Ion-exchange Chromatographic Studies of the $[Co(N)_4(O)_2]^+$-type Complexes

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The following complexes of the $[Co(N)_4(O)_2]^+$ type have been prepared: $[Coox(tn)_2]^+$, *u-fac-*, *s-fac-*, and *mer-*$[Coox(NH_3)(dien)]^+$, *cis-* and *trans-*$[Coox(NH_3)_2(en)]^+$, *u-fac-* and *s-fac-*$[Co(ida)(NH_3)(en)]^+$, *fac-*$[Co(ida)(NH_3)_3]^+$, and *cis*(O)*trans*(N)*cis*(NH_3)-, *cis*(O)*cis*(N)*cis*(NH_3)-, and *cis*(O)*cis*(N)*trans*(NH_3)-$[Co(gly)_2(NH_3)_2]^+$. The geometrical structures have been determined on the basis of the PMR spectra, the absorption spectra, *etc.* Including these new complex species, twenty-six species of the $[Co(N)_4(O)_2]^+$ type have been investigated through ion-exchange chromatographic separation. The elution orders obtained have been discussed in connection with the geometrical configurations.

Recent years have seen a dramatic development in the application of ion-exchange chromatography to the preparation of isomeric complexes of cobalt(III), in particular that of isomeric complexes of the $[Co(N)_4(O)_2]^+$ type consisting of polydentate ligands. In contrast to such practical separations of the isomeric complexes, only a little attention has been focused on the relationship between the order of the chromatographic separation and the geometrical configuration; a few works[1)] were, though, once undertaken in order to establish the elution order of such simple complexes as diacidotetraamminecobalt(III) ions. Very recently, a wide variety of cobalt(III) complexes were investigated by means of high-speed liquid chromatography.[2)]

In the present work, experiments were designed, in the first place, to prepare some complexes of the $[Co(N)_4(O)_2]^+$ type in order to undertake the work systematically. All the complexes including the new ones were classified into several series according to their geometrical structures. Then the order of elution was determined among the complexes of each series. The comparison between the series was done by using suitable complexes as the markers.

Experimental

Preparations. The new complexes designed in this work were prepared by the methods to be described below.

a) Oxalatobis(trimethylenediamine)cobalt(III) Chloride, $[Coox(tn)_2]Cl$. To a suspension of 6.3 g (0.02 mol) of *trans-*$[CoCl_2(tn)_2]Cl$[3)] in 20 ml of water, we added 3.7 g (0.02 mol) of potassium oxalate monohydrate, after which the mixture was stirred at 50 °C for 10 min. After an insoluble material had been removed by filtration, the filtrate was kept in a refrigerator overnight. The purple-red crystals thus deposited were filtered and washed with ethanol and ether. The yield was 3 g.

b) Oxalatoamminediethylenetriaminecobalt(III) Chloride, $[Coox(NH_3)(dien)]Cl$. Method 1: To a solution of 25 g (0.1 mol) of $K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$[4)] in 200 ml of water, we added 35.7 g of the solid material which had been isolated by saturating an aqueous diethylenetriamine with carbon dioxide; thereafter the mixture was stirred at room temperature for a day. To the resulting red solution oxalic acid was added until the solution showed a pH of *ca.* 3. The solution was again stirred at room temperature for a day. After the removal of insoluble white precipitates by filtration, the filtrate was found to be contain three geometrical isomers of the desired complex, their formation ratio being estimated to be *u-fac*: *s-fac*: *mer*=59: 6: 35 by means of ion-exchange chromatography (the symbols *s-* and *u-* indicate the structures with and without a plane of symmetry respectively).

Method 2: To a solution containing 0.7 g (0.005 mol) of ammonium oxalate in 50 ml of 2.8% aqueous ammonia, we added 1.3 g (0.005 mol) of *mer-*$[CoCl_3(dien)]$;[5)] the mixture was then stirred at room temperature for 1.5 hr. The mixture contained mainly two geometrical isomers of the complex, their formation ratio being estimated to be *u-fac*: *mer*=8: 92.

