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Characterization of the Three Isomers of Sodium Bis(L-aspartato)cobaltate(III)[1]

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The bis(L-aspartato)cobaltate(III) complex, $Co(N)_2(O)_4$ type, has been prepared and separated into three optically active isomers by ion-exchange chromatography. The isomers were identified from their electronic absorption, infrared, and circular dichroism spectra.

Varying degrees of stereoselectivity have been reported in the preparation of cobalt(III) complexes containing optically active amino acids functioning as bidentate ligands.[2] Cobalt(III) complexes of optically active amino acids functioning as tridentate ligands have been reported for L-aspartic acid,[3,4] 2,3-diaminopropionic acid,[5,6] 2,4-diaminobutyric acid,[7] and L-histidine.[8] The present paper reports the complete separation of the three possible geometrical isomers of the complex $Na[Co(L\text{-}asp)_2]$ which are characterized by their electronic absorption, infrared, and circular dichroism (CD) spectra. Corresponding enantiomeric complexes of D-aspartic acid were also obtained.

Experimental Section

L- and D-aspartic acids were purchased from Nutritional Biochemicals Corp., Cleveland, Ohio, and were used as received.

Three Isomers of Sodium Bis(L- or L-aspartato)cobaltate(III).—To a hot solution (*ca.* 80°) of 3.2 g (0.024 mol) of L-aspartic acid and 0.48 g (0.012 mol) of NaOH in 25-ml of water were added 1.3 g (0.012 mol) of freshly prepared $Co(OH)_3$[9] and 0.1 g of activated charcoal. The reaction mixture was stirred on a boiling water bath for about 10 min. The mixture was filtered to remove the charcoal after cooling in an ice bath. The filtrate was poured into a column (1.5 × 25 cm) of strong-base anion-exchange resin (Dowex 1X2, 200–400 mesh, chloride form). A small quantity of a complex, for which the spectrum corresponded to that of $H_3Co(asp)_3$,[10] was eluted when the column was flushed with water. The adsorbed band was eluted with 0.1 *M* NaCl solution at a rate of about 0 5 ml/min. Three colored bands, one brick red, one violet, and one blue-violet, were eluted in that order. The three eluates were separately evaporated to dryness in a vacuum desiccator over H_2SO_4. Each of the crude products obtained was dissolved in a small quantity of water with the addition of an equivalent amount of $AgClO_4$. The AgCl was removed by filtration and washed with a small amount of ice water. The filtrate and washings were combined and three volumes of ethanol were added to precipitate the complex. Each of the complexes was recrystallized from as little water as possible by adding a small amount of ethanol. Three isomers of the corresponding D-asparato complex were also isolated by the same procedure. Lithium salts of the three isomers were obtained by elution with 0.1 *M* LiCl solution, followed by evaporation at 30° in a rotatory evaporator. *Anal.* Calcd for $NaC_8H_{10}N_2Co \cdot 3H_2O$: C, 24.13; H, 4.05; N, 7.03. Found: (first isomer eluted) C, 24.59; H, 3.94; N, 7.10; (second isomer eluted) C, 24.14; H, 4.11; N, 6.89; (third isomer eluted) C, 24.01; H, 4.10; N, 6.97. Calcd for $LiC_8H_{10}N_2Co \cdot H_2O$: C, 27.76; H, 3.49; N, 8.09. Found: (first isomer eluted) C, 27.52; H, 4.14; N, 7.92. Calcd for $LiC_8H_{10}N_2Co \cdot 3H_2O$: C, 25.14; H, 4.22; N, 7.33. Found: (second isomer eluted) C, 24.14; H, 4.28; N, 6.93; (last isomer eluted) C, 24.21; H, 4.30; N, 6.98.

Measurements.—The electronic absorption spectra of the complexes in aqueous solution were measured with a Beckman DU spectrophotometer. The CD spectra were recorded with a Roussel-Jouan Dichrograph. The concentrations of solutions were 0.005–0.01 *M* and all measurements were made at room temperature. The infrared spectra were measured with a Hitachi EPI-2 spectrometer with NaCl prisms using KBr disks.

Results and Discussion

The three possible isomers of $Co(L\text{-}asp)_2^-$ are shown in Figure 1. They are designated as trans or cis with respect to the nitrogen atoms. The two cis(N) isomers are distinguished as cis(N)trans(O_6) (oxygens of six-membered chelate rings trans to one another) and cis(N)trans(O_5) (oxygens of five-membered chelate rings trans).

The infrared spectrum of a sample of β'-$H_3Co(asp)_3$ which was prepared by the method of Shibata, *et al.*,[10] shows a strong band at 1625 cm^{-1} which can be assigned to coordinated carboxylate groups of the bidentate ligand and a band at 1710 cm^{-1} which can be assigned to the uncoordinated carboxylic acid groups. The infrared spectrum for the isomer of $Co(L\text{-}asp)_2^-$ from the first eluate (assigned later as the trans(N) isomer) shows a strong band at 1615 cm^{-1}. Each of the isomers from the second and third eluates shows a strong band at 1580 cm^{-1} with a shoulder at about 1640 cm^{-1}. A similar spectrum was reported[11] for $Co(EDDS)^-$, where EDDS is the anion of ethylenediaminedisuccinic acid, prepared by joining two aspartic acid molecules by a C–C linkage to give an EDTA type ligand. They assigned these bands, respectively, to the coordinated carboxylate groups of the six-membered and five-membered chelate rings. For the three isomers of $Co(L\text{-}asp)_2^-$ the infrared spectra gave no indication of the presence of uncoordinated carboxylate or carboxylic acid groups.

