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Preparation and Characterization of Cobalt(III) Complexes with *N*-Carboxylate Derivatives of L-Prolinate

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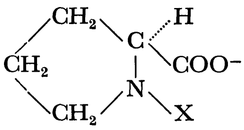
Four cobalt(III) complex anions, bis(L-prolinate-*N*-monopropionato)-, (L-prolinate-*N*-monoacetato)(iminodiacetato)-, (L-prolinate-*N*-monopropionato)(iminodiacetato)- and (L-prolinate-*N*-monoacetato)(L-prolinate-*N*-monopropionato)cobaltate(III) were synthesized. They were isolated as sodium or potassium salts by ion-exchange column chromatography. These complexes were characterized on the basis of their absorption and circular dichroism spectra in the visible and near ultraviolet regions. All the complexes obtained in solid state have *trans(N)*-RR or *trans(N)*-R configuration. Two geometrical isomers were obtained for (L-prolinate-*N*-monopropionato)triamminecobalt(III) complexes.

L-prolinate is a unique aminocarboxylate bidentate ligand, since the secondary amine nitrogen of pyrrolidine ring coordinates stereospecifically to a metal ion with only S configuration. This has been recognized from circular dichroism (CD) studies[1] or X-ray crystal structure analyses[2,3] of several L-prolinato metal complexes. In the course of our study on stereochemistry of six isomers of bis(L-alaninate-*N*-monoacetato)cobaltate(III),[4] we found that an *N*-carboxylate derivative of L-prolinate, L-prolinate-*N*-monoacetate gave only two isomers of the bis(O,N,O-tridentato)cobalt(III) complex. This was explained from the viewpoint that the chiral nitrogen center of the coordinated L-prolinate-*N*-monoacetate takes only R configuration, and the ligand only a *facial* coordination. In the present paper, the stereochemistry of some cobalt(III) complexes of another L-prolinate derivative, L-prolinate-*N*-monopropionate is reported.



X = H : L-prolinate

$X = CH_2COO^-$: L-prolinate-*N*-monoacetate (abbreviated to L-proma^{2-})

$X = CH_2CH_2COO^-$: L-prolinate-*N*-monopropionate (abbreviated to L-promp^{2-})

The difference between L-proma^{2-} and L-promp^{2-} is that the former forms two five-membered chelate rings by coordination, whereas the latter forms a five- and a six-membered chelate ring by an α-aminocarboxylate part and an *N*-propionate foot, respectively.

Experimental

Preparation of Ligands. *(1) L-Proline-*N*-monoacetic Acid*: The preparation was reported previously.[4]

*(2) L-Proline-*N*-monopropionic Acid*: A solution of 25 g of L-proline in 54 ml of 4 N sodium hydroxide was mixed with a solution of 23.5 g of 3-chloropropionic acid in 54 ml of 2 N sodium hydroxide, and 80 ml of 4 N sodium hydroxide was added drop by drop to the mixture with vigorous stirring at 80—85°C on an oil bath. The pH of mixture was maintained in a 8—9 range during the reaction. After the sodium hydroxide solution had been added, the reaction mixture was heated at 85°C for about 20 min. This was cooled to 40°C and 36 ml of concentrated hydrochloric acid was added. The solution was concentrated in a vacuum evaporator at 40°C until white crystals appeared. The product was filtered off and the filtrate was concentrated again. After the operation was repeated six times (about 38 g of white crystals were obtained in total), a large amount of ethanol was added to the final filtrate. The white crystals separated were collected by filtration (26 g). The combined white crystals were contaminated with a small amount of sodium chloride. This was recrystallized from a warm (hydrochloric acid)-water (1 : 100) solution. The pure crystals were washed with ethanol and dried in a vacuum desiccator. $[\alpha]_D^{20} = -55.5°$ (c. 8.7, water). Found: C, 51.22; H, 6.98; N, 7.55%. Calcd for L-prompH$_2$ = $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48%.

Preparation and Separation of Complexes. *(3)* trans(N)-*K[Co(L-proma)$_2$]·3H$_2$O*: The preparation of this complex was already reported.[4] One corresponding *cis(N)* isomer was obtained concurrently in solution, but it was not obtained in solid state because of poor stability.

