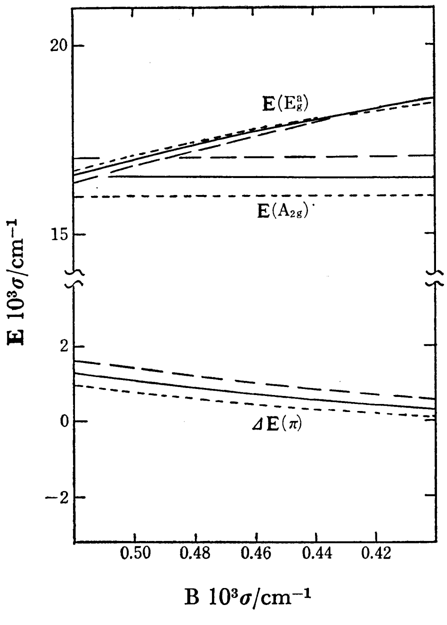


Fig. 7. The variation of $\mathbf{E}(E_g{}^a)$ or $\Delta\mathbf{E}(\pi)$ with B (Case a); ----$\mathbf{E}(A_{2g})=17000$, ——$\mathbf{E}(A_{2g})=16500$ and ······$\mathbf{E}(A_{2g})=16000$ cm^{-1}.

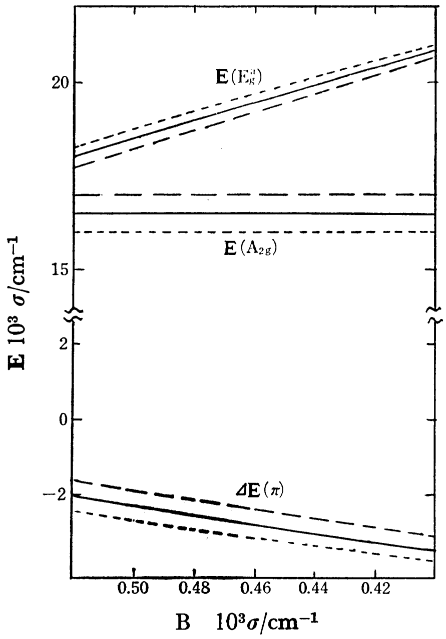


Fig. 8. The variation of $\mathbf{E}(E_g{}^a)$ or $\Delta\mathbf{E}(\pi)$ with B (Case b); ----$\mathbf{E}(A_{2g})=17000$, ——$\mathbf{E}(A_{2g})=16500$ and ······$\mathbf{E}(A_{2g})=16000$ cm^{-1}.

Since the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and the ${}^1A_{1g} \rightarrow {}^1B_{2g}$ transitions correspond to the $xy \rightarrow x^2-y^2$ and the $xy \rightarrow z^2$ transitions respectively, the ratio of the transition oscillator strengths can be derived in a way similar to that used for the O_h transitions:[27]

$$\frac{f_{A_2}}{f_{B_2}} = \frac{3\times\mathbf{E}(A_2)}{\mathbf{E}(B_2)} \times \left(\frac{\mathbf{E}(B_2)-\mathbf{E}(CT)}{\mathbf{E}(A_2)-\mathbf{E}(CT)}\right)^2. \qquad (4)$$

Using this equation, the intensity of the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition can be evaluated for the *trans*-$[\text{Co(ox)}_2(\text{py})_2]^-$ complex; the $\mathbf{E}(A_{2g})$ value is estimated to be *ca.* 17000 cm^{-1} in view of the Ia maxima of the *trans*(*N*)-$[\text{Co(ida)}_2]^-$ and *trans*(*N*)-$[\text{Coox(gly)}_2]^-$ complexes (Table 1). The $\mathbf{E}$(CT) value is assumed to be 41000 cm^{-1}, which corresponds to the CT maximum for the $[\text{Co(ox)}_3]^{3-}$ complex. Thus, the ε_{max} value due to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition is calculated to be *ca.* 42 in Case a and *ca.* 19 in Case b. If the fact that the observed I maximum has $\varepsilon_{max}=57.5$ is taken into consideration, then the ε_{max} in Case a seems to be too large. As to the *trans*-$[\text{Co(CO}_3)_2(\text{py})_2]^-$ complex, it is difficult to adopt the same discussion about the intensity because the symmetry of this complex is actually lower than D_{4h}; in addition, the $\mathbf{E}(A_{2g})$ value is hard to estimate. On the basis of these considerations, we now assign the IIa band to the ${}^1A_{1g} \rightarrow {}^1B_{2g}$ transition and the IIb band to the ${}^1A_{1g} \rightarrow {}^1E_g{}^b$ transition.

