The Preparation and Absorption Spectra of the Mixed *cis*-Dicyano Complexes of Cobalt(III) with Carbonato or Related Ligands

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By the reaction of the $[Co(CO_3)_3]^{3-}$ complex and KCN, the complex anion, $[Co(CN)_2(CO_3)_2]^{3-}$, has been isolated as the tris(ethylenediamine)cobalt(III) salt. From this dicarbonato-complex anion, related dicyano complexes, $[Co(CN)_2(CO_3)(C_2O_4)]^{3-}$ and $[Co(CN)_2(C_2O_4)_2]^{3-}$ have then been obtained as $\Lambda(+)_{589}$-$[Co(en)_3]^{3+}$ salts, with resolutions into the active forms. Other related complexes, $[Co(CN)_2(dtc)_2]^-$ and $[Co(CN)_2(xan)_2]^-$ (dtc=dimethyldithiocarbamate anion, xan=methylxanthate anion), have also been prepared as potassium salts from the dicarbonato complex. The absorption spectra of all of the dicyano complexes have been measured, as have the CD spectra of the resolved dicyano complexes. Based on these spectral data, the geometrical structures of all the dicyano complexes have been identified as of the *cis* form. The $[Co(CN)(malo)_2OH_2]^{2-}$ complex has been isolated as potassium salt. From the PMR spectrum, the structure has been determined as the *trans* form. The polarized spectra of a crystal of this complex have also been measured.

It is generally said that the synthesis of a complex containing two different ligands which are considerably separated in the spectrochemical series[1] is difficult because a disproportionation reaction takes place easily. In fact, several complexes containing the cyanide ion, which occupies the highest position of the series, and ammonia, which is ranked in a middle position, have been prepared by methods which guard against the disproportionation reaction.[2-10] In a previous work,[4] we ourselves used potassium tricarbonatocobaltate(III) as the starting material for the synthesis of cyano-ammine-series complexes. At that time, we observed the formation of some species containing both cyano and carbonato ligands in the midst of the preparation reaction. Recently, we succeeded in isolating a species, the dicyanodicarbonatocobaltate(III) complex, from a reaction mixture of tricarbonatocobaltate(III) and cyanide.[11] Afterward, we attempted to prepare related complexes, such as bis(oxalato) and bis(malonato) complexes, from the dicarbonato complex. Furthermore, other similar dicyano complexes containing the dimethyldithiocarbamato ligand (abbreviated as dtc) or the methylxanthato(xan) were also prepared from the dicarbonato complex. In the present paper the preparation of these dicyano complexes and their electronic absorption spectra will be reported in detail. The spectra of other dicyano complexes containing H_2O ligands will also be reported. The cyanobis(malonato)-aquocobaltate(III) complex is also isolated in this work.

Experimental

Materials. The dimethylammonium dimethyldithiocarbamate, $(CH_3)_2NH_2(CH_3)_2NCS_2$, and potassium methylxanthate, KCH_3OCS_2, were freshly prepared according to the literature methods.[12] The other reagents were of reagent-grade quality.

Preparation. 1) $\Lambda(+)_{589}$-*Tris(ethylenediamine)cobalt(III)* cis-*dicyanodicarbonatocobaltate(III) Dihydrate*, $\Lambda(+)_{589}$-$[Co(en)_3]$·cis-$[Co(CN)_2(CO_3)_2]\cdot 2H_2O$. The preparative method has been described in an earlier paper,[11] but the description will be given here again because this method is the basis for the syntheses of the other complexes. To a cold, green solution of tricarbonatocobaltate(III)[13] ($CoCl_2\cdot 6H_2O$ 10 g (0.048 mol) scale) we added potassium cyanide (7.5 g, 0.12 mol) in portions. The mixture was then stirred vigorously at room temperature for an hour, whereby a deep red solution was obtained. (This solution was used not only in this preparation but also in other preparations to be discussed later.) The solution was carefully neutralized with aqueous perchloric acid and then filtered. The filtrate was charged on an ion-exchange column containing 100—200 mesh Dowex 1-X8 resin in the Cl form (diameter, 5 cm; resin height, 15 cm). By elution with an aqueous solution of KCl (1 M), a red band came out of the column, after a green band. This red effluent was concentrated at about 30 °C. A small amount of ethanol was added to the concentrate, and then the whole was kept in a refrigerator in order to precipitate some salts, such as KCl. After the removal of the precipitates, an aqueous solution of $\Lambda(+)_{589}$-$[Co(en)_3]Br_3\cdot 2H_2O$[14] was added to the filtrate. When the whole was then kept in a refrigerator, needle-like crystals of the desired complex, colored brown-violet, were deposited. These were washed with cold water, ethanol, and ether in turn, and finally dried *in vacuo*. The yield was about 1.5 g. Found: C, 23.93; H, 5.68; N, 22.10%. Calcd for $[Co(C_2H_8N_2)_3]\cdot[Co(CN)_2(CO_3)_2]\cdot 2H_2O$: C, 23.73; H, 5.58; N, 22.13%.