c) Oxalatodiammineethylenediaminecobalt(III) Chloride, $[Coox(NH_3)_2(en)]Cl$. This complex was prepared from *trans*(NH_3)-$[CoCl_2(NH_3)_2(en)]Cl$.[6)] A solution containing 3.0 g (0.015 mol) of the dichloro complex and 2.2 g (0.015 mol) of potassium oxalate monohydrate in 20 ml of water was warmed at 60 °C for 30 min. When the warm solution was allowed to stand at room temperature for some time, pink precipitates appeared. The substance was filtered and washed with ethanol and ether. The yield was 0.8 g. When the filtrate was kept in a refrigerator, red crystals were deposited, along with a small amount of the pink precipitates. The yield of this crude product was 1.2 g. The product was recrystallized twice from water. The pink complex was identified as the *cis*(NH_3) isomer, and the red one, as the *trans*(NH_3) isomer, from their absorption and PMR spectra.

d) Iminodiacetatoammineethylenediaminecobalt(III) Chloride, $[Co(ida)(NH_3)(en)]Cl$. To a green solution of tricarbonatocobaltate(III)[4)] $(Co(NO_3)_2\cdot 6H_2O$, 0.1 mol scale) we added a mixture of 16 g (0.12 mol) of iminodiacetic acid and 20 ml of concd aqueous ammonia; the mixture was then stirred at 50 °C for 10 min. To the resulting blue solution we added 7.2 g (0.12 mol) of ethylenediamine and 1 g of activated charcoal. The mixture was stirred vigorously at room temperature for a day. After the charcoal had then been filtered off, the filtrate was acidified with aqueous perchloric acid until the solution showed a pH of *ca.* 3, and then again filtered to remove the precipitated material. The solution thus obtained contained *u-fac* and *s-fac* isomers in the formation ratio of 88: 12.

e) Iminodiacetatotriamminecobalt(III) Chloride, $[Co(ida)(NH_3)_3]Cl$. To a green solution of tricarbonatocobaltate (III)[4)] $(Co(NO_3)_2\cdot 6H_2O$, 0.1 mol scale) we added a mixture of 16 g (0.12 mol) of iminodiacetic acid and 20 ml of concd aqueous ammonia, after which the whole was stirred at 50 °C to give a blue solution (*ca.* 10 min). Twenty ml of concd aqueous ammonia and 1 g of activated charcoal were then added to the solution, and the mixture was stirred again at 50 °C for 2 hr. After the charcoal has subsequently been removed by filtration, the deep red filtrate was neutralized with aqueous hydrochloric acid and then kept in a refrigerator overnight. The red crystals thus deposited were collected and washed with ethanol and ether. The yield was 10 g. This complex was characterized as the *fac* isomer on the basis of its spectral data.

f) Bis(glycinato)diamminecobalt(III) Chloride, $[Co(gly)_2(NH_3)_2]Cl$. This was readily prepared by modifying the method for the corresponding ethylenediamine complex $[Co(gly)_2(en)]Br$.[7] A solution of 10 g (0.042 mol) of cobalt(II) chloride hexahydrate in 10 ml of water was added to another solution containing 20 ml of concd aqueous ammonia and 6.4 g (0.085 mol) of glycine in 30 ml of water. After the addition of 10 g of lead dioxide, the solution was heated on a water-bath for 30 min. The reaction was completed by adding 10 more grams of lead dioxide and by then warming the solution for an hour. After having been cooled in a refrigerator overnight, the solution was filtered. The red solution thus obtained contained three *cis*(O) isomers; the formation ratio was found to be *cis*(O)*trans*(N)*cis*(NH_3): *cis*(O)*cis*(N)*cis*(NH_3): *cis*(O)*cis*(N)*trans*(NH_3)=46: 49: 5.

The other known complexes used in this work were as follows: $[CoCO_3(NH_3)_4]Cl$, $[CoCO_3(en)_2]Cl$, $[Coox(NH_3)_4]Cl$, $[Coox(en)_2]Cl$, $[Comal(NH_3)_4]NO_3$, $[Comal(en)_2]I$, α-[Coox(trien)]Cl, β-$[Coox(trien)]ClO_4$, [Co(ida)(dien)]Cl and $[Co(gly)_2(en)]Cl$. They were all prepared according to the known methods.

Elution. The columns used in this work were those containing 100—200 mesh Dowex 50W- X 8 in sodium form (diameters, 2.0—7.0 cm; resin heights, 10—50 cm). The elutions were carried out with 0.3—0.4 M NaCl aqueous solutions at rates in the range of *ca.* 0.3—1.2 ml/min. The complexes were classified into several series, and the chromatographic separation was carried out with each series.