(4) trans(N)-*Na[Co(L-promp)$_2$]·3H$_2$O*: A solution of 10 g (0.042 mol) of $CoCl_2 \cdot 6H_2O$ in 10 ml of water was added to a solution of L-proline-*N*-monopropionic acid (0.084 mol) which was neutralized in advance by the addition of sodium hydroxide. To this was gradually added 10 g of lead dioxide and the resulting mixture was constantly stirred at about 50°C for an hr, whereupon the color of the solution turned from dark red to violet. After having been kept for 30 min at room temperature, the mixture was filtered to remove an excess of lead dioxide. A large amount of ethanol-acetone (1 : 1) mixture was added to the filtrate and a small amount of the resulting sodium chloride was filtered off. The filtrate was concentrated in a vacuum evaporator at about 30°C and poured into a column (25 mm × 1500 mm) containing strong-base anion exchange resin (Dowex 1X8 200—400 mesh, chloride form). After the column had been swept with water, the adsorbed band was eluted with 0.075 N aqueous solution of sodium chloride at a rate of 2.5 ml per min. Only one violet band was eluted. The sodium chloride in the eluate was fractionally separated by adding an appropriate amount of ethanol to the concentrated solution. The desired complex was obtained by concentrating the filtrate almost to dryness. The product was washed with ethanol

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and then dried in a vacuum desiccator.

(5) trans(N)-$K[Co(\text{L-proma})(ida)]\cdot 2.5H_2O$: A solution of 0.042 mol of iminodiacetic acid neutralized by sodium hydroxide was mixed with a neutralized solution of 0.042 mol of L-proline-*N*-monoacetic acid. To this was added gradually a solution of 10 g (0.042 mol) of $CoCl_2\cdot 6H_2O$ in 10 ml of water and then 10 g of lead dioxide. After the mixture was constantly stirred at about 50°C for an hr, its pH was adjusted to 6.5 with 6 N hydrochloric acid. This was stirred again for an hr to complete the reaction. The solution turned violet. An excess of lead dioxide was filtered off. When a large amount of ethanol was added to the filtrate, a bluish violet deposit was obtained, which was filtered. It was confirmed from column chromatography and absorption measurements that the bluish violet deposit consisted of *trans(N)*- and *cis(N)*-Na[Co(ida)$_2$]. The concentrated filtrate was poured into a column (35 mm × 500 mm) containing the same resin as used in (4). Five colored bands *viz.*, a brownish red one (i) in a small amount, two red ones (ii) and (iii) and two violet ones (iv) and (v) in small amounts, were eluted in this order with 0.07 N aqueous solution of potassium chloride. The first spin-allowed d-d absorption band of each eluate showed that the first three, (i), (ii) and (iii), are of *trans(N)* type and the latter two (iv) and (v) of *cis(N)*. Of the three *trans(N)* eluates, (i) was confirmed to be *trans(N)*-[Co(ida)$_2$]$^-$[5] and (iii) *trans(N)*-[Co(L-proma)$_2$]$^-$[4]. Eluate (ii) was then concentrated in a vacuum evaporator. The coexisting potassium chloride was fractionally precipitated by adding ethanol to the concentrated solution and filtered off. Finally, a saturated solution of silver acetate was added drop by drop to the concentrated filtrate and the resulting silver chloride was filtered off. The desired complex was obtained by adding a large amount of ethanol to the filtrate and recrystallized from a small amount of water by adding ethanol. The pure complex was washed with ethanol and dried in a vacuum desiccator. Eluates (iv) and (v) were so unstable that they were not obtained in solid state.

(6) trans(N)-$K[Co(\text{L-promp})(ida)]\cdot 2H_2O$: This complex was prepared and separated by a similar procedure to that for *trans(N)*-K[Co(L-proma)(ida)]. Four colored bands, a violet one (i), a reddish violet one (ii), a brownish red one (iii) in a small amount, and another violet one (iv) were eluted in this order. The absorption measurements of the eluates indicated that (i) contained *trans(N)*-[Co(L-promp)$_2$]$^-$, (iii) *trans(N)*-[Co(ida)$_2$]$^-$ and (iv) *cis(N)*-[Co(ida)$_2$]$^-$. Eluate (ii) was concentrated to dryness in a vacuum evaporator. The complex was extracted with a large amount of absolute ethanol and solidified by adding ether to the extract. After the resulting suspension was centrifuged, the complex was filtered and dried in a vacuum desiccator. The isolated potassium salt was hygroscopic.