This compound showed the same CD spectrum as the $\Lambda(+)_{589}$-$[Co(en)_3]^{3+}$ complex itself. Attempts to obtain an usual compound such as potassium (or calcium) salt ended in failure because of the great solubility of such salt and because of the instability of the species in an aqueous solution.

2) $\Lambda(+)_{589}$-*Tris(ethylenediamine)cobalt(III)* cis-*dicyanocar-*

1) Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).
2) P. R. Ray and B. Sarma, *J. Indian Chem. Soc.*, **28**, 59 (1951).
3) H. Siebert, *Z. Anorg. Allg. Chem.*, **327**, 63 (1964).
4) M. Shibata, E. Kyuno, and M. Mori. *Inorg. Chem.*, **3**, 1573 (1964).
5) K. Ohkawa, J. Fujita, and Y. Shimura, This Bulletin, **38**, 66 (1965).
6) K. Ohkawa, J. Hidaka, and Y. Shimura, *ibid.*, **39**, 1715 (1966).
7) H. Nishikawa, K. Konya, and M. Shibata, *ibid.*, **41** 1492 (1968).
8) K. Konya, H. Nishikawa, and M. Shibata, *Inorg. Chem.*, **7**, 1165 (1968).
9) N. Maki, J. Hamazaki, and S. Sakuraba, This Bulletin, **41**, 1735 (1968).
10) M. Muto, T. Baba, and H. Yoneda, *ibid.*, **41**, 2918 (1968).
11) S. Fujinami and M. Shibata, *Chem. Lett.*, **1970**, 219.
12) "Beilsteins Handbuch," III, 216, 209.
13) M. Shibata, *Nippon Kagaku Zasshi*, **87**, 771 (1966).
14) "Inorganic Syntheses," VI, 186.

bonatooxalatocobaltate(III) Monohydrate, $\Lambda(+)_{589}$-[*Co(en)*$_3$]·cis-[*Co(CN)*$_2$*CO*$_3$(*C*$_2$*O*$_4$)]·*H*$_2$*O*. To a deep red solution obtained by the procedure described in 1), we added ground powder of oxalic acid (12 g, 0.1 mol) little by little. Then the solution was stirred vigorously at room temperature for 4—5 hours. After that, a chromatographic separation similar to that described in 1) was carried out using an aqueous solution of KCl (2 M). The effluent was quickly dried at about 30 °C, and the residue was extracted with methanol several times. The extracted solution was dried up again, and the remaining material was dissolved in a minimum amount of water. After a saturated aqueous solution of the $\Lambda(+)_{589}$-[Co(en)$_3$]Br$_3$ complex and a little ethanol had been added to the solution, it was kept in a refrigerator until brown-red crystals deposited. This crude complex was then recrystallized from water. The compound exhibited a different CD spectrum from that of $\Lambda(+)_{589}$-[Co(en)$_3$]$^{3+}$ itself, indicating the successful resolution of this dicyano complexes. Yield, about 0.03 g. Found: C, 25.11; H, 5.05; N, 20.94%. Calcd for [Co(C$_2$H$_8$N$_2$)$_3$]·[Co(CN)$_2$CO$_3$(C$_2$O$_4$)]·H$_2$O: C, 24.82; H, 4.92; N, 21.05%.

3) $\Lambda(+)_{589}$-*Tris(ethylenediamine)cobalt(III)* cis-*Dicyanobis(oxalato)cobaltate(III) Hexahydrate*, $\Lambda(+)_{589}$-[*Co(en)*$_3$]·cis-[*Co(CN)*$_2$(*C*$_2$*O*$_4$)$_2$]·6*H*$_2$*O*. A deep red solution obtained by the procedure described in 1) was acidified with ground powder of oxalic acid until the resulting solution showed pH 5; the solution was then stirred at room temperature for 5 hours. After that, the reacted solution was treated in the same way as has been described in 2). When the final solution was kept in a refrigerator, a foliate red crystal was deposited. The compound showed a CD spectrum different from that of the precipitant, indicating a successful resolution. Yield, about 0.03 g. Found: C, 22.38; H, 5.13; N, 17.53%. Calcd for [Co(C$_2$H$_8$N$_2$)$_3$][Co(CN)$_2$(C$_2$O$_4$)$_2$]·6H$_2$O: C, 22.72; H, 5.32; N, 17.66%.