Resolution. The optical resolution of the *cis*(O)*trans*(N)*cis*(NH_3) isomer of the $[Co(gly)_2(NH_3)_2]^+$ complex was carried out successfully by means of ion-exchange chromatography; the complex dissolved with a small amount of water was charged on a column of Dowex 50W- X 8 resin (100—200 mesh, Na-form, 2.5×50 cm). When being eluted by an aqueous solution of sodium antimony $(+)_{589}$-tartrate (0.25 M) at the rate of 0.3 ml/min, a band adsorbed on the top of the column was clearly separated into two bands. The first band corresponded to the $(-)_{589}$-antipode, and the second band, to the $(+)_{589}$-antipode.

Measurements. The absorption spectra were measured with a Hitachi EPU-2A spectrometer. The circular dichroism spectrum (CD) was recorded on a JASCO Model ORD/UV-5 spectrometer with a CD attachment. The proton magnetic resonance spectra (PMR) were recorded on a JEOL JNM-PS-100 MNR spectrometer at about 22 °C, using D_2O or a mixture of D_2O and 30% D_2SO_4 as the solvent. The values of the chemical shifts were determined in relation to the sodium D_4-trimethylsilylpropionate (TMSP) used as an internal reference.

Results and Discussion

Characterization of Complexes. The results of the elemental analysis and numerical data of the absorption spectra for the new complexes are summarized in Table 1. The geometrical structures of these complexes were determined mainly on the basis of their absorption and PMR spectra. For convenience, the PMR spectra will be discussed in the succeeding section.

The possible geometrical forms regarding the present complexes are shown in Fig. 1: There are three isomers for the $[Coox(NH_3)(dien)]^+$ complex. Among those, the *u-fac* isomer was easily characterized by its PMR spectrum, but the *s-fac* and *mer* isomers were not by their PMR spectra. However, we have found that the preparation from the *mer*-$[CoCl_3(dien)]$ complex produced one isomer predominantly. Considering this fact, the *mer*-form was tentatively assigned to that isomer obtained in a predominant yield.

Two isomers may be expected for the $[Coox(NH_3)_2(en)]^+$ complex. The complexes obtained were characterized by comparing their PMR spectra.

TABLE 1. ELEMENTAL ANALYSES AND ABSORPTION SPECTRAL DATA

Complex	Found (calcd) %			ν_I		ν_{II}		ν_{CT}	
	C	H	N	$\tilde{\nu}/10^3\,cm^{-1}$	log ε	$\tilde{\nu}/10^3\,cm^{-1}$	log ε	$\tilde{\nu}/10^3\,cm^{-1}$	log ε
$[Coox(tn)_2]Cl\cdot H_2O$	27.87 (27.55)	6.66 (6.37)	16.02 (16.07)	19.5	1.93	27.9	2.23	41.1	4.43
u-fac-$[Coox(NH_3)(dien)]Cl\cdot H_2O$	22.84 (22.47)	6.04 (5.67)	17.21 (17.84)	19.9	2.12	28.2	2.24	44.2	4.35
s-fac-$[Coox(NH_3)(dien)]Cl$[a]	—	—	—	20.0	—	28.2	—	44.3	—
mer-$[Coox(NH_3)(dien)]Cl\cdot H_2O$	22.60 (22.47)	6.06 (5.67)	17.36 (17.48)	20.0	2.09	28.0	2.15	44.0	4.32
cis-$[Coox(NH_3)_2(en)]Cl\cdot 1/2H_2O$	17.24 (16.82)	5.50 (5.30)	19.47 (19.10)	19.8	2.03	28.1	2.17	44.7	4.34
trans-$[Coox(NH_3)_2(en)]Cl\cdot 2H_2O$	15.67 (15.37)	6.18 (5.81)	18.10 (17.92)	19.9	1.88	28.3	2.02	45.2	4.36
u-fac-$[Co(ida)(NH_3)(en)]Cl\cdot H_2O$	22.69 (22.47)	6.05 (5.67)	17.48 (17.48)	*ca.* 17.9 20.1	sh 1.88	28.4	2.01	47.2	4.41
s-fac-$[Co(ida)(NH_3)(en)]Cl\cdot H_2O$	22.84 (22.47)	6.05 (5.67)	17.05 (17.48)	19.4	2.07	28.1	2.13	48.4	4.35
fac-$[Co(ida)(NH_3)_3]Cl\cdot H_2O$	16.68 (16.31)	5.76 (5.49)	18.66 (19.02)	19.8	1.93	28.1	2.07	49.0	4.39
cis(O)*trans*(N)*cis*(NH_3)-$[Co(gly)_2(NH_3)_2]Cl$	17.54 (17.37)	5.33 (5.11)	20.22 (20.26)	20.1	1.95	28.2	2.13	49.0	4.35
cis(O)*cis*(N)*cis*(NH_3)-$[Co(gly)_2(NH_3)_2]Cl$	17.49 (17.37)	5.53 (5.11)	19.97 (20.26)	19 6	2.03	27.8	2.11	47.6	4.34
cis(O)*cis*(N)*trans*(NH_3)-$[Co(gly)_2(NH_3)_2]Cl$	17.43 (17.37)	5.27 (5.11)	19.81 (20.26)	19.7	2.00	28.4	1.75	47.4	4.36