(7) trans(N)-$K[Co(\text{L-proma})(\text{L-promp})]\cdot 3H_2O$: A solution of 10 g (0.042 mol) of $CoCl_2\cdot 6H_2O$ in 10 ml of water was added to a neutralized equimolar mixture (0.042 mol) of L-proline-*N*-monoacetic acid and L-proline-*N*-monopropionic acid. To this was added 10 g of lead dioxide and the resulting mixture was mechanically stirred at about 40°C for an hr. The color of the solution turned from dark red to reddish purple. An excess of lead dioxide was filtered off and the filtrate was treated with a column as described in (4) and (5). Three colored bands, a violet one (i), a purple one (ii), and a red one (iii), were eluted in this order. It was confirmed from the absorption measurements that (i) contained *trans(N)*[Co(L-promp)$_2$]$^-$ and (iii) *trans(N)*-[Co(L-proma)$_2$]$^-$. Eluate (ii) was concentrated to dryness in a vacuum evaporator. Solidification was carried out by a similar procedure to that for *trans(N)*-K[Co(L-promp)(ida)]. The complex was obtained as hygroscopic potassium salt.

(8) trans(O)-$[Co(\text{L-promp})(NH_3)_3]ClO_4$ *and* cis(O)-$[Co(\text{L-promp})(NH_3)_3]ClO_4\cdot 1/2H_2O\cdot 1/4C_2H_5OH$: A solution of 9 g (0.17 mol) of ammonium chloride and 10 ml of 28% aqueous ammonia (0.15 mol) in 15 ml of water was mixed with a neutral solution of 0.042 mol of L-proline-*N*-monopropionic acid. To this were added a solution of 10 g (0.042 mol) of $CoCl_2\cdot 6H_2O$ in 10 ml of water and 10 g of lead dioxide. The reaction mixture was constantly stirred at about 40°C for an hr. The color of the solution turned from dark red to reddish yellow and finally to red. After having been allowed to stand at room temperature for 30 min, the mixture was filtered to remove an excess of lead dioxide, and the filtrate was kept in a refrigerator. A small amount of yellow depoint, $[Co(NH_3)_6]Cl_3$, was filtered off. The filtrate was poured into a column (35 mm × 500 mm) containing strong-acid cation exchange resin (Dowex 50WX8 200—400 mesh, sodium form). After the column had been swept with water, the adsorbed band was eluted with 0.1 N aqueous solution of sodium perchlorate at a rate of 2.5 ml per min. Two red bands, (i) in a small amount and (ii) in a large amount were eluted in this order. When eluate (i) was concentrated in a vacuum evaporator, red crystals appeared. Eluate (ii) was also concentrated in a vacuum evaporator; the desired complex was obtained in this case by adding a large amount of ethanol to the concentrated solution. This was recrystallized from a small amount of water by adding ethanol. Both the complexes were washed with ethanol and dried in a vacuum desiccator. On the basis of absorption measurements, isomers (i) and (ii) were confirmed to be *trans(O)* and *cis(O)* ones, respectively; the absorption maxima of isomer (i) are at 18.5 and $27.0\times 10^3\ cm^{-1}$ with a shoulder at about $21.0\times 10^3\ cm^{-1}$, and of isomer (ii) 19.3 and $27.3\times 10^3\ cm^{-1}$.

The analytical results for the six new cobalt(III) complexes are given in Table 1.

Measurements. The electronic absorption spectra were measured by a Beckman DU spectrophotometer and Shimadzu spectrophotometer UV-200. The CD spectra were recorded with a Roussel-Jouan dichrograph. All the measurements were carried out in aqueous solutions at room temperature.

Results and Discussion

The *trans(N)* and *cis(N)* isomers of a $[Co^{III}(O)_4(N)_2]$ type complex can be identified by the splitting pattern of their first spin-allowed d-d absorption bands.[6,7] All the $[Co^{III}(O)_4(N)_2]$ type complexes show well-separated splitting components in their first absorption bands (Figs. 1 and 2, and Table 2); these are therefore assigned to the *trans(N)* structure. The corresponding *cis(N)* isomers are expected to be unstable because of a rather short contact (from molecular model considerations) of the pyrrolidine ring to another ligand coordinated.[4] No *cis(N)* isomers were detected in column chromatographic

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Table 1. Analytical results (amounts in %)