4) *Potassium* cis-*Dicyanobis(dimethyldithiocarbamato)cobaltate (III) Monohydrate*, cis-*K*[*Co(CN)*$_2$*(dtc)*$_2$]·*H*$_2$*O*. To a cold, deep red reaction mixture, we added an aqueous solution of the dimethyldithiocarbamate (16 g, 0.1 mol) in portions. The mixture was stirred at room temperature for half an hour and then filtered. The filtrate was quickly dried up at ca. 25 °C, and the residue was extracted with methanol several times. After the concentration of the extracted solution to a small volume, the solution was poured into a column of alumina for chromatography (5×25 cm). By elution with methanol, a red band of the desired complex, next to a green band, came out. The eluted solution was then concentrated, and ether was added. When the solution was then kept in a refrigerator, dark red crystals were deposited. They were collected and washed with cold methanol and ether in turn. Yield, about 3 g. Found: C, 23.45; H, 3.51; N, 13.40; S, 31.82%. Calcd for K[Co(CN)$_2$(C$_3$H$_6$NS$_2$)$_2$]·H$_2$O: C, 23.52; H, 3.46; N, 13.71; S, 31.39%.

5) *Potassium* cis-*Dicyanobis(methylxanthato)cobaltate(III) Monohydrate*, cis-*K*[*Co(CN)*$_2$*(xan)*$_2$]·*H*$_2$*O*. The method was quite similar to that in 4); the xanthate ligand (14 g, 0.1 mol) was, however, used instead of the dtc ligand. Yield, 1 g. This complex is very unstable, even in the solid state. Found: C, 19.28; H, 2.55; N, 7.65; S, 33.78%. Calcd for K[Co(CN)$_2$(C$_2$H$_3$OS$_2$)$_2$]·H$_2$O: C, 18.84; H, 2.11; N, 7.33; S, 33.53%.

6) *Potassium* trans-*Cyanobis(malonato)aquocobaltate(III) Monohydrate*, trans-*K*$_2$[*CoCN(*malo*)*$_2$*OH*$_2$]·*H*$_2$*O*. To the cold, deep red solution mentioned in 1), we added finely ground malonic acid until the resulting solution showed pH 5. The mixture was stirred at room temperature for 3 hours, and then the solution was chromatographed in the same manner as has been described in 1). A blue-violet band came out upon elution with a KCl solution (1 M). This effluent was evaporated to dryness at 30 °C, and the residue was extracted with methanol several times. The extract was then again dried up, and the residue was dissolved in a minimum amount of water. After acetone was added, the solution was kept in a refrigerator until needle-like crystals had been deposited. They were collected and washed with methanol, acetone, and ether in turn. Yield, 1 g. Found: C, 20.68; H, 2.10; N, 3.81%. Calcd for K$_2$[CoCN(C$_3$H$_2$O$_4$)$_2$-OH$_2$]·H$_2$O: C, 20.84; H, 2.00; N, 3.47%.

Measurements. The infrared absorption spectra (IR) were measured by means of a JASCO IRA-2 grating infrared-spectrophotometer. The KBr disk method was used in the range of 400—4000 cm^{-1}. For the measurement of the electronic absorption spectra in solution, a Hitachi EPU-2A spectrophotometer was used. The circular dichroism spectra (CD) were recorded on a JASCO Model ORD/UV-5 spectrophotometer with a CD attachment, with samples converted to sodium salts in solution. The proton magnetic resonance spectra (PMR) were recorded on a JEOL C-60H spectrometer (60 Mc/sec) using sodium 3-(trimethylsilyl)propanesulfonate as the internal reference at room temperature. The electronic absorption spectra of single crystals were measured through the good offices of Professor Yukio Kondo of Rikkyo University, Tokyo.