a) Because of the poor yield, no elemental analysis was carried out.

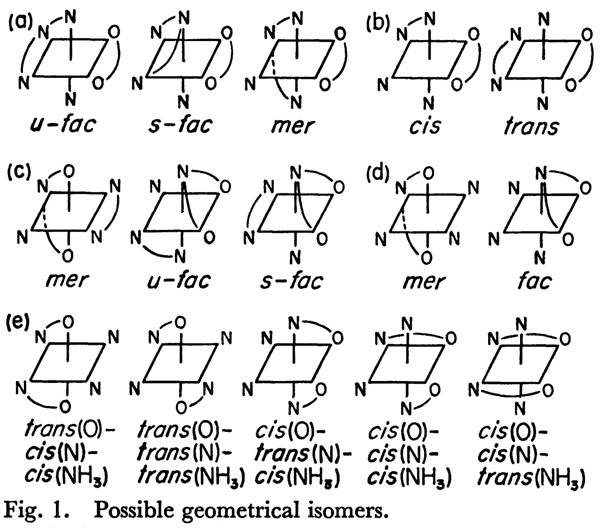

Fig. 1. Possible geometrical isomers.
(a) $[Coox(NH_3)(dien)]^+$ (b) $[Coox(NH_3)_2(en)]^+$
(c) $[Co(ida)(NH_3)(en)]^+$ (d) $[Co(ida)(NH_3)_3]^+$
(e) $[Co(gly)_2(NH_3)_2]^+$.

The $[Co(ida)(NH_3)(en)]^+$ complex can exist in three geometrical isomers. In the absorption spectrum of the *mer* isomer of the $[Co(ida)(NH_3)(en)]^+$ complex, a clear splitting of the first absorption band is to be expected from the *trans*(O) structure. In the spectrum of the known $[Co(ida)(dien)]^+$ complex,[8)] the separation of the split of the first band is estimated to be about 2900 cm^{-1}. In the spectra of the present two compounds, no such remarkable separation is observed, as may be seen in Fig. 2. This suggests that both the compounds are of facial forms. It is well known that the ida chelating in the *mer*-position is very strained.[8,9)] This suggests the preferential chelation of the ida in the facial configuration for the present compounds.

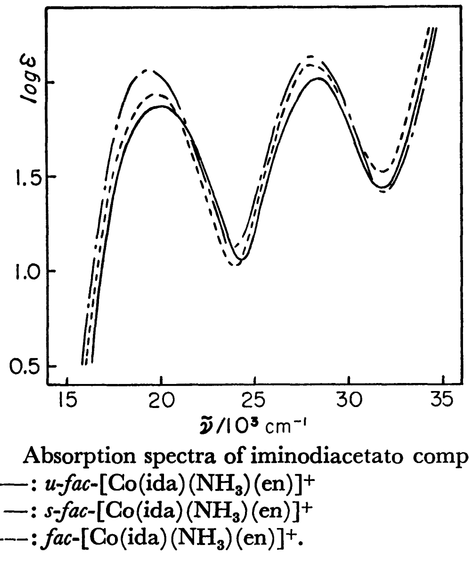

Fig. 2. Absorption spectra of iminodiacetato complexes.
———: *u-fac*-$[Co(ida)(NH_3)(en)]^+$
— • —: *s-fac*-$[Co(ida)(NH_3)(en)]^+$
------: *fac*-$[Co(ida)(NH_3)_3]^+$.

With the $[Co(ida)(NH_3)_3]^+$ complex, two geometrical isomers can exist, but only one was actually obtained; it was identified as having the *fac* form on the basis of the absorption spectrum (Fig. 2).

