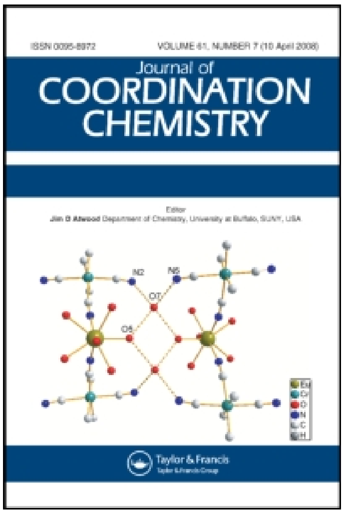

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Hidaka, Jinsai , Yamada, Shoichi and Douglas, Bodie E.(1972) 'CHARACTERIZATION OF THE THREE ISOMERS OF LITHIUM L-ASPARTATO(IMINODIACETATO)COBALTATE(III)[1]', Journal of Coordination Chemistry, 2: 2, 123 — 127

To link to this Article: DOI: 10.1080/00958977208072961

URL: http://dx.doi.org/10.1080/00958977208072961

J. Coord. Chem., 1972, Vol. 2, pp. 123–127

CHARACTERIZATION OF THE THREE ISOMERS OF LITHIUM L-ASPARTATO(IMINODIACETATO)COBALTATE(III)[1]

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(*Received July* 6, 1971; *in final form January* 4, 1972)

The L-aspartato(iminodiacetato)cobaltate(III) complex ion has been prepared and separated into three optically active isomers by ion-exchange chromatography. These isomers were identified from their electronic absorption, circular dichroism and pmr spectra. Their spectra are compared to those of the three isomers of the bis(L-aspartato)-cobaltate(III) complex ion.

INTRODUCTION

A few reports have been presented for cobalt (III) complexes of optically active amino acids functioning as tridentate ligands containing five- and six-membered rings.[3, 4, 5, 6] For the mixed Co(III) complex with D-aspartate ion and diethylenetriamine the three isomers were isolated and it was suggested that the vicinal and configurational contributions were essentially additive in their circular dichroism (CD) spectra.[3] The present paper is concerned with the isolation of the three geometrical isomers of the mixed complex, Li[Co(L-asp)(ida)][L-asp = $NH_2CH(CO_2)$-$(CH_2CO_2)^{2-}$ and ida = $NH(CH_2CO_2)_2{}^{2-}$]. Their absorption, pmr and CD spectra will be discussed in relation to those of the three isomers of Co(L-asp)$_2{}^-$.[7,8] Only facial isomers are considered since L-aspartate ion cannot span meridional positions.

EXPERIMENTAL SECTION

The preparation and separation of the isomers were carried out by procedures similar to those used for the bis(L-asparatato)cobaltate(III)[7] ion. Freshly prepared $Co(OH)_3$[9] (0.41 g) was suspended in 10 ml of water and to this suspension was added a hot solution (*ca.* 75°) containing 0.15 g of NaOH, 0.5 g of L-aspartic acid, and 0.5 g of iminodiacetic acid in 40 ml of water, and finally 0.1 g of activated charcoal was added. The resulting mixture was stirred at 75° on a water bath for about 20 min. The blue-violet mixture was filtered, after cooling in an ice bath, to remove the charcoal. The filtrate was poured into a column (2 × 30 cm) of strong base anion-exchange resin (Dowex 1X4, 100–200 mesh, chloride form). After the column had been flushed with water, the adsorbed band was eluted with 0.1 M LiCl solution at a rate about 0.5 ml per min. Seven coloured bands were eluted at similar intervals and the eighth red-violet band followed the seventh band after a longer interval. It was confirmed, by the measurements of the CD and visible absorption spectra of these eluates, that the second, brown eluate is *trans*(N)-Co(ida)$_2{}^-$,[10] the third, violet one *cis*(N)*trans*(O_6)-Co(L-asp)$_2{}^-$,[7] the fourth, blue-violet one *cis*(N)*trans*(O_5)-Co(L-asp)$_2{}^-$,[7] and the seventh, violet one *cis*(N)-Co(ida)$_2{}^-$.[11] The eighth red-violet eluate contains some intermediate species for which the absorption spectrum is similar to a *trans*(N) type complex with L-aspartate, but not *trans*(N)-Co(L-asp)$_2{}^-$. The first, brick-red (F1), the fifth, violet (F5), and the sixth, blue-violet (F6) eluates were concentrated separately to about 5 ml in a vacuum evaporator below 30°. The crude products from F5 and F6 were precipitated by adding a large amount of ethanol. The complexes from F5 and F6 were recrystallized from as little water as possible by adding gradually a large amount of ethanol. The crude complex from F1 was dissolved in a small amount of water and three volumes of ethanol were added to it. The solution was filtered after standing for several minutes. The desired complex was obtained from the filtrate by adding a small amount of ethanol-ether (1:1) mixture. *Anal.* Calcd. for $LiC_8H_{10}N_2Co \cdot 3H_2O$: C, 25.14; H, 4.22; N, 7.33. Found: C, 25.48; H, 3.95; N, 7.42 for the F1 isomer with $\Delta\varepsilon_{546} = +0.60$; C, 24.94; H, 4.30; N, 7.32 for the F5 isomer with $\Delta\varepsilon_{546} = -1.08$ and C, 24.96; H, 4.01; N, 7.40 for the F6 isomer with $\Delta\varepsilon_{546} = +1.35$.