Results and Discussion

Characterization. The IR spectra of the present [Co(CN)$_2$(O–O)$_2$]$^{3-}$-type complexes are very complicated because of the existence of the [Co(en)$_3$]$^{3+}$ complex as their counter ions, but it was possible to confirm the chelation of CO_3^{2-} or $C_2O_4^{2-}$ ions according to the methods of the literature.[15,16] The ν(CN) band was observed at 2155, 2140, and 2150 cm^{-1} for the dicarbonato, the carbonatooxalato, and bis(oxalato) complexes respectively. The IR spectra of the [Co(CN)$_2$(S–S)$_2$]$^-$-type complexes resembled those of the corresponding tris(dtc) and tris(xan) complexes in the spectra due to ligand absorption. The ν(CN) band was observed at 2110 and 2115 cm^{-1} for the xan and dtc complexes respectively. It is worthy of notice that the ν(CN) bands of these (S–S) chelated complexes appear in a region lower by *ca.* 30 cm^{-1} compared with those of the (O–O) chelated complexes. This fact may be related to the nephelauxetic effects[17] of the dtc and xan ligands. Evidence for the chelated malonate ion and the coordinated water molecule in the [CoCN-(malo)$_2$OH$_2$]$^{2-}$ complex was obtained from its IR spectrum. The ν(CN) band was observed at 2145 cm^{-1}.

Since the [Co(CN)$_2$CO$_3$(C$_2$O$_4$)]$^{3-}$ and [Co(CN)$_2$-(C$_2$O$_4$)$_2$]$^{3-}$ complexes could be resolved with the $\Lambda(+)_{589}$-[Co(en)$_3$]$^{3+}$ ion, the geometrical structures of these complexes were identified as of the *cis*-form. With the [Co(CN)$_2$(CO$_3$)$_2$]$^{3-}$ complex, the resolution

15) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, **79**, 4900 (1957).

16) J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Phys. Chem.*, **61**, 1014 (1957).

17) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, London, New York, Paris (1962).

Table 1. Absorption and CD spectral data of cyano complexes (10^3 cm^{-1})

Complex	Ia		Ib		II	
	ν_{max} (log ε)	ν_{ext}^{CD} ($\Delta\varepsilon$)	ν_{max} (log ε)	ν_{ext}^{CD} ($\Delta\varepsilon$)	ν_{max} (log ε)	ν_{ext}^{CD} ($\Delta\varepsilon$)
$[Co(CN)_2(CO_3)_2]^{3-}$	18.3 (1.96)		22.5 (2.03)		27.5 (2.20)	
$[Co(CN)_2CO_3(C_2O_4)]^{3-}$	18.7 (1.90)	19.3 (−0.66)	23.0 (2.07)	22.9 (+2.17)	28.1 (2.25)	28.4 (−0.47)
$[Co(CN)_2(C_2O_4)_2]^{3-}$	18.8 (1.84)	19.1 (−1.74)	23.4 (2.14)	23.5 (+3.03)	28.4 (2.37)	29.0 (−0.57)
$[Co(CN)_2(malo)_2]^{3-}$	18.7 (1.60)		23.3 (2.08)		sh	
$[Co(CN)_2C_2O_4(OH)_2]^{-}$	18.5 (1.70)		23.8 (2.00)		sh	
$[Co(CN)_2(OH_2)_4]^{+}$	18.6 (1.53)		24.0 (1.86)		*ca.* 30 (1.50)	
$[Co(CN)_2(dtc)_2]^{-}$	19.4 (2.52)		sh		—	
$[Co(CN)_2(xan)_2]^{-}$	19.7 (2.34)		sh		—	
	I ν_{max} (log ε)		II ν_{max} (log ε)			
$[CoCN(malo)_2OH_2]$	18.8 (2.20)		25.8 (1.94)			

was unsuccessful, but its structure was regarded as *cis*-form from the fact that the electronic absorption spectrum of this complex was very similar to those of the resolved complexes.

In the PMR spectrum of the $[CoCN(malo)_2OH_2]^{2-}$ complex, resonance signals due to the methylene groups in the chelated malonate rings were observed at 2.98, 3.29, 3.66, and 3.97 ppm; these are classified as an AB pattern with a coupling constant of $J=18.6$ Hz. This pattern suggests a structure *trans* with respect to CN^- and H_2O; two sets of AB patterns may be expected for *cis* structure of the complex. In fact, the $[Cogly(malo)_2]^{2-}$ complex[18] exhibits very complicated methylene signals because of the malonato ligand.

