# The Preparation and Absorption Spectra of the Cyanocarbonatotriammine- and Cyanooxalatotriammine-type Complexes of Cobalt(III)

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The complexes of the [CoCN(O–O)(N)$_3$] type (O–O represents $CO_3^{2-}$ or $C_2O_4^{2-}$, and (N)$_3$ represents three $NH_3$, one $NH_3$ plus one en, or one dien) have been prepared starting from the [Co(CO$_3$)$_3$]$^{3-}$ complex, and their characterization has been achieved on the basis of the absorption and PMR spectra. Among these, each of the *fac*(N) isomers of the carbonato complexes shows a shoulder in the second absorption band and no shoulder in the first absorption band. In contrast, each of the corresponding *fac*(N) isomers of the oxalato complexes shows no such shoulder in the second absorption band, but does show a shoulder in the first absorption band. The same phenomena have been found in the spectra of the *trans*(N)-[Co(O–O)(mda)(NH$_3$)]$^-$ complexes (mda stands for the methyliminodiacetate ion).

In our previous studies concerning the preparation of mixed-ligand cobalt(III) complexes containing the cyanide ion as a ligand, we succeeded in obtaining such complexes as [CoCN(NH$_3$)$_5$]$^{2+}$,[1] *mer*-[Co(CN)$_3$(NH$_3$)$_3$],[1] *cis*-[Co(CN)$_2$(CO$_3$)$_2$]$^{3-}$,[2] and *cis-cis*-[Co(CN)$_2$(CO$_3$)(NH$_3$)$_2$]$^-$.[3] The present work was undertaken in connection with those studies and in order to prepare the cyanocarbonatotriammine-type and the cyanooxalatotriammine-type complexes, which are represented by the formula [CoCN(O–O)(N)$_3$] ((N)$_3$ represents three NH$_3$, one NH$_3$ plus one en, or one dien). These complexes are of interest not only in such preparative work, but also in electronic spectroscopy: Since the three kinds of donor atoms differ greatly in their ligand-field strengths, marked splittings of both the first and second absorption bands were expected for some of these complexes. In practice, the carbonato complexes with a geometrical form with respect to donor atoms showed shoulders in their second absorption bands, whereas the corresponding oxalato complexes showed shoulders in their first absorption bands.

## Experimental

*Preparation.* 1) *Cyanocarbonatotriamminecobalt(III), [CoCN(CO$_3$)(NH$_3$)$_3$]*: To a cold, green solution of tricarbonatocobaltate(III) (0.1 mol scale)[4] we added potassium cyanide (13 g, 0.2 mol) in portions; the mixture was then stirred vigorously at room temperature for 20 min, whereby a deep red solution was obtained. To this solution we added conc. aqueous ammonia (40 ml, 0.56 mol), after which the mixture was stirred at 50 °C for 40 min. The resulting dark red solution was carefully neutralized with aqueous perchloric acid under an iced condition and then filtered to remove any precipitated material. The filtrate was charged on a column of Dowex 50 WX-8 resin (100—200 mesh, Na-form, 50×400 mm). With careful washing with water, two bands colored yellow-brown and red, descended after the minor band of negatively charged species had been effused. These two bands were collected in fractions labeled A-1 and A-2. Each fraction was concentrated to a small volume, and a small amount of ethanol was added to the concentrate. When the mixture was kept in a refrigerator, fine crystals were deposited. The complexes thus obtained were also named A-1 and A-2. The formation ratio of A-1/A-2 was found to be about 1/5.

2) *Cyanocarbonatoammineethylenediaminecobalt(III), [CoCN(CO$_3$)(NH$_3$)(en)]·H$_2$O*: Concentrated aqueous ammonia (20 ml, 0.28 mol) was added to a deep red solution prepared in the same way (0.1 mol scale) as in 1), and the mixture was stirred at 40 °C for 30 min. The resulting solution was neutralized with aqueous perchloric acid and filtered. To the filtrate ethylenediamine (0.1 mol) was added, after which the mixture was stirred at 40 °C for an hour. The resulting dark red solution was neutralized again with aqueous perchloric acid under an iced condition and filtered to remove any precipitates. The filtrate was chromatographed in the same manner as in 1); two bands, colored yellow-brown and red, were collected in fractions labeled B-1 and B-2. When each concentrate from the fractions was kept in a refrigerator, crystals of the desired complex were deposited. The formation ratio of B-1/B-2 was about 1/10.