Complex salt	C		H		N	
	Found	Calcd	Found	Calcd	Found	Calcd
trans(*N*)-Na[Co(L-promp)$_2$]·3H$_2$O	37.67	37.95	5.53	5.57	5.56	5.53
trans(*N*)-K[Co(L-proma)(L-promp)]·3H$_2$O	35.10	35.44	5.03	5.15	5.57	5.51
trans(*N*)-K[Co(L-proma)(ida)]·2.5H$_2$O	29.57	29.67	4.32	4.30	6.34	6.29
trans(*N*)-K[Co(L-prmp)(ida)]·2H$_2$O	32.33	32.01	4.55	4.48	6.06	6.22
trans(*O*)-[Co(L-promp)(NH$_3$)$_3$]ClO$_4$	24.19	24.35	5.25	5.11	14.24	14.20
cis(*O*)-[Co(L-promp)(NH$_3$)$_3$]ClO$_4$· 1/2H$_2$O·1/4C$_2$H$_5$OH	24.46	24.59	5.43	5.46	13.40	13.49

Table 2. Absorption maxima of *trans*(*N*)-[Co(*O*,*N*,*O*-tridentato)$_2$]type complexes

Complex ion	I Band		II Band		Ref.
	ν_{max} a)	(log ε_{max})	ν_{max} a)	(log ε_{max})	
[Co(L-proma)$_2$]$^-$	*ca.* 16.7 sh 19.8	(1.1) (1.79)	27.1	(1.86)	(4)
[Co(L-promp)$_2$]$^-$	*ca.* 15.7 sh 18.2	(1.5) (2.13)	25.1	(2.29)	
[Co(L-proma)(L-promp)]$^-$	*ca.* 16.0 sh 18.8	(1.2) (1.95)	26.1	(2.08)	
[Co(L-proma)(ida)]$^-$	*ca.* 16.7 sh 19.8	(1.2$_5$) (1.93)	27.6	(1.98)	
[Co(L-promp)(ida)]$^-$	*ca.* 16.0 sh 19.2	(1.2$_5$) (1.94)	26.2	(2.06)	
[Co(ida)$_2$]$^-$	16.7 20.4	(1.06) (1.72)	27.8	(1.75)	(5)

a) The wave numbers are given in 10^3 cm^{-1}.

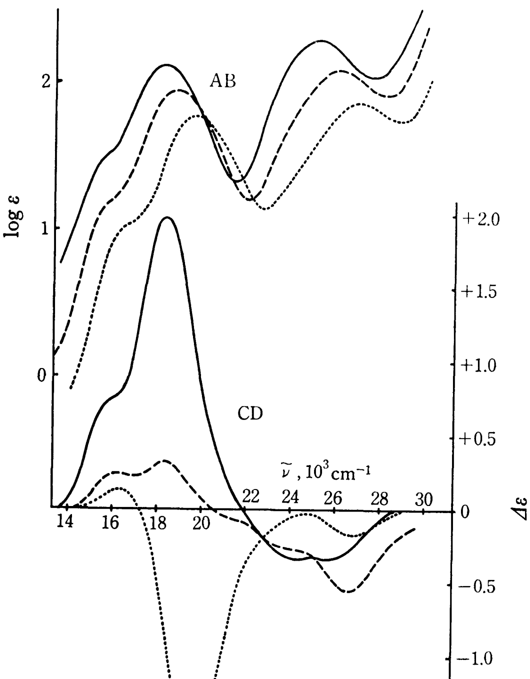

Fig. 1. Absorption and CD curves of *trans*(*N*)-RR-[Co(L-promp)$_2$]$^-$ (——), *trans*(*N*)-RR-[Co(L-proma)(L-promp)]$^-$ (— — —) and *trans*(*N*)-RR-[Co(L-proma)$_2$]$^-$ (----).

experiments of [Co(L-proma)(L-promp)]$^-$ and [Co-(L-promp)$_2$]$^-$. Some indication of *cis(N)* isomers was obtained in the column chromatography of the ida-mixed complexes, but they were too unstable to isolate, except for the case of *cis(N)*-[Co(ida)$_2$]$^-$.