Five geometrical isomers can exist for the $[Co(gly)_2(NH_3)_2]^+$ complex. Much as in the absorption spectra of the above ida complexes, the spectra of the three isomers show no splittings in their first absorption bands (Fig. 3); therefore, they may be regarded as the *cis*(O) isomers. With the related $[Co(gly)_2(en)]^+$ complex, its *trans*(O) isomer and *cis*(O) isomers were isolated,[7)] but with the present diammine complex no *trans*(O) isomers were obtained. One of the three *cis*(O) isomers, *cis*(O)-*cis*(N)*cis*(NH_3), was easily assigned on the basis of its PMR spectrum. Of the other two isomers, the *cis*(O)-*trans*(N)*cis*(NH_3) isomer can be resolved into antipodes. In fact, the resolution was successful using a chromatographic method. Accordingly, the distinction between the resolvable *cis*(O)*trans*(N)*cis*(NH_3) isomer and the unresolvable *cis*(O)*cis*(N)*trans*(NH_3) isomer was made on the basis of such resolution experiments. The CD spectrum of the antipode eluted earlier is shown in Fig. 3. The spectrum shows a lower-energy negative component ($\Delta\varepsilon = -1.23$, 19300 cm^{-1}) and a higher-energy positive component ($\Delta\varepsilon = +0.41$, 22000 cm^{-1}) in the region of the first absorption band.

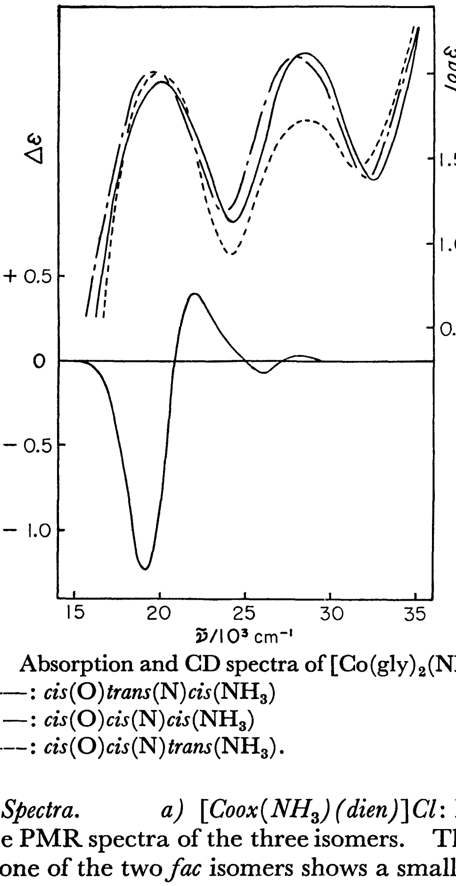

Fig. 3. Absorption and CD spectra of $[Co(gly)_2(NH_3)_2]^+$.
———: *cis*(O)*trans*(N)*cis*(NH_3)
— • —: *cis*(O)*cis*(N)*cis*(NH_3)
------: *cis*(O)*cis*(N)*trans*(NH_3).

PMR Spectra. *a) [Coox(NH_3)(dien)]Cl*: Figure 4 shows the PMR spectra of the three isomers. The spectrum of one of the two *fac* isomers shows a small peak at 6.78, two small peaks at 4.68 and 4.50, and a sharp peak at 3.63 ppm, with an integrated ratio of 1: 2: 2: 3. The spectrum of the other *fac* isomer exhibits a small peak at 6.9, a somewhat large peak at 4.94 and a sharp peak at 3.50 ppm, with a ratio of 1: 4: 3. The spectrum of the *mer* isomer exhibits a small peak at 6.27, a rather large peak at 4.90, and a sharp peak at 3.20 ppm, with a ratio of 1: 4: 3. From an inspection of the intensities, the peaks at 6.2—7.0 ppm are assignable to the NH proton resonances, the ones at 4.2—5.2 ppm, to the NH_2 proton resonances, and the ones at 3.1—3.7 ppm, to the NH_3