The Absorption and CD Spectra for the Dicyano Complexes. The absorption spectra of the $[Co(CN)_2(O\text{-}O)_2]^{3-}$-type complexes were measured in aqueous solutions of the tris(ethylenediamine) salts and in solutions of the sodium salts obtained by means of ion exchange. A spectrum obtained by subtracting the spectrum of the $[Co(en)_3]^{3+}$ complex itself from the observed spectrum for the tris(ethylenediamine) salt coincided with the spectrum for the sodium salt. Therefore, only the spectra of the sodium salts are shown in Fig. 1, while the numerical data are summarized in Table 1. The spectra show three well-separated maxima at *ca.* 18, 23, and 28 kK. No such marked splitting has ever been reported with the *cis*-form complexes. Hereafter, these three maxima (or bands) will be represented by Ia, Ib, and II from the lower energy. After the $[Co(CN)_2(CO_3)_2]^{3-}$ and the $[Co(CN)_2CO_3(C_2O_4)]^{3-}$ had been dissolved in aqueous perchloric acid, the resulting solutions were submitted to spectrum measurements. (The results are shown in Fig. 2 and Table 1.) It was ascertained that the complex species thus formed were chromatographically pure, and that the observed spectra were completely reformed into the spectra of the parent complexes, when excess Na_2CO_3 was added to the $HClO_4$ solution. From these facts, the spectra in Fig. 2 may be considered to be those for the tetra-

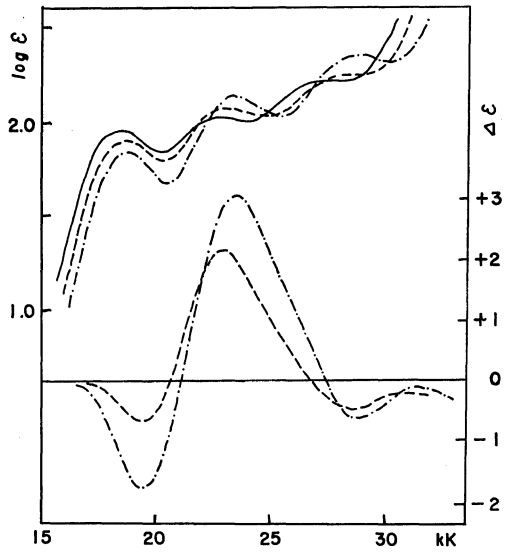

Fig. 1. Absorption and CD spectra of dicyano complexes.
——: $[Co(CN)_2(CO_3)_2]^{3-}$, – – –: $[Co(CN)_2CO_3(C_2O_4)]^{3-}$, –·–·–: $[Co(CN)_2(C_2O_4)_2]^{3-}$, (Na salts).

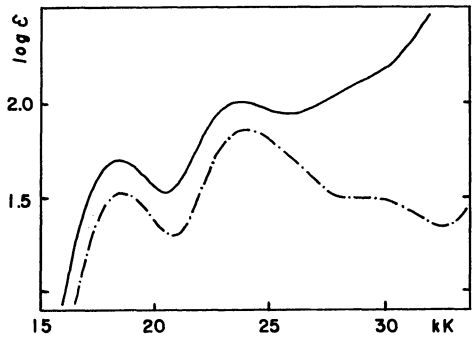

Fig. 2. Absorption spectra of dicyanoaquo complexes.
——: $[Co(CN)_2C_2O_4(OH_2)_2]^{-}$ (Na salt), –·–·–: $[Co(CN)_2(OH_2)_4]^{+}$.

aquo and diaquo complexes, *cis*-$[Co(CN)_2(OH_2)_4]^{+}$ and $[Co(CN)_2(C_2O_4)(OH_2)_2]^{-}$. A characteristic difference of these spectra from those of the present complexes is the decreased intensity of the II band. The dicyanobis(malonato) complex species, the attempt at the isolation of which was unsuccessful, exhibits a spectrum rather more similar to that of the tetraaquo complex species (Fig. 5) than to that of the dicarbonato (or bis(oxalato)) complex. This fact suggests that the intensity of the II band is related to the rigidity of

18) K. Yamasaki, J. Hidaka, and Y. Shimura, This Bulletin, **42**, 119 (1969).

the O–O ligand. Krishnamurthy and his co-workers[19] have reported the absorption spectrum of the *cis*-$[Cr(CN)_2(OH_2)_4]^+$ complex, which is very similar to the spectrum of our cobalt(III) complex. They said that one component of the second absorption band might be hidden under the middle maximum (corresponding to the Ib band), which is a component of the first absorption band; they based their suggestion on the meagerness of the third maximum (II Band). However, we consider that the Ib bands in our dicyano complexes are due to a split component of the first absorption band, judging from the fact that the Ib maxima for the $[Co(CN)_2(C_2O_4)_2]^{3-}$ and $[Co(CN)_2CO_3(C_2O_4)]^{3-}$ complexes coincide with their CD maxima (Fig. 1). However, it is interesting that the intensities of the Ib maxima are greater than those of the Ia bands.