3) *Cyanocarbonatodiethylenetriaminecobalt(III), [CoCN(CO$_3$)(dien)]*: The procedure was the same as that in 1), except for the use of diethylenetriamine (10.3 g, 0.1 mol) instead of conc. ammonia. The chromatographic separation gave three bands, colored yellow-brown, red, and red. These were collected in fractions labeled C-1, C-2, and C-3. Very fine crystals were obtained from C-1 and C-3, whereas no complex was isolated from C-2 because the species was too unstable to be isolated. The formation ratio of C-1/C-3 was found to be about 1/5.

4) *Cyanooxalatotriammine-type Complexes, [CoCN(ox)(N)$_3$]*: A cyanocarbonato complex, A-1 (10 g, 0.05 mol), which had been obtained in *1)*, was treated with 60% perchloric acid (0.1 mol), and then potassium oxalate (18.4 g, 0.1 mol) was added to the acid-hydrolyzed solution. The resulting solution was stirred at 40 °C for 2 h and then neutralized with an aqueous solution of potassium hydroxide. After the precipitated material had been removed by filtration, the filtrate was chromatographed in the same manner as that in *1)*; two yellow-brown bands, labeled A′-1 and A′-2, were thus obtained. The amount of the second band (A′-2) formed was less than that of the first one (A′-1). One yellow-brown band was obtained when the A-2 complex was used as the starting material, and the complex obtained from this band was the same as A′-2. The other oxalato complexes, labeled B′-1 and B′-2 for the [CoCN(ox)(NH$_3$)(en)] complex, and C′-1 and C′-3 for the [CoCN(ox)(dien)] complex, were obtained in the same manner as above. The oxalato complexes thus obtained were less soluble in water than the corresponding carbonato complexes. Therefore, the recrystallization of the oxalato complexes was achieved by dissolving them in an aqueous solution of sulfuric acid and by then adding ethanol.

5) *Potassium Carbonatomethyliminodiacetatomonoamminecobaltate (III), K[Co(CO$_3$)(mda)(NH$_3$)]·2.5H$_2$O*: The ligand, methyliminodiacetic acid (H$_2$mda), was prepared from methylamine and sodium monochloroacetate according to the method

in the literature.[5] To a solution of K[Co(CO$_5$)$_2$(NH$_3$)$_2$]·H$_2$O[6] (13.5 g, 0.05 mol) in water, we added an aqueous solution of the ligand (K$_2$mda, 0.05 mol); the mixture was then stirred for 4 h at 45 °C, whereby a red-blue solution was obtained. It was carefully neutralized with aqueous perchloric acid under an iced condition and then filtered. The filtrate was charged on a column of an anion-exchange resin (Dowex 1X-8, 100—200 mesh, Cl-form, 50×400 mm). When the adsorbed band was eluted with a 0.07 M aqueous KCl solution, one red-violet band was obtained. This fraction was concentrated to a small volume at *ca.* 40 °C. A small amount of methanol was added to remove the KCl used for the elution. When the solution was then kept in a refrigerator, the desired complex was deposited. The recrystallization was performed from water.

*6) Potassium Oxalatomethyliminodiacetatomonoamminecobaltate (III), K[Co(ox)(mda)(NH$_3$)]*: This complex was easily obtained by treating an aqueous solution of the carbonato complex obtained in *5)* with a little excess of oxalic acid.

*Measurements.* The absorption spectra were measured with a Hitachi Model 323 spectrophotometer. The proton magnetic resonance spectra were recorded on a JEOL JNM-PS-100 NMR spectrometer at *ca.* 22 °C, with 20% D$_2$SO$_4$ in D$_2$O as the solvent. The values of the chemical shifts were referred to internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) or sodium D$_4$-trimethylsilylpropionate (TMSP).

