

OPTICAL ACTIVITY OF Co(III) AMMINE COMPLEXES AND CHIRAL LIGANDS. CIRCULAR DICHROISM SPECTRA OF SOME CoN_3O_3 AND CoN_4O_2 CHROMOPHORES.

S. BUNEL, C. IBARRA, V. CALVO AND L. LARREA

Departamento Química Inorgánica y Analítica,
Facultad de Ciencias Químicas y Farmacéuticas
Universidad de Chile, Casilla 233, Santiago.

ABSTRACT

Ammine complexes of Co(III) containing the chiral ligands L-aspartate (L-asp), L-asparaginate (L-aspn) and L-malate (L-mal) ions were prepared. They are characterized by analysis, conductivity measurements, absorption and circular dichroism (CD) spectra, and IR spectrum of the L-malate complex.

Absorption and CD spectra of these complexes are compared with those of an aminocomplex of Co(III) containing D-ribose as a second ligand. The first excited state of Co(III) is split in two levels in the complexes formed by L-aspartate, L-asparaginate and D-ribose, the sign of the CD signals being opposite in this last compound to those of the aminoacidate complexes. All of them behave as if the metallic center were influenced by a field of tetragonal symmetry. The complex formed by the L-malate ion shows only one CD signal corresponding to the first excited state indicating that it has octahedral average microsymmetry.

The second excited state shows enhancement of the rotatory strength when there is an optically active charge transfer (CT) transition of similar energy, as with the L-malate and D-ribose complexes, which have an optically active second d-d band.

RESUMEN

A partir de complejos amoniacaes de Co(III) se sintetizaron compuestos que contienen los ligantes quirales L-aspartato, L-asparaginato y L-malato como segundo ligante. Los compuestos se identificaron por medio de análisis, mediciones de conductividad, espectros de absorción y de dicroismo circular (DC) y de espectro IR sólo para el complejo que forma el ion L-malato.

Los espectros de absorción y de dicroismo circular de estos complejos se compararon entre sí y con el aminocomplejo de Co(III) que contiene D-ribosa como segundo ligante.

El primer estado excitado del Co(III) se divide en dos en los complejos formados por los iones L-aspartato, L-asparaginato y D-ribosa; pero en este último caso las señales de DC son de signo opuesto a las de los aminoacidato-complejos, comportándose todos ellos como si el centro metálico estuviera sometido a un campo de simetría tetragonal.

El complejo formado por el ion L-malato muestra una sola señal de DC correspondiente al primer estado excitado, lo que indica que el ion Co(III) experimenta una microsimetría promedio octaédrica.

El segundo estado excitado cobra fuerza rotatoria sólo cuando el complejo presenta una banda de transferencia de carga de energía cercana. Ello ocurre con los complejos formados por el ion L-malato y por la ribosa, cuya segunda banda de absorción d-d es ópticamente activa.

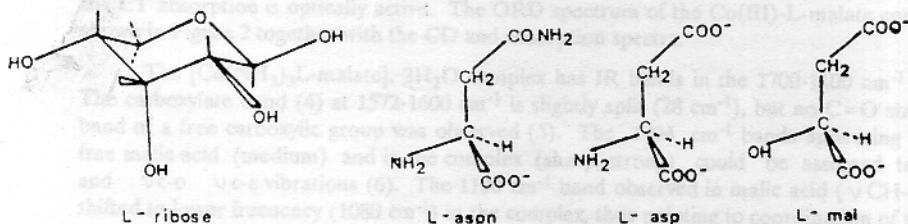
INTRODUCTION

The original aim of this study was to compare the optical activity in the visible spectral region of the ammine complexes of Co(III) with a chiral acid or aminoacid as a second ligand with that of Co(III) ammine complexes and a monosaccharide (1).

In all these complexes except that formed by L-asparaginate, chelation leads to a rigid structure of the chiral ligand around the metallic center.

We had observed earlier that the spectra of Co(III) ammine complexes containing either L-aspartate, L-asparaginate, L-malate ions or D-ribose as ligands have similar visible absorption bands, whereas the corresponding CD spectra are different. The intention was to find a correlation between the CD signal signs corresponding to the first excited state of Co(III) and the conformation of the chelate rings. On these grounds it could then be possible to predict the structure of a chiral chelate compound of this type from the knowledge of its CD spectrum in the visible region. However, the comparative study of optical activity in the charge transfer region of these compounds was also interesting: There are charge transfer absorptions in the four complexes we are comparing, but in only two of them there are low energy charge transfer transitions which are optically active. The second excited state of Co(III), magnetically forbidden, becomes optically active in these two cases. The rotatory strength probably originates in its mixing with the charge transfer states as it is discussed later on.