Spectral Measurements—Electronic absorption spectra were measured with a Cary Model 14 recording spectrophotometer and the CD spectra were recorded on a Roussel-Jouan Dichrographe using a Sylvania Sun Gun light source. Pmr spectra were recorded on a JEOLCO NMR spectrometer at 100 MHz in the frequency sweep mode with a frequency lock on the methyl resonance of t-butyl alcohol (TBA) at δ 1.234 ppm (with respect to DSS at 0). Solutions contained *ca.* 10 wt % of the lithium salts of the isomers in D_2O (*ca.* 0.5 ml) with TBA added as an internal standard.

RESULTS AND DISCUSSION

Of the three geometrical isomers of the mixed complex, the lowest energy band of the F1 isomer is split into two well-separated components and the splitting pattern agrees with that of *trans*(N)-$Co(L\text{-}asp)_2^{-}$[7] (Figure 1 and Table I). The band maxima are shifted toward those of *trans*(N)-$Co(ida)_2^{-}$ which are at higher energies[10] compared to those of *trans*(N)-$Co(L\text{-}asp)_2^{-}$. The F1 isomer, therefore, can be assigned confidently as the *trans*(N)

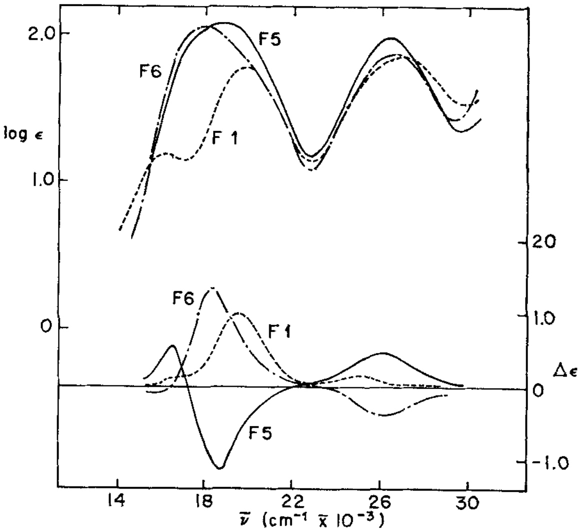

FIGURE 1 Absorption and CD spectra for the three isomers of $Li[Co(L\text{-}asp)(ida)]\cdot 3H_2O$ identified as *trans*(N) (F1) (- - -), *cis*(N)*trans*(O_5O_6) (F5) (—), and *cis*(N)*trans*(O_5O_5) (F6) (— · — ·).