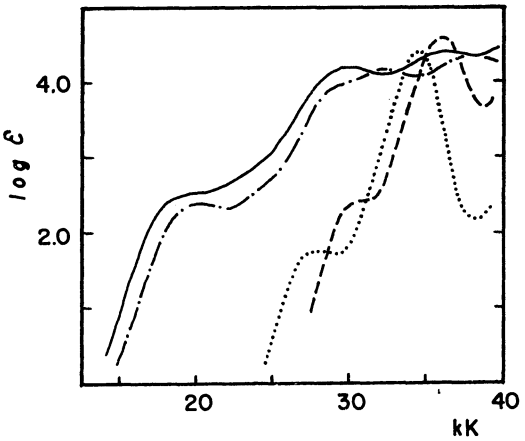

Fig. 3. Absorption spectra of sulfur-contained complexes.
——: $K[Co(CN)_2(dtc)_2]$, –·–·–: $K[Co(CN)_2(xan)_2]$,
·····: KCH_3OCS_2, ----: $(CH_3)_2NH_2(CH_3)_2NCS_2$.

The spectra of the $[Co(xan)_3]$ and $[Co(dtc)_3]$ complexes have been reported by Kida *et al.*,[20] but there has been no report on mixed complexes with the xan (or dtc) ligand and another ligand. In a complex containing such a (S–S) ligand, the d-d transition bands are covered, at a higher energy, by the allowed transition bands of the ligand. In fact, each absorption spectrum of the $[Co(CN)_2(dtc)_2]^-$ and $[Co(CN)_2(xan)_2]^-$ complexes (Fig. 3, Table 1) shows a well-defined maximum at a lower energy and a shoulder at a higher energy. However, by a comparison of these spectra with those of the carbonato (or oxalato) complex, the present dtc and xan complexes may be regarded as *cis* complexes. If the complexes are *trans*, entirely different spectra from those of the *cis*-$[Co(CN)_2(O\text{–}O)_2]$-type complexes may be expected.

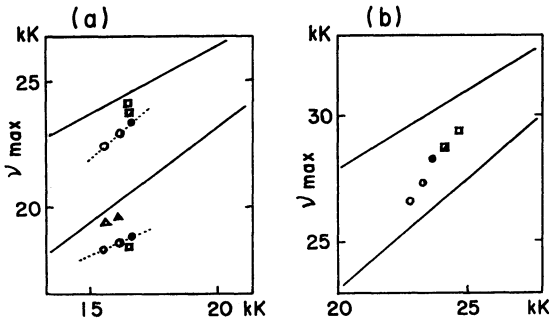

Fig. 4. The relationships between the absorption maxima of the dicyano complexes (ν_{max}) and the predicted values.
○: $[Co(CN)_2(CO_3)_2]^{3-}$, ◑: $[Co(CN)_2CO_3(C_2O_4)]^{3-}$,
●: $[Co(CN)_2(C_2O_4)_2]^{3-}$, ◪: $[Co(CN)_2C_2O_4(OH_2)_2]^-$,
□: $[Co(CN)_2(OH_2)_4]^+$, △: $[Co(CN)_2(dtc)_2]^-$,
▲: $[Co(CN)_2(xan)_2]^-$.

In order to discuss further the d-d bands of the present dicyano complexes, we divided each absorption curve into three symmetrical Gaussian[21,22] within a 3% error. The results of the analysis are summarized in Table 2. These analysed values are taken on a vertical axis in Fig. 4, while the absorption maxima for the $[Co(O)_6]$- and $[Co(S)_6]$-type complexes are placed on a horizontal line; (a) concerns the Ia and Ib bands, and (b), the II band. The solid lines in Fig. 4 represent the predicted values according to Yamatera's treatment.[23] However, the δ_π parameter was ignored and only the δ_σ parameter was taken into consideration for the second absorption band. Thus, the separation from a solid line on the vertical axis is a measure of the deviation from the theoretical treatment. That is, it indicates the distortion from octahedral symmetry or the degree of covalency between metal and ligand bonding. It is commonly considered that, in this figure, the distortion is removed upon the change in ligands from CO_3^{2-} to $C_2O_4^{2-}$.