The ligands are shown in Figure 1.



EXPERIMENTAL

Materials. Chiral ligands were from Merck, BDH and Aldrich, and used without further purification.

Cis-[Co(NH₃)₄(H₂O)₂]₂(SO₄)₃ · 3H₂O was prepared according to Greenway and Lancashire (2). Purity was checked as previously reported (1).

Methods. Visible absorption spectra were measured on a Carl Zeiss PMQ-2 spectrophotometer using 10⁻² M aqueous solutions in the visible range, and 10⁻⁵ M solutions in the UV range. Optical rotatory dispersion (ORD) measurements were run on a Cary 60 spectropolarimeter, using 1 and 0.1 cm pathlength cells, with 10⁻² M aqueous solutions. The circular dichroism, CD spectra were recorded on a Cary 60 spectropolarimeter using 10⁻² M and 10⁻⁵ M aqueous solutions in 1.0 and 2.0 cm pathlength cells.

Carbon, hydrogen and nitrogen were analysed on a Perkin Elmer 240-C analyzer. The Co content was determined by atomic absorption spectroscopy with a Perkin Elmer 305 spectrometer. The sulphate and hydroxide ion contents were determined by conductimetric titration in a YSI model 32 conductivity meter. The IR spectra were measured either on a Bruker FTIR spectrophotometer (2 cm^{-1} resolution) or on a Leitz Wetzlar spectrometer with KBr pellets.

Preparation of the Co(III)-L-aspartate complex.

L-aspartic acid (0.44 g, $3.3 \cdot 10^{-3}$ mole) was dissolved in 20 cm^3 water, heated and neutralized with dilute ammonia solution. After the solution was cool, (1.1 g, $1.65 \cdot 10^{-3}$ mole) cis-[Co(NH₃)₄(H₂O)₂]₂(SO₄)₃·3H₂O was added. pH was adjusted to 7.0 with ammonia and the solution diluted to 30 cm^3 with distilled water. The solution was kept at 45°C in a water bath for three hours, then left 24 hours at room temperature after which 20 cm^3 methanol was added and the resulting solid was filtered off. This product is the well-known insoluble polynuclear complex: [Co((OH)₂CO(NH₃)₄)₄](SO₄)₃·nH₂O (3). The filtered solution was evaporated to dryness under air flow. The solid residue was redissolved in a minimum amount of water and 100 cm^3 methanol was added with constant stirring. The microcrystalline solid thus formed was filtered off and dried in a desiccator. The yield was approximately 700 mg.

Preparation of the Co(III)-L-asparagine complex.

L-asparagine (0.9 g, $6 \cdot 10^{-3}$ mole) in 30 cm^3 water was heated to 70°C until the amino acid dissolved. The solution was cooled to room temperature, (2.2 g, $3.3 \cdot 10^{-3}$ mole) cis-[Co(NH₃)₄(H₂O)₂]₂(SO₄)₃·3H₂O was added and the pH adjusted to 7.0 with ammonia. The volume was adjusted to 60 cm^3 and kept in a water bath for 3 hours at 45°C. The final pH was 9.10. The solution was kept for 24 hours at room temperature. The polymeric compound previously described separated and 60 cm^3 methanol was added to complete its precipitation, and then filtered off. Methanol (150 cm^3) was added to the filtered solution maintaining constant stirring. The asparagine complex crystallized and it was isolated by filtration, washed with 5 cm^3 methanol and dried in a desiccator. The yield was nearly 300 mg.

Preparation of the Co(III)-L-malate complex.

L-malic acid (0.8 g, $6 \cdot 10^{-3}$ mole) and (2.2 g, $3.3 \cdot 10^{-3}$ mole) cis-[Co(NH₃)₄(H₂O)₂]₂(SO₄)₃·3H₂O were dissolved in 40 cm^3 water adjusted to pH 7.0 with a final volume of 60 cm^3 . The solution was kept at 45°C in a water bath for 3 hours. Although formation of the polymeric compound was not observed, the pH of the solution rose to 9.3. The preparation was allowed to stand overnight at room temperature and 20 cm^3 methanol was added to precipitate insoluble reagents which were filtered off. The solvent was evaporated from the filtered solution, a small amount of water was then added to dissolve impurities and the solution was then filtered. The crystals were dried in a desiccator. The product was further purified by dissolution in a minimum amount of water, addition of methanol, and concentration. Large prismatic crystals were then obtained. The yield was 1 g. Preparation and analysis of the complex [Co(NH₃)₄-D-ribose]₂(SO₄)₃·4H₂O were already described in reference (1). Only the visible ORD curve of the complex was then shown, and the CD maxima in the same spectral region were measured as extinction coefficient differences with a low-sensitivity spectrophotometer, fitted with CD attachment.