As is seen in Fig. 3, two isomers are possible for the *trans(N)* complex with two O,N,O-tridentate ligands. It is recognized[4,5,8] that the tridentate ligand such as ida^{2-} or L-proma^{2-} is hardly coordinated meridionally in Co(III) complexes, except for the case of *trans(O)*-[Co(ida)(dien)]$^{+}$[8]. L-promp^{2-} here employed forms a five- and a six-membered chelate ring by coordination. A molecular model examination reveals that the *N*-propionate moiety of L-promp^{2-} spans in a less strained circumstance than the *N*-acetate one of L-proma^{2-}. Thus it seems that a *meridional* coordination (Fig. 3a) is less improbable for L-promp^{2-} than for L-proma^{2-}. The preparation of [Co(L-promp)(NH$_3$)$_3$]$^+$ revealed the formation of the meridionally coordinated isomer, though the yield was very low. It was confirmed from the ion-exchange column chromatography and absorption measurements in the visible region that a major portion of the obtained triammine complex consists of the *cis(O)* isomer with *facial* coordination of L-promp^{2-} and that the *trans(O)* one with *meridional* coordination is formed in only a trace amount. Thus, it is assumed that the stable *trans(N)* complexes obtained in good yield take the

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[8] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

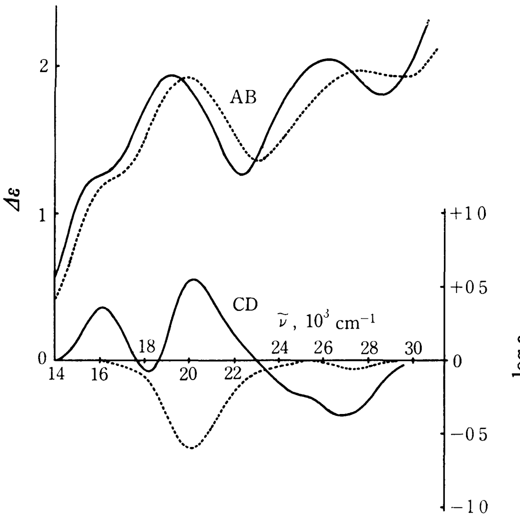
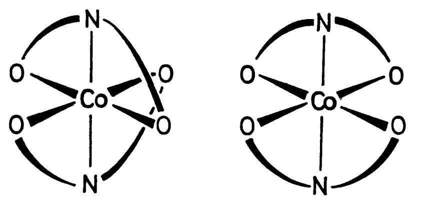


Fig. 2. Absorption and CD curves of *trans*(*N*)-R-[Co(L-promp)(ida)]$^-$ (——) and *trans*(*N*)-R-[Co(L-proma)(ida)]$^-$ (----).



(a) (b)

Fig. 3. Two possible isomers for a *trans*(*N*)-[Co(O,N,O-tridentato)$_2$] type complex: (a) *meridional-trans*(*N*), and (b) *facial-trans*(*N*).

facial coodinations (Fig. 3b) of L-promp^{2-}, L-proma^{2-} and ida^{2-} ligands.

The nitrogen atom of L-proma^{2-} or L-promp^{2-} is a chiral center in the present complexes. It can be considered that three isomers, RR, RS, and SS, with respect to the two coordinated nitrogen atoms, are possible for each bis(O,N,O-tridentato) complex. But it is well-established[1–4] that L-prolinate and its *N*-carboxylate derivatives cannot take configurations R and S, respectively, of the coordinated nitrogen atom. Consequently, only the RR type is possible for each of the *facial trans(N)* complexes. In fact, only one *trans(N)* isomer was obtained for each of the [Co(L-proma)$_2$]$^-$, [Co(L-proma)(L-promp)]$^-$ and [Co(L-promp)$_2$]$^-$ complexes. A quite similar consideration can be applied the mixed complexes with an ida^{2-} ligand, [Co(L-proma)(ida)]$^-$ and [Co(L-promp)(ida)]$^-$; thus each of them is assigned to *facial trans-(N)*-R configuration.

Absorption and CD spectra. The five *facial trans-(N)* complexes show reasonable correlation among their absorption spectra. The first and second spin-allowed d-d absorption bands of the bis type complexes are shifted to lower energy and intensified, in the order ida^{2-}→L-proma^{2-}→L-promp^{2-} (Figs. 1 and 2, and Table 2). A mixed complex, R-[Co(L-promp)(ida)]$^-$, shows its first band in a middle position between the first bands of parent complexes, RR-[Co(L-promp)$_2$]$^-$ and [Co(ida)$_2$]$^-$. Similar relationships are also substantiated for the other mixed complexes, R-[Co(L-proma)(ida)]$^-$ and RR-[Co(L-proma)(L-promp)]$^-$.