## Results and Discussion

The possible geometrical isomers of the [CoCN(O–O)(N)$_3$] type complexes are illustrated in Fig. 1, where *mer* and *fac* represent *trans-cis* and *cis-cis* arrangements of the three N atoms, and where the *s*- and *u*- symbols are used to distinguish between the isomer with a plane of symmetry and the one without such a plane.

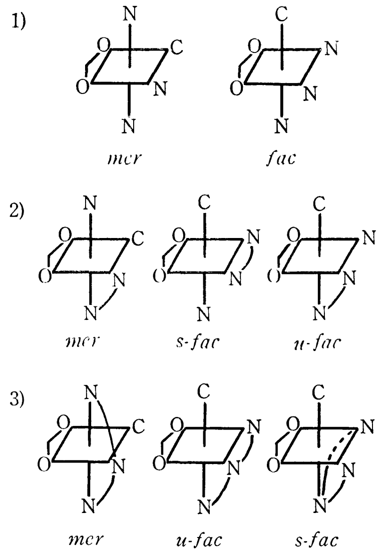

Fig. 1. Possible geometrical isomers of the [CoCN(O–O)(N)$_3$]-type complexes; 1) triammine complex, 2) ammine-ethylenediamine complex, and 3) diethylenetriamine complex.

The results of elemental analysis are given in Table 1 (no elemental analysis of the B′-1 complex was carried out because of the poor yield); these figures are in close agreement with the calculated values. The absorption spectral data are also summarized in Table 1, but that of the A′-1 complex was not measured because of its low solubility. Figure 2 shows the absorption spectra of the cyanocarbonato complexes, A-2, B-2, and C-3. Each spectrum shows a shoulder and a maximum in the second absorption band region. A similar feature of the

Table 1. Elemental analyses and absorption spectral data

| Label | Complex | Elemental analyses, %[a)] C | H | N | I band $\tilde{\nu}/10^3$ cm$^{-1}$ | I band log ε | II band $\tilde{\nu}/10^3$ cm$^{-1}$ | II band log ε |
|---|---|---|---|---|---|---|---|---|
| A-1 | *mer*(N)-[CoCN(CO$_3$)(NH$_3$)$_3$]·H$_2$O | 11.76<br>(11.22) | 4.98<br>(5.18) | 26.03<br>(26.17) | 20.6 | 2.05 | 28.8 | 2.05 |
| A-2 | *fac*(N)-[CoCN(CO$_3$)(NH$_3$)$_3$] | 12.42<br>(12.25) | 4.85<br>(4.63) | 28.83<br>(28.58) | 20.2 | 2.03 | 29.0<br>sh26.5 | 2.20 |
| A′-2 | *fac*-(N)-[CoCN(ox)(NH$_3$)$_3$]·0.5H$_2$O | 16.10<br>(15.46) | 4.27<br>(4.32) | 24.26<br>(24.04) | 21.2<br>sh18.0 | 1.95 | 29.4 | 2.15 |
| B-1 | *mer*(N)-[CoCN(CO$_3$)(NH$_3$)(en)]·H$_2$O | 20.26<br>(20.01) | 5.40<br>(5.46) | 23.64<br>(23.33) | 20.6 | 2.06 | 28.8 | 2.08 |
| B-2 | *u-fac*-(N)-[CoCN(CO$_3$)(NH$_3$)(en)]·H$_2$O | 19.95<br>(20.01) | 5.91<br>(5.46) | 23.18<br>(23.33) | 20.6 | 2.07 | 29.0<br>sh26.5 | 2.16 |
| B′-2 | *u-fac*-(N)-[CoCN(ox)(NH$_3$)(en)]·0.5H$_2$O | 23.42<br>(23.18) | 4.64<br>(4.67) | 21.64<br>(21.62) | 21.4<br>sh18.0 | 2.07 | 29.4 | 2.26 |
| C-1 | *mer*(N)-[CoCN(CO$_3$)(dien)] | 29.02<br>(29.04) | 5.49<br>(5.28) | 22.00<br>(22.58) | 20.4 | 2.18 | 28.6 | 2.20 |
| C-3 | *s-fac*(N)-[CoCN(CO$_3$)(dien)] | 29.04<br>(29.04) | 5.45<br>(5.28) | 22.79<br>(22.58) | 20.8 | 2.21 | 29.0<br>sh26.5 | 2.26 |
| C′-1 | *mer*(N)-[CoCN(ox)(dien)]·H$_2$O | 28.32<br>(28.58) | 5.46<br>(5.14) | 19.32<br>(19.05) | 20.6 | 2.13 | 29.0 | 2.26 |
| C′-3 | *s-fac*-(N)[CoCN(ox)(dien)]·H$_2$O | 28.68<br>(28.58) | 5.22<br>(5.14) | 18.52<br>(19.05) | 21.4<br>sh18.3 | 1.82 | 29.4 | 1.99 |
|  | *trans*(N)-K[Co(CO$_3$)(mda)(NH$_3$)]·2.5H$_2$O | 20.32<br>(20.23) | 4.34<br>(4.24) | 7.95<br>(7.86) | 18.4 | 2.06 | 26.4<br>sh23.9 | 1.99 |
|  | *trans*(N)-K[Coox(mda)(NH$_3$)] | 24.28<br>(24.15) | 3.11<br>(2.89) | 7.98<br>(8.05) | 18.2<br>sh16.5 | 2.08 | 25.6 | 2.32 |