The three newly synthesized compounds are red-purple microcrystals, very soluble in water and pinsoluble in most organic solvents.

Analysis.

The elemental analysis results of C, H, N, and cobalt and sulphate content, plus conductimetric titration data are shown in Table 1. The calculated formulae fit the equivalent conductivity.

TABLE 1. Elementary Analysis.

	[Co-L-asp]		[Co-L-aspn]		[Co-L-mal]	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Co%	17.63	18.06	17.63	16.89	21.26	20.30
N %	16.75	16.15	16.76	17.13	15.16	15.13
H %	5.73	5.26	5.73	5.04	5.82	5.20
C %	14.37	13.73	14.37	14.43	17.33	17.29
SO ₄ %	14.37	14.00	14.75	14.69	0	0
Conductivity (mho·cm ² ·eq ⁻¹)	109.4		129.4		0	
[Co(NH ₃) ₃ -L-aspartate] ₂ SO ₄ ·5H ₂ O = [Co-L-asp]						
[Co(NH ₃) ₂ (H ₂ O)(OH)L-asparaginate] ₂ SO ₄ ·3H ₂ O = [Co-L-aspn]						
[Co(NH ₃) ₃ -L-malate]·2H ₂ O = [Co-L-mal]						

RESULTS

Table 2 shows the absorption and CD values of the three complexes. In the visible spectral region the typical first d-d band of Co(III) exhibit two optically active components of opposite sign in the complexes containing L-aspartate and L-asparaginate. Only one CD signal is observed for the L-malate complex. The second visible absorption band appears as a shoulder in the L-aspartate and L-asparaginate complexes and has very weak optical activity. The second d-d band of the L-malate complex, on the contrary, shows one intense CD signal.

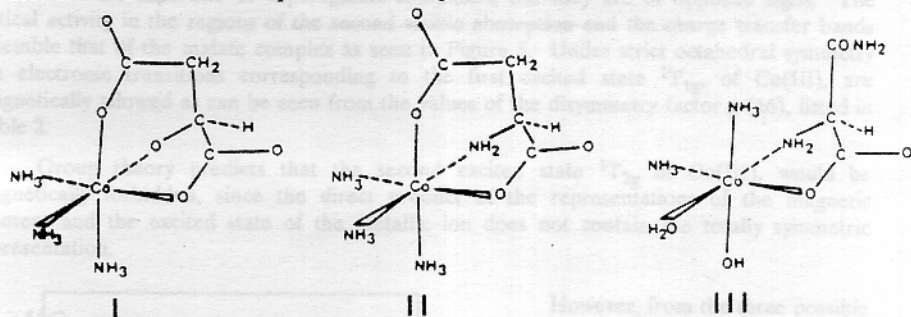
The two complexes with aminoacids (L-aspartate and L-asparaginate) show optically inactive CT in the near UV and UV regions respectively. However, in the L-malate complex, the CT absorption is optically active. The ORD spectrum of the Co(III)-L-malate complex is shown in Figure 2 together with the CD and absorption spectra.

The [Co(NH₃)₃L-malate]·2H₂O complex has IR bands in the 1700-1100 cm⁻¹ region. The carboxylate band (4) at 1572-1600 cm⁻¹ is slightly split (28 cm⁻¹), but no C=O stretching band of a free carboxylic group was observed (5). The 1404 cm⁻¹ bands appearing both in free malic acid (medium) and in the complex (sharp, strong) could be assigned to δ OH and ν_{c-o} ν_{c-c} vibrations (6). The 1100 cm⁻¹ band observed in malic acid (ν CH-O) was shifted to lower frequency (1080 cm⁻¹) in the complex, thus pointing to coordination of the OH group (5). There are characteristic bands at 1290 cm⁻¹, 1080 cm⁻¹, 568 and 505 cm⁻¹ which were previously assigned to metal-alkoxide stretching vibrations (7,8).