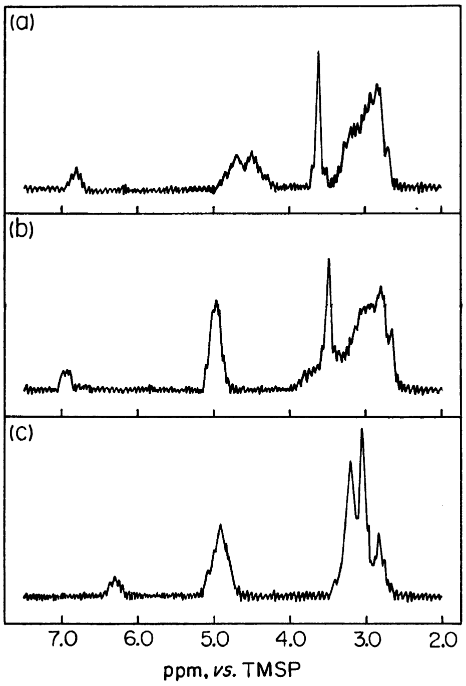

Fig. 4. PMR spectra of $[Coox(NH_3)(dien)]^+$.
(a) *u-fac* (b) *s-fac* (c) *mer* (D_2O–30% D_2SO_4).

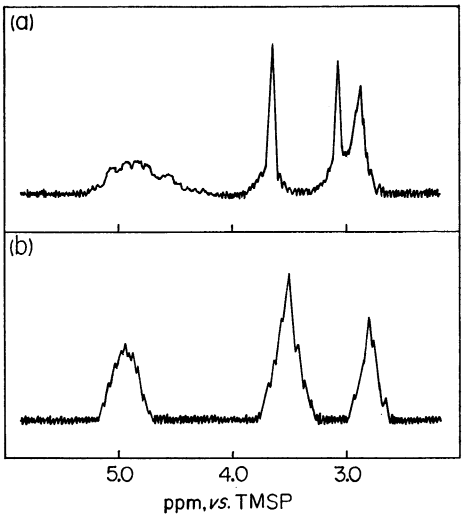

Fig. 5. PMR spectra of $[Coox(NH_3)_2(en)]^+$.
(a) *cis* (b) *trans* (D_2O–30% D_2SO_4).

proton resonances. The peaks due to the C_2H_4 groups appear at 2.6—3.4 ppm. On this basis, the *u-fac* configuration, with two non-equivalent NH_2 groups (Fig. 1), can be assigned to the complex whose spectrum shows the two peaks due to the NH_2 groups.

b) [*Coox*(*NH*$_3$)$_2$(*en*)]*Cl*: The PMR spectra of the two isomers are shown in Fig. 5. The spectrum of one of the two isomers shows a broad peak at 4.2—5.2 ppm, and two sharp peaks at 3.64 and 3.06 ppm, in which the integrated ratio is 4: 3: 3. The spectrum of the other isomer exhibits a broad peak at 4.94 and a sharp one at 3.51 ppm, with a ratio of 4: 6. From the intensities, the peaks at 4.2—5.2 ppm can be assigned to the NH_2 proton resonances, and those at 3.0—3.7 ppm, to the NH_3 proton resonances. The resonances due to the C_2H_4 groups appear at 2.5—3.0 ppm. The structures illustrated in Fig. 1 suggest that both the NH_2 and the NH_3 proton resonances split into two for the *cis*(NH_3) isomer. On this basis, the former complex is identified as the *cis*(NH_3) isomer. In the spectrum of the latter complex, each peak appears, in accord with the *trans*-(NH_3) structure.

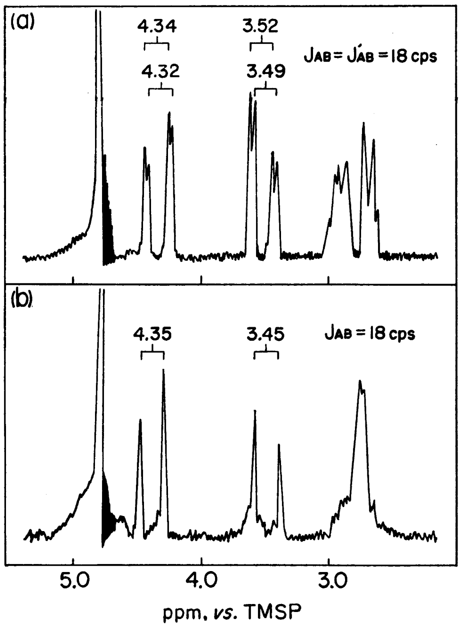

Fig. 6. PMR spectra of $[Co(ida)(NH_3)(en)]^+$.
(a) *u-fac* (b) *s-fac* (D_2O).