TABLE I

Absorption and CD Data of the Three Isomers of $Co(L\text{-}asp)(ida)^-$

Complex Ion	First Band				Second Band			
	absorption		CD		absorption		CD	
	ν_{max} (cm^{-1})	ϵ_{max}	ν_{max} (cm^{-1})	$\Delta\epsilon_{max}$	ν_{max} (cm^{-1})	ϵ_{max}	ν_{max} (cm^{-1})	$\Delta\epsilon_{max}$
trans(N)-Co(L-asp)(ida)$^-$	16,100	16.4	*ca.* 16,400	+0.09	27,000	74.2	24,800	+0.14
(Fl)	19,800	63.8	19,500	+1.01				
trans(N)-Co(L-asp)$_2^-$ Ref 7	15,870	14.5	16,500	+0.35	26,460	79	25,100	+0.42
	19,530	79.5	19,400	+1.43			28,400	−0.10
trans(N)-Co(ida)$_2^-$ Ref 14	16,670	11.5			27,770	56.3		
	20,400	52.5						
cis(N)*trans*(O$_5$O$_6$)-Co(L-asp)(ida)$^-$	*ca.* 17,700		16,400	+0.57	26,300	102.4	26,000	+0.47
(F5)	18,700	125.8	18,500	−1.11				
cis(N)trans(O$_6$)-Co(L-asp)$_2^-$ Ref 7	*ca.* 16,700	79	17,900	−1.36	26,180	74.5	26,000	+0.62
	19,230	180	20,300	+0.96				
cis(N)*trans*(O$_5$O$_5$)-Co(L-asp)(ida)$^-$	17,700	120	*ca.* 15,900	−0.04	26,500	79.6	26,500	−0.36
(F6)	*ca.* 19,600		18,300	+1.35				
cis(N)*trans*(O$_5$)-Co(L-asp)$_2^-$ Ref 7	17,240	124	17,300	+3.71	26,460	63.5	25,000	−0.54
	ca. 20,000	76	20,400	−1.72				
cis-Co(ida)$_2^-$ Ref 12	17,800	151.4	17,100	−2.72	26,340	134.9	26,300	−0.79
			19,600	+2.94				
Co(EDTA)$^-$ Ref 12	18,600	347	17,300	−1.51	26,650	246	24,050	−0.29
			19,830	+0.76			27,900	−0.33

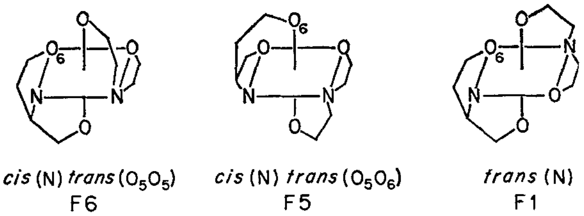

FIGURE 2 The three isomers of Li[Co(L-asp)(ida)]. The oxygen donor-atoms of the five- and six-membered rings are designated O_5 and O_6, respectively.

complex (Figure 2). The lowest energy band of the remaining two isomers (F5 and F6) show small splittings. The band of the F5 isomer shows a shoulder on the lower energy side of the major peak and that of the F6 isomer has a shoulder on the higher energy side. The maximum position of the major peak of F5 is close to that of Co(EDTA)$^-$ and that of F6 is closer to that of *cis*(N)-Co(ida)$_2^-$.[11] The relationship in lowest energy band between the two *cis*(N) isomers agrees with that of the two *cis*(N) isomers of Co(L-asp)$_2^-$,[7] though the splittings of the *cis*(N) isomers of the mixed complexes are smaller. These absorption trends suggest that the F5 isomer is *cis*(N)*trans*(O_5O_6), corresponding to *cis*(N)*trans*(O_6)-Co(L-asp)$_2^-$, and the F6 isomer is *cis*(N)*trans*-(O_5O_5), corresponding to *cis*(N)*trans*(O_5)-Co(L-asp)$_2^-$ [7] (Figure 2). Zompa tentatively assigned the configurations of the three isomers of the bis(L-histidinato)cobalt(III) ion, [Co(N)$_4$(O)$_2$] type, for which the reverse splitting pattern of the L-aspartato complex is expected, from their absorption spectra.[6] The absorption spectral splittings in the present series are consistent with the assignments of the bis(L-histidinato)cobalt(III) isomers.

TABLE II

Coupling Constants[a] and Chemical Shifts[b] for the ABX Protons of Co(L-asp)(ida)$^-$

	trans(N)	*cis*(N)*trans*(O_5O_6)	*cis*(N)*trans*(O_5O_5)
	(F1)	(F5)	(F6)
δ_A (ppm)	3.148	3.134	3.004
δ_B	2.720	2.785	2.718
δ_X	4.067	3.715	3.761
$\delta_A - \delta_B$	0.428	0.349	0.286
J_{AB} (Hz)	18.8	18.9	19.0
J_{AX}	5.5	5.3	5.2
J_{BX}	2.3	2.1	2.2

[a] Values in Hz; signs have not been determined.

[b] Values are ppm downfield from TBA at δ 1.234 ppm (wrt DSS at O).