a) ( ): calcd. sh: shoulder.

spectrum has been reported for the *mer*(*trans*)-[Co(CO$_3$)(α-am)(NH$_3$)$_2$] complexes (*trans* refers to the NH$_3$ groups, and α-am represents the glycinate, alaninate, or valinate ion),[7,8] and also with the *mer*(N)-[Co(CO$_3$)(*i*-dtma)] complexes (*i*-dtma stands for *N*,*N*-bis(2-aminoethyl)glycinate ion).[9] The spectrum of the *i*-dtma complex is included in Fig. 2 as an example. Moreover, it has been reported[10] that the absorption spectrum of the *trans*-[Co(CO$_3$)$_2$(py)$_2$]$^-$ complex shows an explicit shoulder in the second absorption band region and that the shoulder is assignable to a split component of the second band on the basis of Yamatera's predictions.[11] Therefore, the band positions for the present [CoCN(CO$_3$)(NH$_3$)$_3$] complex were calculated by means of Yamatera's predictions; the parameters concerning the first and second bands, $\delta^{\mathrm{I}}$ and $\delta^{\mathrm{II}}$, were treated as $\delta^{\mathrm{I}}=\delta^{\mathrm{I}}_{\sigma}+\delta^{\mathrm{I}}_{\pi}$ and $\delta^{\mathrm{II}}\approx\delta^{\mathrm{II}}_{\sigma}$. The numerical values were estimated from the absorption maxima of the [Co(NH$_3$)$_6$]$^{3+}$, [Co(CO$_3$)$_3$]$^{3-}$,[4] and *fac*-[Co(CN)$_3$(NH$_3$)$_3$][12] complexes ($\delta^{\mathrm{I}}$(NH$_3$−CO$_3$)$=4466$, $\delta^{\mathrm{II}}$(NH$_3$−CO$_3$)$=6700$ cm$^{-1}$; $\delta^{\mathrm{I}}$(CN−NH$_3$)$=10770$, $\delta^{\mathrm{II}}$(CN−NH$_3$)$=10130$ cm$^{-1}$). The predicted positions are given in Table 2.

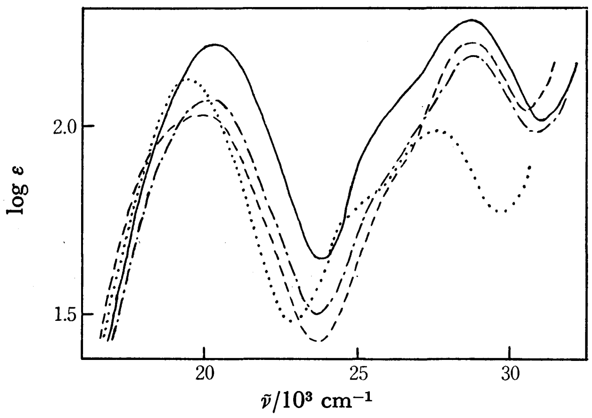

Fig. 2. Absorption spectra of [CoCN(CO$_3$)(N)$_3$]-type complexes, A-2 (------), B-2 (-·-·-) and C-3 (——), and of *mer*(N)-[Co(CO$_3$)(*i*-dtma)] (······).