In contrast to these absorption behaviors, their CD spectra in the corresponding region differ significantly from each other (Figs. 1 and 2, and Table 3). In the first absorption band region, the lower energy CD bands commonly have a positive sign, though it seems that R-[Co(L-proma)(ida)]$^-$ lacks this CD band. Another common feature in the CD spectra of five *facial trans(N)*-R or -RR complexes is observed in the second absorption band region; namely all of them have negative CD. In contrast, the CD pattern in the region 17—22×10^3 cm^{-1} changes remarkably with substitution of ligands. That is, RR-[Co(L-proma)$_2$]$^-$ shows an intense negative CD band and RR-[Co(L-(promp)$_2$]$^-$ an intense positive one (Fig. 1 and Table 3). In the corresponding region, the mixed complex, RR-[Co(L-proma)(L-promp)]$^-$, shows two CD components, a positive one at 18.4×10^3 cm^{-1} and a negative one at about 27.1×10^3 cm^{-1}. R-[Co(L-proma)(ida)]$^-$ shows a negative major CD band which corresponds well to the major one of bis(L-proma) com-

TABLE 3. CD DATA OF *trans*(*N*)-[Co(*O*,*N*,*O*-TRIDENTATO)$_2$] TYPE COMPLEXES

Complex ion	I Band region		II Band region		Ref.
	ν_{ext}[a]	($\Delta\varepsilon_{\text{ext}}$)	ν_{ext}[a]	($\Delta\varepsilon_{\text{ext}}$)	
RR-[Co(L-proma)$_2$]$^-$	16.2	(+0.14)	26.7	(−0.20)	4
	19.5	(−1.72)			
RR-[Co(L-promp)$_2$]$^-$	*ca.* 16.0 sh	(+0.75)	*ca.* 24.6 sh	(−0.34)	
	18.3	(+2.01)	*ca.* 25.7	(−0.34)	
RR-[Co(L-proma)(L-promp)]$^-$	16.2	(+0.23)	*ca.* 24.0 sh	(−0.28)	
	18.4	(+0.33)	26.7	(−0.56)	
	ca. 21.3 sh	(−0.06)			
R-[Co(L-proma)(ida)]$^-$	19.9	(−0.59)	27.5	(−0.05)	
R-[Co(L-promp)(ida)]$^-$	16.1	(+0.41)	*ca.* 25.0 sh	(−0.22)	
	18.2	(−0.08)	26.8	(−0.37)	
	20.2	(+0.57)			

a) The wave numbers are given in 10^3 cm^{-1}.

plex, while R-[Co(L-promp)(ida)]$^-$ shows two CD bands in the region 17—22$\times 10^3$ cm^{-1} (Fig. 2 and Table 3). It seems that the sign reversal of the major CD band between RR-[Co(L-promp)$_2$]$^-$ and RR-[Co(L-proma)$_2$]$^-$ arises from the difference in the *N*-carboxylate moieties, since both the L-promp^{2-} and L-proma^{2-} ligands take the *facial* R(*N*) form by coordination and the resulting complexes take quite a similar configuration to each other. A similar sign reversal was reported[9] for the major CD bands in the visible region between copper(II) complexes of L-prolinate and its *N*-methyl derivative. Thus one should be surprised at the poor additivity of CD curves in the present complexes, rather than at the sign reversal between L-proma^{2-} and L-promp^{2-} complexes. The sum of CD curves of *trans(N)*-R-[Co(L-proma)(ida)]$^-$ and -[Co(L-promp)(ida)]$^-$ poorly reproduces the observed curve of *trans(N)*-RR-[Co(L-proma)(L-promp)]$^-$. A similar treatment for the CD curves of *trans(N)*-RR-[Co(L-proma)$_2$]$^-$ and -[Co(L-promp)$_2$]$^-$ also cannot reproduce the curve for the mixed complex *trans(N)*-RR-[Co(L-proma)(L-promp)]$^-$. These facts present a strange contrast to almost perfect additivity observed for several cobalt(III) complexes with some simple α-aminocarboxylates or their derivatives; for instance Koine *et al.*[10] showed that the CD curve of *trans(N)*-(L-alaninate-*N*,*N*-diacetato)(L-prolinato)-cobaltate(III) was clearly reproduced by summing up those of *trans(N)*-(L-alaninate-*N*,*N*-diacetato)(glycinato)cobaltate(III) and *trans(N)*-(ammoniatriacetato)(L-prolinato)cobaltate(III). Poor additivity of the present complexes would be related to less rigid conformations of the L-prolinate derivative tridentate ligands in a complicated sector spaces, which were produced by a rather low symmetry of the complexes, and which should have different space distributions of sector signs from one complex to another.

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