The three mixed isomers have C_1 symmetry (Figure 2). It is expected, therefore, that the pmr spectra of each of the isomers should consist of one ABX pattern due to the CH—CH$_2$ moiety of L-asp and two AB patterns due to the two CH$_2$ of ida. This expectation was completely realized in their spectra (Figure 3 and Table II). Each of the isomers shows a twelve line pattern at 100 MHz which is readily amenable to interpretation as an ABX pattern due to the CH—CH$_2$ moiety of the coordinated L-aspartate. Framework Molecular Models reveal that the relationships in shielding effects among the CH—CH$_2$ moieties of the three isomers are quite similar to those in the case of the three Co(L-asp)$_2^-$ isomers.[8] δ_A is farthest downfield for the F1 isomer and farthest upfield for the F6 isomer. The F5 isomer gives δ_A between those of the other two isomers. δ_X and δ_B of the three isomers also show the same trends as those of the Co-(L-asp)$_2^-$ isomers (Figure 4 and Table II). On the basis of their pmr spectra, the assignments of the isomers are: F1, *trans*(N); F5, *cis*(N)*trans*-(O_5O_6); and F6, *cis*(N)*trans*(O_5O_5) (Figure 2). These assignments coincide with those from their absorption spectra and are also supported from

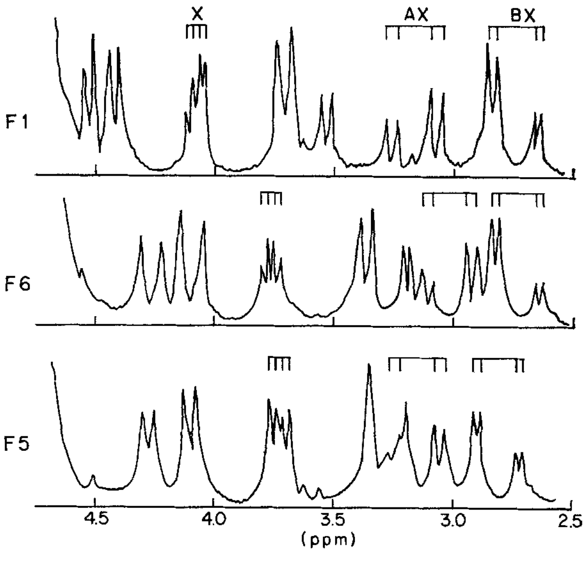

FIGURE 3 Proton magnetic resonance spectra (100MHz) of the three isomers of Li[Co(L-asp)(ida)].

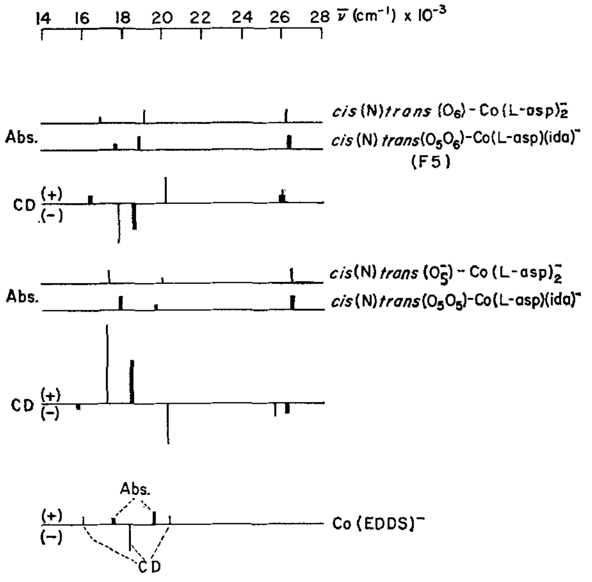

FIGURE 4 ABX patterns of the three isomers of Li-[Co(L-asp)(ida)] compared to those of the isomers[8] of Co(L-asp)$_2^-$.

the fact that the elution order of the three isomers is in accord with that of the three isomers of Co(L-asp)$_2^-$.[7]

Circular Dichroism Spectra—The configurations of the three mixed isomers are stereospecifically regulated by the coordinating L-aspartate. The mirror images of the isomers would have the opposite chirality of chelate rings and must contain D-aspartate as in the case of Co(L-asp)$_2^-$ isomers.[7]

The CD pattern of the *trans*(N) isomer is the same as that of *trans*(N)-Co(L-asp)$_2^-$, just as in the case of their absorption spectra, though the CD intensities of the mixed complexes are lower than the latter (Figure 1 and Table I). This suggests that, assuming additivity,[12] the vicinal contributions to the CD intensities for the *trans*(N) isomers are rather large compared to the contribution from the chiral ring configuration.