Table 2. Predicted band positions for [CoCN(CO$_3$)(NH$_3$)$_3$]

| Geometry | I band (in cm$^{-1}$) | II band (in cm$^{-1}$) |
|---|---|---|
| *fac*(N) | 18700, 22500, 22500 | 27500, 27500, 31700 |
| *mer*(N) | 19900, 21400, 22500 | 27500, 29200, 30000 |

From the table it may be seen that the separations between the lowest-energy and highest-energy components in both the first and the second band for the *fac*(N) geometry are considerably greater than those for the *mer*(N) geometry. This fact suggests that a splitting of the second absorption band is to be expected for the *fac*(N) complex (namely, A-2). Thus, the remaining complexes, B-2 and C-3, may also be regarded as *fac*(N) isomers from the similarity in the spectrum. It is, however, not possible to differentiate between the *s*- and *u*-configurations for the B-2 and C-3 complexes.

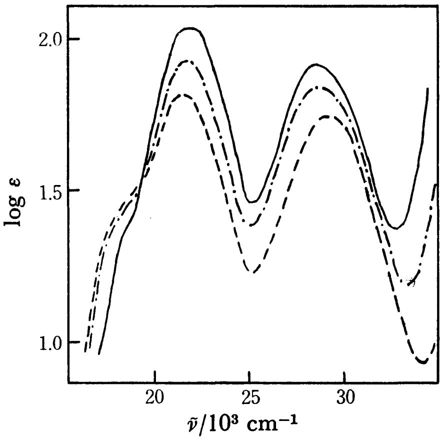

Fig. 3. Absorption spectra of [CoCN(H$_2$O)$_2$(N)$_3$]-type complexes derived from A-2 (------), B-2 (-·-·-), and C-3 (——).

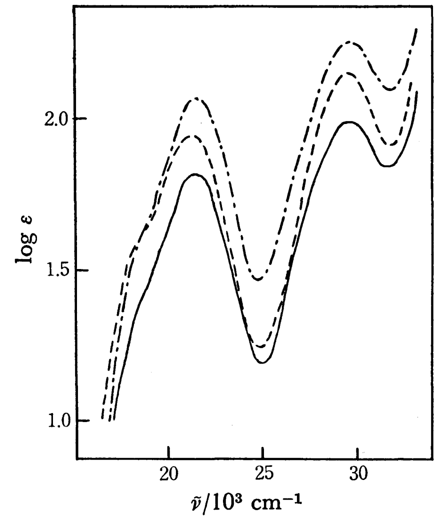

Fig. 4. Absorption spectra of [CoCN(ox)(N)$_3$]-type complexes, A′-2 (------), B′-2 (-·-·-), and C′-3 (——), in *ca.* 20% H$_2$SO$_4$.

Figure 3 shows the absorption spectra measured with solutions of the *fac*(N)-[CoCN(CO$_3$)(N)$_3$] complexes (A-2, B-2, and C-3) acidified with aqueous perchloric acid to give acid-hydrolyzed species. Figure 4 shows the spectra of the [CoCN(ox)(N)$_3$] complexes, A′-2, B′-2, and C′-3. In both figures, each spectrum reveals a shoulder in the first absorption band and no shoulder in the second absorption band. Similar splitting of the first absorption bands have been observed in the spectra of the *mer*(*trans*)-[Co(α-am)(H$_2$O)$_2$(NH$_3$)$_2$]$^{2+}$ and of the *mer*(*trans*)-[Coox(α-am)(NH$_3$)$_2$] complexes.[8] On this basis, the A′-2, B′-2, and C′-3 complexes can be identified as the *fac*(N) isomers which correspond, in geometrical configuration, to the above-mentioned *mer*(*trans*) isomers.