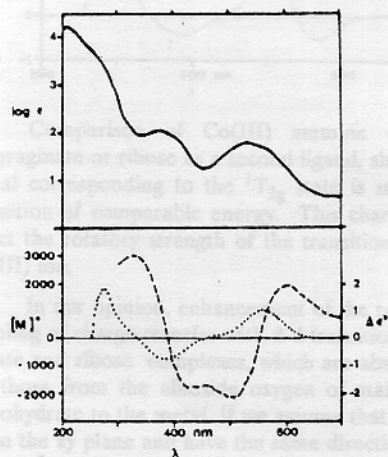
DISCUSSION

Conductivity of the L-malate-containing complex [Co(NH₃)₃L-malate] indicates that it is nonionic with L-malate behaving as a tridentate ligand. This implies that deprotonation of the OH group is induced by chelation, in agreement with the IR spectral results mentioned above (5). The observed splitting of the carboxylate signal might arise from a slight distortion of the Oh symmetry imposed by strain of the tridentate ligand (6). As expected both in malate and tartrate-containing complexes, bands at 1290-1080 cm⁻¹ remain active, while those at 1450 and 1240 cm⁻¹ disappear; these bands were assigned to OH stretching (8). Further evidence of metal-alkoxide coordination comes from the 600-400 cm⁻¹ spectral region. The reported cobalt-alkoxide vibrations (7) consist of ν m-o + ν c-c and m-o bands in the 600-400 cm⁻¹ range. The L-malate-containing complex shows bands at 568 and 505 cm⁻¹. Various

complexes formed by Co(III), 1,10-phenanthroline and malate (4,9) also give evidence of alkoxide-metal coordination, with formation of a five membered chelate ring. In this complex the three ammonia molecules plus the tridentate malate ligand lead to only one possible structure I, where the three nitrogen atoms of the ammonia ligands and the three oxygen atoms of the malate ion adopt a "facial" configuration around Co(III).



Only one CD signal is observed under the first absorption band (530 nm) of the Co(III) complex ion, corresponding to the first excited state, ${}^1T_{1g}$, and the ORD curve clearly shows the presence of a single Cotton effect whose zero rotation point coincides with the CD signal maximum, as seen in Figure 2.



Provided that the ORD curve is the resultant of contributions of every optically active electronic transition of a chiral species, it may be concluded that the experimental curve is due to only one excited state of the Co(III) ion. This means that the Co(III) ion is affected by an average ligand field of octahedral symmetry (10). Therefore the compound behaves as an orthoaxial complex in spite of the fact that the interaxial angles involving the chelate ring are smaller than 90° (11).

One should bear in mind that, in general, "facial" isomers of tris-aminoacidates of Co(III) also show a single CD signal under the first absorption band (545 nm), except for the tris-prolinates, where the proline ring causes greater distortion (12).

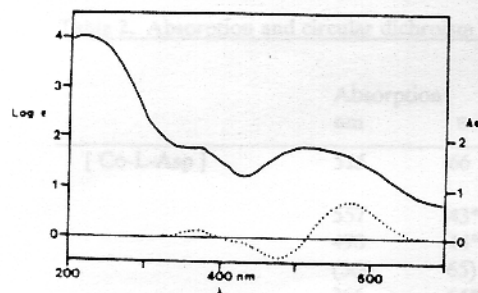
Figure 2. $[\text{Co}(\text{NH}_3)_3\text{L-mal}]$: Absorption spectrum (—); ORD curve (---); CD spectrum (.....).

The second visible absorption band (390 nm), corresponding to the ${}^1T_{2g}$ state, has a negative CD signal of intensity comparable to that of the first. The Cotton effects are well separated. The malate-containing complex has a third positive CD signal under a shoulder in the UV region (289 nm).

In the $[\text{Co}(\text{NH}_3)_3\text{L-aspartate}]^+$ complex the aspartate ion also behaves as a tridentate ligand leading to only one possible structure II, with the carboxylate group oxygen atoms in the "cis" position and the ammonia molecules in "facial" positions. There are two CD signals of opposite sign under the absorption band at 515 nm. The signal at longer wavelength (570 nm) is positive, as seen in Figure 3. The complex behaves as an orthoaxial one, with D_{4h}

holohedrized microsymmetry, which means that the first excited state ${}^1T_{1g}$ of Co(III) splits into its 1A_2 and 1E components.

The energy difference between these states is $35/4 D_t$.