c) [*Co*(*ida*)(*NH*$_3$)(*en*)]*Cl*: The PMR spectra of the two isomers are shown in Fig. 6. The peaks due to the CH_2 proton resonances of the acetate rings of the ida appear at a lower field (3.3—4.5 ppm) than the C_2H_4 proton resonances of the en (2.6—3.0 ppm) because of the combined deshielding effects on the acetate protons from the carboxylate and amine groups.[8] When the geminal acetate protons are in magnetically different situations, the spectrum shows symmetrical AB quartets due to two spin-coupled protons. One of the two *fac* isomers exhibits two overlapping AB quartets, indicating that the two CH_2 groups are in slightly different environments, while the other isomer exhibits one quartet (Fig. 1). On this basis, the former complex is assigned to the *u-fac* isomer, and the latter, to the *s-fac* isomer.

In the spectrum of the *u-fac* isomer thus assigned, the

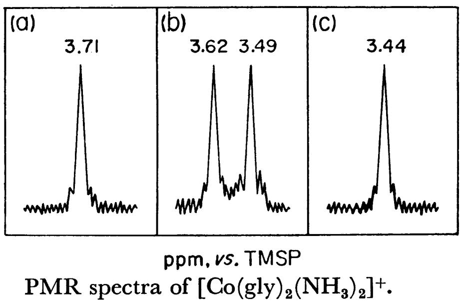

Fig. 7. PMR spectra of $[Co(gly)_2(NH_3)_2]^+$.
(a) *cis*(O)*trans*(N)*cis*(NH_3) (b) *cis*(O)*cis*(N)*cis*(NH_3)
(c) *cis*(O)*cis*(N)*trans*(NH_3) (D_2O).

C_2H_4 protons of the en give two complicated peaks because of the inequality of the two CH_2 groups, while in the spectrum of the *s-fac* isomer the C_2H_4 protons give a symmetrical peak because of the equality of the two CH_2 groups.

d) $[Co(gly)_2(NH_3)_2]Cl$: The PMR spectra of the three *cis*(O) isomers show only peaks due to the CH_2 protons of the glycinate rings (Fig. 7); one of the three isomers shows two peaks, at 3.62 and 3.49 ppm, indicating different situations of the CH_2 groups, while the other two isomers exhibit only one peak each, at 3.71 and 3.44 ppm respectively. On this basis, the *cis*(O)-*cis*(N)*cis*(NH_3) configuration can be assigned to the former one.

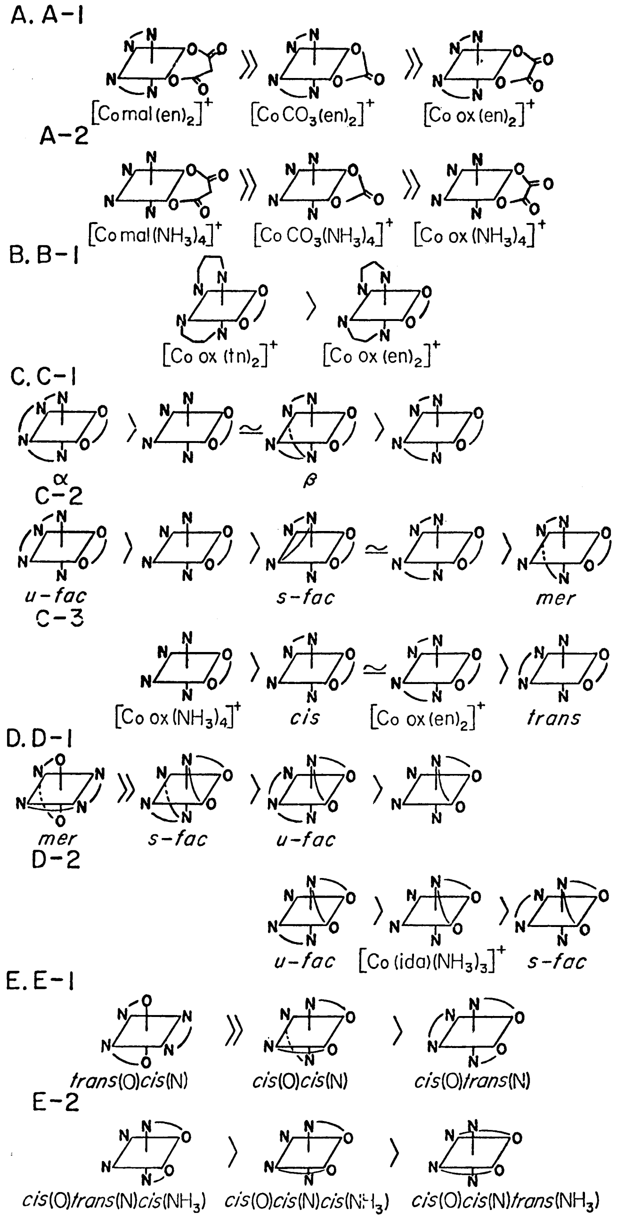

Fig. 8. Elution orders.