Figure 5 shows the spectrum of the [CoCN(CO$_3$)(dien)] complex, C-1, and that of the corresponding oxalato complex, C′-1. There are no shoulders in either the first or second absorption band. Similarly shaped spectra have been reported with the *fac*(N)-[Co(CO$_3$)(α-am)(NH$_3$)$_2$][8] and also with the *fac*(N)-[Co(CO$_3$)(*i*-dtma)].[9] As for *cis*-[Co(CO$_3$)$_2$(py)$_2$]$^-$, no shoulders have been reported in the first and second absorption bands.[10] Thus, the C-1 and C′-1 complexes can be identified as the *mer*(N) isomers. The same

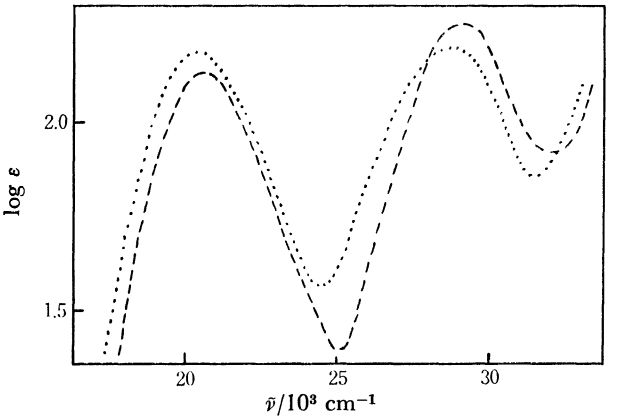

Fig. 5. Absorption spectra of [CoCN(CO$_3$)(dien)] complex, C-1 (······) and [CoCN(ox)(dien)] complex, C′-1 (------).

assignment can be made for the remaining complexes (A-1, B-1, A′-1, and B′-1). In addition the elution orders in the chromatographic separations support the foregoing assignments; the earlier eluted species in each run of the chromatographic separations is the *mer*(N) isomer.[7–9)]

The PMR spectrum of the *mer*(N)-[CoCN(ox)(dien)] complex, whose structural assignment could be made on the basis of the absorption spectrum, is presented in Fig. 6-a, the spectrum of the corresponding *fac*(N) complex being presented in Fig. 6-b. By a comparison of the two spectra, each peak resonating in a down field (5.7 ppm for the *mer* and 6.9 ppm for the *fac*) is attributed to the NH proton, the two peaks resonating in a middle field (4.8 and 4.4 ppm for the *mer* and 4.3 and 4.1 ppm for the *fac*) being attributed to the NH$_2$ protons. The integrated ratio of these three peaks is estimated to be 1: 2: 2.

A molecular model for the *mer*(N) isomer indicates that the two protons of each of the two NH$_2$ groups of the chelated dien are not equivalent with respect to the complexed CN$^-$ ion; one of the protons is located in a position near to the CN$^-$ ion, while the other is far from the CN$^-$ ion. Thus, the observed two peaks for the *mer*(N) complex can be interpreted in terms of such environmentally different situations of the NH$_2$ protons by assuming the effect of the CN$^-$ ion on the NH$_2$ resonances. Provided the *fac*(N) complex has the *s-fac*(N) structure, the two peaks due to the NH$_2$ protons can be interpreted in the same way. If the *u-fac*(N) structure is assumed, its spectrum would have three peaks due to the NH$_2$ resonances with the integrated ratio of 1: 1: 2. The fact that the CN$^-$ ion affects the NH$_2$ resonances is clearly recognized in the PMR spectrum of the *cis-cis*-[Co(CN)$_2$(H$_2$O)$_2$(en)]$^+$ complex[13)] (Fig. 6-c); there are four peaks corresponding to the four protons of the two NH$_2$ groups of the chelated en. This fact supports the *s-fac*(N) structure of the C′-3 complex. As to the corresponding carbonato complex, the PMR spectrum was measured in 20% D$_2$SO$_4$ (under this condition the complex was converted into [CoCN(H$_2$O)$_2$(dien)]$^{2+}$ species). The spectrum exhibited two broad peaks due to the NH$_2$ resonances, although one peak at a lower field contained a weak peak due to the NH resonance. On the basis of this obervation, the structure of the carbonato complex (C-3) is regarded as of the *s-fac*(N) form.