In this case this is equivalent to $5/2 (Dq^0 - Dq^{NH_2})$ (13), where Dq^0 refers to the carboxylate and Dq^{NH_2} to the amino group ligand parameters.

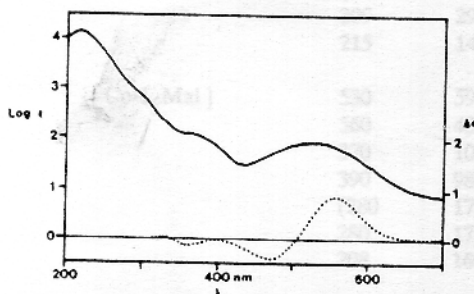
From the parameters calculated by Ban and Csaszar (14) for different ligands in the Co(III) orthoaxial complexes as a basis set, the relationship $Dq^{NH_2} > Dq^0$ is always satisfied: As a result, $35/4 D_t < 0$.

Figure 3. $[Co(NH_3)_3L-asp]^+$: Absorption spectrum (—); CD spectrum (.....)

Therefore the 1A_2 state is of lower energy than the 1E state, and the positive CD signal (570 nm) corresponds to the 1A_2 state and the negative one (480 nm) to the 1E state.

A weak positive CD signal (368 nm) can be detected under the second excited state of Co(III), appearing in this complex as a shoulder on top of the high intensity charge transfer band. Hawkins et al. (20) have arrived at a similar energy state assignment in studying the circular dichroism of the *cis*- CoN_4Cl_2 chromophore.

The spectral region 300-200 nm does not show CD signals similar to those of the malate complex.



In the L-asparagine complex $[Co(NH_3)_2(H_2O)(OH)L-asparinate]^+$, the aminoacidate anion behaves as a bidentate ligand, coordinating through the carboxylate and amino groups; the $CONH_2$ group does not coordinate to Co(III) (15).

Figure 4. $[Co(NH_3)_2(H_2O)(OH)L-asparn]^+$: Absorption spectrum (—); CD spectrum (.....)

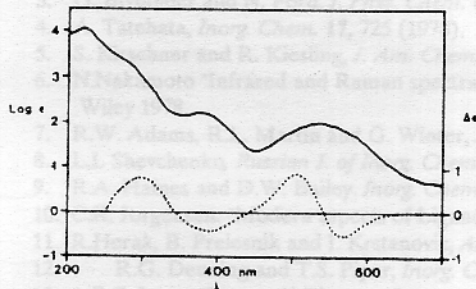
There are four possible distributions of the atoms directly bonded to Co(III): two of them with "facial" disposition of the nitrogen atoms and the other two with "meridional" arrangement. The CD spectrum under the first excited state is, however, similar to that of the complex of L-aspartate with a first positive signal at lower and a negative one at higher energy, as seen in Figure 4. Spectral evidence then shows that the field generated by the asparaginate ligand is similar to that produced by the aspartate ion. This result is consistent with a model where charged oxygen ligands, of the carboxylate and OH groups, are in "cis" positions to one another and trans to the ammonia molecules, structure III.

If the holohedrized symmetry had been lower, i.e. D_{2h} , the three axial contributions would have been different. In that case a third CD signal of negative sign should have been present in the region near 700 nm, but it was not seen. A very weak negative CD signal is seen

at 360 nm, under the spectral region corresponding to the ${}^1T_{2g}$ state of Co(III). There are no other CD signals in the 300-200 nm region.

Comparing the malate, aspartate and asparaginate-Co(III) complexes with $[\text{Co}(\text{NH}_3)_4\text{D-ribose}]_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ (1) it is interesting to note that the CD spectrum of the last complex under the first visible absorption band (530 nm) has the same number of components as those of the aspartate or asparaginate-complexes, but they are of opposite signs. The optical activity in the regions of the second visible absorption and the charge transfer bands resemble that of the malate complex as seen in Figure 5. Under strict octahedral symmetry the electronic transitions corresponding to the first excited state ${}^1T_{1g}$ of Co(III), are magnetically allowed as can be seen from the values of the dissymmetry factor g (16), listed in Table 2.

Group theory predicts that the second excited state ${}^1T_{2g}$ of Co(III), would be magnetically forbidden, since the direct product of the representations of the magnetic moment and the excited state of the metallic ion does not contain the totally symmetric representation.



However, from the three possible transitions making up the T_{2g} state, only the $dx_y \rightarrow dz^2$ transition has a zero magnetic moment whereas the $dx_z \rightarrow dz^2$ and $dy_z \rightarrow dz^2$ transitions have non-zero values and are polarized in the xy plane (17).