Upon first consideration the CD curves for the *cis*(N) isomers are disturbingly different from those of the corresponding *cis*(N)-Co(L-asp)$_2^-$ isomers. The absorption and pmr spectra, second band CD peaks (*ca.* 26,000 cm^{-1}), and order of elution relate F6 to *cis*(N)*trans*(O$_5$)-Co(L-asp)$_2^-$ and F5 to *cis*(N)*trans*(O$_6$)-Co(L-asp)$_2^-$, but for each pair the CD peaks in the first band region are shifted in energy to a greater extent than expected from the absorption bands and the signs are *reversed.* A clue to this behaviour is found by comparing CD and absorption peaks in the first band region for F6 and *cis*(N)*trans*(O$_5$) Co(L-asp)$_2^-$ (Figure 5). In the latter case the positions of the CD peaks correspond closely to the two components of the absorption band. In the case of F6 there is no CD peak corresponding to the absorption shoulder at *ca.* 19,600 cm^{-1}, but the weak negative CD peak is on the opposite side of the main absorption and CD components. In each case for the *cis*-N isomers (Figure 5) there are only two CD peaks in the first band region, but it is apparent that there must be three transitions, the dominant centre transition is flanked by two transitions of the opposite sign. In the case of the Co(L-asp)$_2^-$ isomers, the splitting is smaller and the lowest energy CD peak is swamped by the dominant peak. The lowest energy transition shows up in the CD spectra of the *cis*(N)-Co(L-asp)(ida)$^-$ isomers, but the highest energy CD peak in this region is missing. The presence of three transitions in the first band region for compounds of the *cis*-[CoN$_2$O$_4$] type is probably general, although most complexes related to Co(EDTA)$^-$ seem to show CD peaks[11] corresponding to the higher energy pair. The presence of three CD peaks in this region is unmistakable for Coen(malonate)$_2^-$ [13] and Co(EDDS)$^-$.[14] The ligand

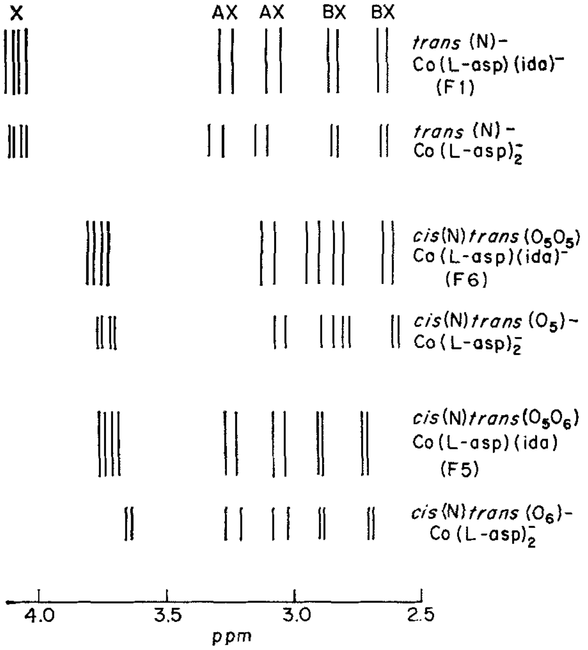

FIGURE 5 Comparison of the absorption and CD spectra of the three isomers of Co(L-asp)(ida)$^-$ with those of the corresponding isomers[7] of Co(L-asp)$_2^-$ and of Co(EDDS)$^-$.[14]

EDDS, ethylenediaminedisuccinate ion, was prepared by joining two L-asp by an ethylene bridge.

On the basis of a dominant central CD peak with a weaker peak of the opposite sign on either side, the CD spectra (Figure 5) are consistent with the correspondence of F5 (Figure 1) with *cis*(N)-*trans*(O_6)-Co(L-asp$)_2^-$ and F6 (Figure 1) with *cis*(N)*trans*(O_5)-Co(L-asp$)_2^-$.

There is a significant reduction in CD intensities for the mixed complex, *cis*(N)*trans*(O_5O_5)-Co(L-asp)(ida$)^-$, corresponding to *cis*(N)*trans*-(O_5)-Co(L-asp$)_2^-$, but not for the *cis*(N)*trans*-(O_5O_6) isomer, compared to *cis*(N)*trans*(O_6)-Co(L-asp$)_2^-$, suggesting a greater contribution of the fixed ring conformation of L-asp in the former case. However, the extensive mutual cancellation of CD peaks of alternating signs makes comparison of intensities uncertain.

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