In establishing the structures of the isomers of the *fac*(N)-[CoCN(ox)(NH$_3$)(en)] complex, the PMR spectral approach did not play a part because similar spectra were expected for both the *s*- and *u*-geometries; the spectrum measured showed two peaks due to the NH$_2$ groups and one peak due to the NH$_3$ molecule. Taking into consideration the fact that the *u-fac*(N) isomer of the [CoCN(ox)(dien)] could not be isolated, the present NH$_3$-en complex may be regarded as a *u-fac*(N) isomer which corresponds to the *s-fac*(N) isomer of the dien complex. From the same point of view, the [CoCN(CO$_3$)(NH$_3$)(en)] complex (B-2) may be regarded as a *u-fac*(N) isomer.

When the absorption spectra of the [CoCN(CO$_3$)(N)$_3$] type complexes are again examined in relation to their established structures, it is found that every complex exhibiting a shoulder in the second absorption band has such a configuration that no chelate ring is formed in a co-plane with the carbonate chelate ring and that the axial positions are occupied by the donor atoms exerting stronger ligand fields than the other donor atoms on the planar positions.

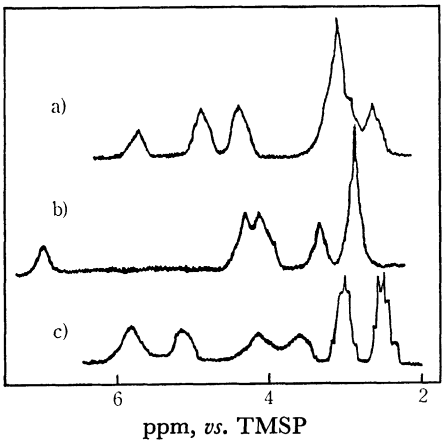

Fig. 6. PMR spectra of;
a) *mer*(N)-[CoCN(ox)(dien)], (b) *s-fac*(N)-[CoCN(ox)-(dien)], c) *cis-cis*-[Co(CN)$_2$(H$_2$O)$_2$(en)]$^+$.

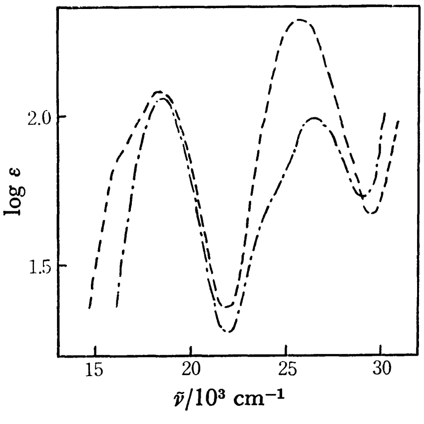

Fig. 7. Absorption spectra of mda complexes of;
*trans*(N)-[Co(CO$_3$)(mda)(NH$_3$)]$^-$ (-·-·-) and *trans*(N)-[Coox(mda)(NH$_3$)]$^-$ (------).

In order to confirm such restrictions in configuration, an additional experiment was designed to prepare the $[Co(CO_3)(mda)(NH_3)]^-$ complex; three geometrical isomers, two *cis*(N) and one *trans*(N), can possibly exist, but only one isomer was isolated, as has been mentioned in the Experimental section. The absorption spectrum of the complex is shown in Fig. 7, together with the spectrum of the corresponding oxalato complex. The splitting of the second absorption band is observed for the carbonato complex, whereas that of the first absorption band is observed for the oxalato complex. These facts correspond to those observed for the cyanotriammine complexes and indicate that both the mda complexes are to be their *trans*(N) isomers. This assignment is supported by the PMR spectrum of the oxalato complex (where there is observed an AB pattern due to the two $CH_2$ groups of the chelated mda).

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