In this connection, the same procedure was applied to the spectral data for the *trans*(*N*)-$[\text{CoCO}_3(\text{mda})(\text{NH}_3)]^-$ (mda=*N*-methyliminodiacetate ion) complex[28] in order to find the variation in $\mathbf{E}(E_g{}^a)$ or $\Delta\mathbf{E}(\pi)$ with B. The results were quite similar; this fact suggests the minor contribution of the π bonding character due to coordinated py molecules in the present bis(pyridine) complexes.

We adopt the more reasonable B value, 480 cm^{-1}. The $\langle xy|\mathbf{A}|xy\rangle$ value is assumed to be zero, because two p orbitals of any O donor in xy molecular plane are already used for σ hybridizations and so cannot be of any use in the π bondings. Using such a value, the π antibonding energy in the yz plane is evaluated to be:

$$\langle yz|\mathbf{A}|yz\rangle = -2200\ \mathrm{cm}^{-1}. \qquad (5)$$

This is expressed alternatively in terms of ligand-field parameters;

$$\Delta(\mathrm{O}) + \Delta(\mathrm{N}) = -4400\ \mathrm{cm}^{-1}. \qquad (6)$$

This value is more negative than the Δ(N) value (-3400—-2000 cm^{-1}) for the *trans*-$[Cr(py)_4AB]^{n+}$-type complexes.[23] When the energies from the ligand to metal-charge-transfer transitions are compared between the $[Co(acac)_3]$ and $[Cr(acac)_3]$ complexes,[29] it is found that the metal orbitals in the cobalt(III) complex lie at rather lower levels than those in the chromium(III) complex, suggesting the existence of π-bonding contributions due to O–O donors in the present cobalt(III) complexes.

Let us next consider the spectrum of the *trans*-$[Co(mal)_2(py)_2]^-$ complex. No shoulder is observed in the I band, but the maximum shifts to a longer wavelength compared with those for the other *trans* isomers, and the half-width is enhanced. These facts suggest that the absorption due to the $^1A_{1g}\rightarrow{}^1A_{2g}$ transition gains a certain amount of intensity. The II band maximum also shifts to a considerably longer wavelength compared with the maxima of the IIb bands for the other isomers, and the half-width is also enhanced. These facts suggest that the absorptions due to the $^1A_{1g}\rightarrow{}^1B_{2g}$ and $^1A_{1g}\rightarrow{}^1E_g{}^b$ transitions occur in a closely-neighboring region with the comparable intensities. The same facts can be found more clearly in the spectrum of the *trans*-$[Coox(H_2O)_2(py)_2]^+$ complex (Fig. 5 and Table 1).

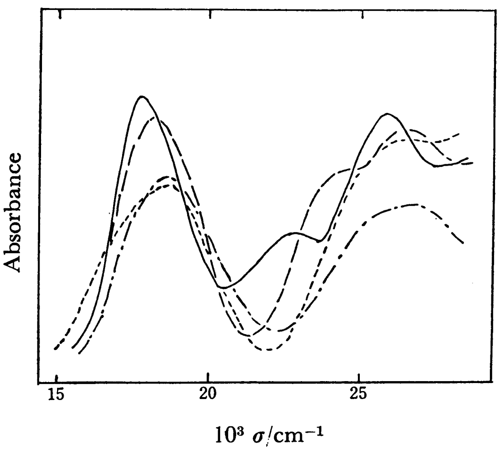


Fig. 9. Crystal spectra of *trans* isomers of;
—— $K[Co(CO_3)_2(py)_2]\cdot3H_2O$,
– – – $K[CoCO_3ox(py)_2]\cdot2.5H_2O$,
-·-·- $K[Co(ox)_2(py)_2]\cdot3H_2O$,
······ $K[Co(mal)_2(py)_2]\cdot2H_2O$.

Figure 9 shows the nonpolarized crystal spectra of the *trans*-isomers; every spectrum resembles the corresponding solution spectrum in shape, but it is noteworthy that the spectrum of the *trans*-$[Co(mal)_2(py)_2]\cdot2H_2O$ shows a shoulder on the longer-wavelength side (*ca.* 16400 cm^{-1}) of the main I band (18600 cm^{-1}). This may be due to the $^1A_{1g}\rightarrow{}^1A_{2g}$ transition, which disappears in the solution spectrum.

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