Table 2. Calculated absorption maxima and half-width for the dicyano complexes (10^3 cm^{-1})

Complex	Ia		Ib		II	
	ν_{max} (log ε)	half-width	ν_{max} (log ε)	half-width	ν_{max} (log ε)	half-width
$[Co(CN)_2(CO_3)_2]^{3-}$	18.3 (1.93)	3.07	22.4 (2.04)	3.63	26.6 (2.11)	3.67
$[Co(CN)_2CO_3(C_2O_4)]^{3-}$	18.6 (1.90)	3.10	22.9 (2.07)	3.67	27.3 (2.14)	3.77
$[Co(CN)_2(C_2O_4)_2]^{3-}$	18.7 (1.84)	2.90	23.4 (2.14)	3.53	28.2 (2.29)	3.93
$[Co(CN)_2(malo)_2]^{3-}$	18.7 (1.60)	3.00	23.3 (2.08)	3.40	27.6 (1.82)	4.40
$[Co(CN)_2C_2O_4(OH_2)_2]^-$	18.5 (1.69)	3.17	23.7 (1.99)	3.83	28.6 (1.97)	4.37
$[Co(CN)_2(OH_2)_4]^+$	18.6 (1.53)	3.13	24.2 (1.86)	3.77	29 (1.50)	6.3
$[Co(CN)_2(dtc)_2]^-$	19.5 (2.51)	3.27	—	—	—	—
$[Co(CN)_2(xan)_2]^-$	19.6 (2.34)	3.33	—	—	—	—

19) K. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967).
20) S. Kida and H. Yoneda, *Nippon Kagaku Zasshi*, **76**, 103 (1955).
21) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).
22) Y. Shimura and R. Tsuchida, This Bulletin, **28**, 572 (1955).
23) H. Yamatera, *ibid.*, **31**, 95 (1958).

Concerning the Ia bands, the analysed values for the complexes containing carbonate and oxalate ions make a line with a considerable separation, one which becomes larger from the CO_3^{2-} ligand to the $C_2O_4^{2-}$ ligand. The analysed values for the aquo complexes will be found below. On the other hand, the analyzed values for the dtc and xan complexes could be found in a place close to the corresponding solid line. From these relations, it may be said that a complex containing a ligand ranking in a higher position in the nephelauxetic series exhibits much less deviation of the Ia-band maximum than would be predicted.

Concerning the Ib bands, a line connecting the analysed values for the complexes with the carbonato and oxalato ligands is also not parallel to the solid line, and it has a narrower separation upon the change in ligands from CO_3^{2-} to $C_2O_4^{2-}$. The separation between the Ia and the Ib, consequently, becomes larger in that order.

The analysed values of the II band are found between the two solid lines, and the rule of average environment[17,24] does not hold.

Figure 1 shows the CD spectra of the resolved dicyano complexes, as measured with aqueous solutions of sodium salts prepared by means of ion-exchange chromatography. Each spectrum reveals three peaks, with the signs (−), (+), (−) corresponding to the Ia, Ib, and II bands. It is noteworthy that the second peak dominates the first in each spectrum, and that the dominant peaks coincide perfectly with the Ib maxima. The $\Lambda(+)_{589}$-$[Co(C_2O_4)_2(NH_3)_2]^-$ complex[13] exhibits two peaks, with (+) and (−) signs, in the first absorption band region. The CD spectrum of the $\Lambda(+)_{589}$-$[Co(CN)_2(en)_2]^+$ complex[25] shows two positive peaks in the region, and suggests cancellation with a considerably large band with a minus Cotton sign. By comparing these spectra with those of our dicyano complexes, the dominant peak can be assigned to the B_1 component in C_{2v} symmetry, while the lower energy peak can be assigned to the (A_2+B_2) component. Thus, from the sign in the transition (*i.e.*, minus), the Λ configuration can be assigned to the complexes concerned.