Figure 5. $[\text{Co}(\text{NH}_3)_4\text{D-rib}]^{3+}$: Absorption spectrum (—); CD spectrum (.....).

Comparison of Co(III) ammine complexes containing either malate, aspartate, asparaginate or ribose as a second ligand, shows that in those of L-malate or D-ribose the CD signal corresponding to the ${}^1T_{2g}$ state is strengthened whenever there is a charge transfer transition of comparable energy. This charge transfer transition, however intense, does not effect the rotatory strength of the transitions corresponding to the first excited state of the Co(III) ion.

In our opinion, enhancement of the rotatory strength of the ${}^1T_{2g}$ transitions is due to a coupling of charge-transfer with d-d transitions. The possible charge transfer transitions of the malate and ribose complexes, which are absent in the aspartate and asparaginate complexes, are those from the alkoxide oxygen of malate ion or the oxygen of the OH group of the carbohydrate to the metal. If we assume that these correspond to a $\sigma \rightarrow 3d_{eg}$ transition, they lie on the xy plane and have the same direction as the magnetic moments of the $dx_z \rightarrow dx^2$ and $dy_z \rightarrow dz^2$ transitions. Comparison of the absorption spectra and optical activity of the three acidate complexes suggest that the number of CD signals under the first d-d absorption band of Co(III) is determined by the microsymmetry around Co(III). The origins of the oxide ions, whether carboxylate, alkoxide or hydroxide residues are not important, the situation is the same for nitrogen residues from ammonia or a chiral aminoacid. Complexes of D-ribose and of the aminoacids L-aspartate and L-asparaginate have the same number of CD signals under the first absorption band as required by this hypothesis. We suggest that similar surroundings of the metal ion, giving the same microsymmetry, determine the same splitting scheme of the energy levels and, therefore, the same number of CD signals.

Regarding the origin of the sign of the CD signals of the first visible excited state in the monosaccharide complex, the sign sequence is related to the rigid δ conformation of the chelate ring. We have shown that the sign sequence is inverted as a result of anomerization of the D-arabinose complex in solution (18).

Table 2. Absorption and circular dichroism values

	Absorption		Circular Dichroism		g x100
	nm	ϵ	nm	$\Delta\epsilon$	
[Co-L-Asp]	515	66	570	+0.376	
			480	0.191	
	557	43*	565	+0.378*	0.879
	490	44*	483	0.211*	0.479
	(360	65)	368	+0.031	
	366	64*	366	+0.061*	0.095
	(280	1257)	---	-----	
	280	195*	---	-----	
215	9923	---	-----		
[Co-L-Aspa]	520	86	560	+0.427	
			470	0.200	
	540	47*	557	+0.420*	0.875
	478	48*	478	0.208*	0.433
	(360	103)	360	0.033	
	380	65*	363	0.044*	0.067
	(310	439)	---	-----	
	309	290	---	-----	
215	14080	---	-----		
[Co-L-Mal]	530	59	560	+1.007	
	560	48*	558	+1.011*	2.11
	370	109	390	0.741	
	390	98*	389	0.801*	0.77
	(280	1756)	275	+1.847	
	280	1756*	278	+2.088*	0.10
	208	16913	---	-----	
[Co-D-Rib]	530	94	568	0.530	
			505	+0.856	
	549	44*	560	0.665*	1.520
	517	48*	510	+0.947*	1.958
	375	166	390	0.428	
	371	166*	385	0.440*	0.265
			300	+0.760	
			297	+0.773*	
	220	11585	---	-----	

Values in parenthesis are shoulders in a $\log(\epsilon)$ vs. wave length spectrum. Calculated* values were obtained by deconvolution of experimental curves (19). $g = \Delta\epsilon/\epsilon$

Even though the L-asparaginate-complex does not have a second chelate ring the optical activity requires that the ring corresponds to an asymmetric envelope conformation.

ACKNOWLEDGEMENTS

This research work was supported by projects N° 230 - 1988 FONDECYT and N° 2741-8823 DTI. We thank Dr. Clifford A. Bunton for helpful discussions. This collaboration was supported by the National Science Foundation Office of International Programs.

We also thank Ms. Fresia Pérez and Mr. Claudio Telha for help with the english version of the manuscript.

Two of the authors (C.I. and S.B.) worked under the "Dedicación Exclusiva" regime during the development of this research. They acknowledge Universidad de Chile for that.

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