A. A-1: $[Co(O\text{-}O)(en)_2]^+$ A-2: $[Co(O\text{-}O)(NH_3)_4]^+$
B. B-1: $[Coox(diamine]_2]^+$
C. C-1: $[Coox(trien)]^+$ C-2: $[Coox(NH_3)(dien)]^+$
C-3: $[Coox(NH_3)_2(en)]^+$
D. D-1: $[Co(ida)(dien)]^+$ D-2: $[Co(ida)(NH_3)(en)]^+$
E. E-1: $[Co(gly)_2(en)]^+$ E-2: $[Co(gly)_2(NH_3)_2]^+$.

Elution Order. The elution orders were investigated with the series classified A—E. The results are summarized in Fig. 8, where the $>$notation indicates an earlier elution of a complex species written on the left side than that on the right side ($\gg$indicates a separation with a long distance, and$\simeq$means nearly the same order of elution).

In the A series, the carbonato, oxalato, and malonato complexes of a tetraammine type were compared. In the B series, the oxalato–ethylenediamine, and –trimethylenediamine complexes were compared. In the C series, the ox ligand was fixed and the other ligands were varied, being trien in the C-1, NH_3+dien in the C-2, and $2NH_3$+en in the C-3 series. In addition, the $[Coox(NH_3)_4]^+$ and $[Coox(en)_2]^+$ complexes were used as markers in order to compare the elution orders among the series. In the D series, the ida ligand was fixed and the other ligands were varied, being dien in the D-1 and NH_3+en in the D-2 series. In the E series, the *bis*-(glycinato)-en (E-1) and -diammine (E-2) complexes were examined.

In both the *bis*(ethylenediamine) and tetraammine complexes (A-1 and A-2), the elution order was found to be malonato$\gg$carbonato$\gg$oxalato. This fact indicates that such a variety of dicarboxylate ions makes the separation of the complexes may clear. In the B series, the elution order was found to be tn$>$en; the more bulky tn complex was eluted earlier. Between the two markers used in the C series, the $[Coox(en)_2]^+$, with two en chelate rings, was eluted later than the $[Coox(NH_3)_4]^+$, which has no such chelate rings, while the $[Coox(trien)]^+$, with three such chelate rings, was eluted faster than the $[Coox(en)_2]^+$.

In both D-1 and E-1, the *trans*(O) isomers, *mer*-$[Co(ida)(dien)]^+$ and *trans*(O)*cis*(N)-$[Co(gly)_2(en)]^+$, were eluted faster than the corresponding *cis*(O) isomers. The same results have previously been reported by other workers[7,8]; this order is in accordance with the general tendency found in the *cis* and *trans* isomers of the simple complexes.[1]

So far as the elution order of the *cis*(O) isomers is concerned, only a little discussion has been done; Legg and Cooke[8] stated that, in the $[Co(ida)(dien)]^+$ complex, the *u-fac* isomer was eluted later than the *s-fac* one because of more unsymmetrical charge distribution. This explanation is applicable to the present C-1 and D-1 series. However, in the C-2, C-3, D-2, and E series, their *cis*(O) isomers, in which more symmetrical change distributions are to be expected, were eluted later.

It is well known that a chelated dien ring situated in the *mer*-position is very distorted.[10] It is considered that, in the present C-2 series, the *mer* isomer is in such a strained configuration. In the D-1 series, the *u-fac* isomer is known to have a strained configuration because of steric repulsion between the amine substituent of the chelated ida and the $-CH_2-$ protons of the chelated dien.[8] In the D-2 series, the *s-fac* isomer may have the most strained structure for the same reason. Corresponding to these strained structures, the last eluted species in each series was the isomer mentioned above.

It is noticeable that a partial reverse in the elution orders between the E-1 and E-2 series was observed; the *cis*(O)*cis*(N) isomer was eluted faster than the *cis*(O)-*trans*(N) isomer in the E-1 series,[7)] but the corresponding two isomers of the E-2 series were eluted in the reverse order.

References

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