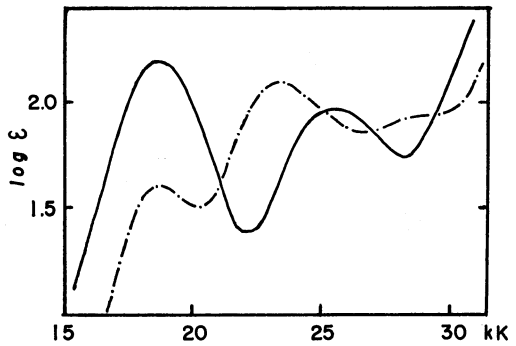

Fig. 5. Absorption spectrum of *trans*-cyanoaquobis(malonato)-cobaltate(III) complex.
——: $K_2[CoCN(malo)_2OH_2]$, –·–·–: $[Co(CN)_2(malo)_2]^{3-}$, (Na salt).

24) N. Matsuoka, J. Hidaka, and Y. Shimura, *ibid.*, **40**, 1868 (1967).

25) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094.

Absorption Spectra of the $[CoCN(malo)_2OH_2]^{2-}$ *Complex.* Figure 5 shows the absorption spectrum in solution. The spectrum exhibits no apparent splitting of the d-d bands, and the second absorption band has a rather weaker intensity and a broadened shape compared with the first absorption band. The maximum of the first band (Table 1) is at middle position between the A_2 and E component (C_{4v} symmetry), as predicted by Yamatera's treatment. On the other hand, this maximum coincides well with the Ia maximum for the $[Co(CN)_2(malo)_2]^{3-}$ complex, as may be seen in Fig. 5. This fact suggests that the first band of this cyano-aquo complex comes dominantly from the E component if this chromophore is treated as being tetragonal.

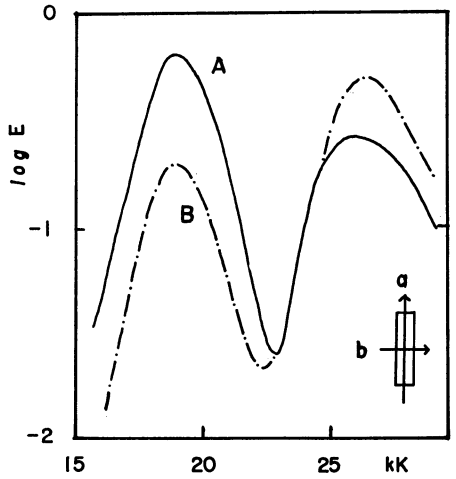

Fig. 6. Polarized single crystal spectra of *trans*-$K_2[CoCN(malo)_2OH_2]\cdot H_2O$ complex at *ca.* 90 K.
(A): along a axis ——; (B): along b axis (b⊥a)–·–·–.
log *E* represents observed absorbancy.

The polarized spectra of a crystal of this complex are shown in Fig. 6. The dichroism of the complex can be clearly observed. It can also be seen from the spectra that the relations between the intensities of the first and second bands are reversed according to the axes of polarization. Furthermore, the spectrum measured along the axis of the crystal (a) shows a red shift and a broadened shape, compared with the spectrum along the (b) axis in the region of the second absorption band. These crystal spectra are not understood precisely, because no X-ray analysis was done. However, in order to explain the observed spectra, let us now suppose that all the molecular axes of this complex are parallel to each other in the crystal. Under the C_{4v} symmetry, the A_2 and B_2 components become forbidden transitions, while the E component becomes an allowed transition; this can not, however, explain the reversed intensities and the broadened unsymmetrical second band. On the other hand, when the C_{2v}[26] molecular symmetry is adopted for this complex, only the A_2 component of the first band (corresponding to A_2 in C_{4v}) becomes a forbidden transition, while the B_1 and B_2 components (corresponding to E in C_{4v}) become allowed. From this, the first band in the

26) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, Toronto, London (1955), p. 334.

spectrum (A) may be attributed to the (B_1, B_2) components. From the group-theoretical consideration, the inflation at the second band in the same spectrum (A) can also be attributed to the (B_1, B_2) components. Consequently, the second band in the spectrum (B) must be mainly due to the A_1 transition (B_2 in C_{4v}). Judging from the coincidence of the second absorption band maxima between the solution and the crystal spectra, the intensity of the II band in the solution spectrum should come dominantly from the B_2 component (in C_{4v}). With the $[Co(L)(NH_3)_5]$- and *trans*-$[Co(L)_2(NH_3)_4]$-type complexes, Piper *et al.*[27] have reported that, if L represents CN^-, the effect of δ_π should serve to increase the splitting of the second absorption band. Accordingly, it would seem to be reasonable to observe the splitting of the second absorption band in the present $[Co(C)(O)_5]$-type complex.

27) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 1524 (1965).