The first (lowest energy) absorption band of a trans-$Co(N)_2(O)_4$ type complex is known to show much greater splitting than that of a corresponding cis isomer.[12] This band is split into two distinct peaks only for the isomer from the first eluate (Figure 2, Table I). The observed splitting pattern agrees well with results for trans(N) isomers in a series of mixed amino acid

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[1] This work was supported in part by a research grant (GM-10829) from the Division of General Medical Studies, U. S. Public Health Service.

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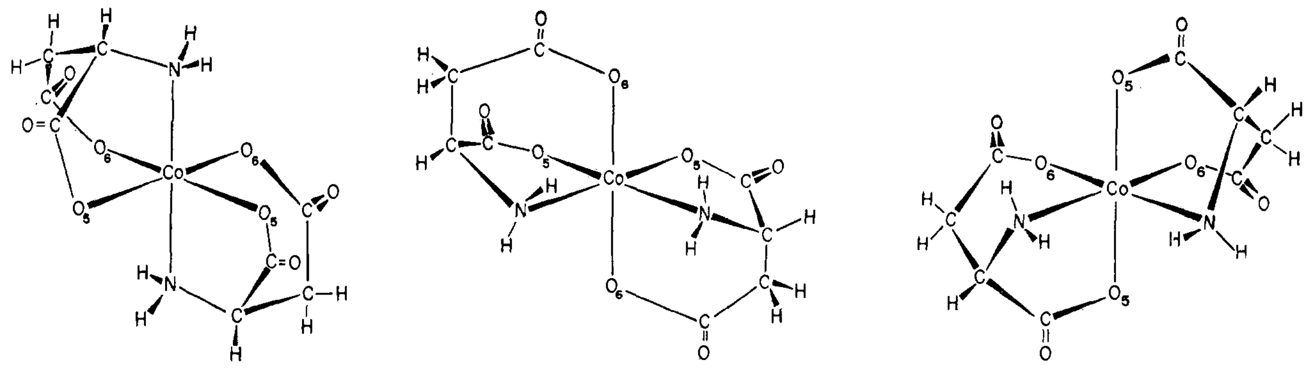

Trans (N) Cis (N) Trans (O_6) Cis (N) Trans (O_5)

Figure 1.—Geometrical isomers of Co(L-asp)$_2^-$.

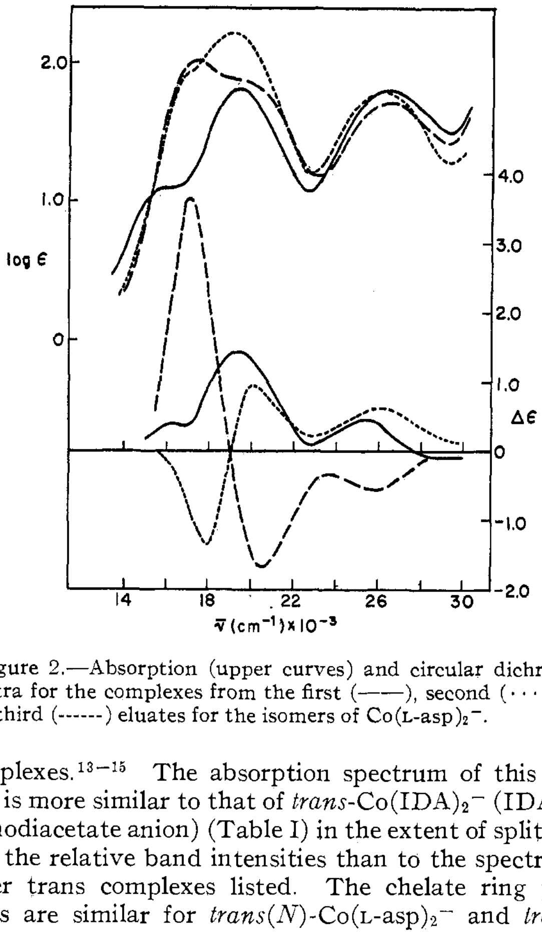

Figure 2.—Absorption (upper curves) and circular dichroism spectra for the complexes from the first (——), second (· · · · · ·), and third (------) eluates for the isomers of Co(L-asp)$_2^-$.

complexes.[13–15] The absorption spectrum of this isomer is more similar to that of *trans*-Co(IDA)$_2^-$ (IDA = iminodiacetate anion) (Table I) in the extent of splitting and the relative band intensities than to the spectra of other trans complexes listed. The chelate ring patterns are similar for *trans(N)*-Co(L-asp)$_2^-$ and *trans*-Co(IDA)$_2^-$. The isomer from the first eluate can be assigned confidently as the trans(N) isomer from the great splitting of the first absorption band and this is supported by the fact that only this isomer gave an infrared spectrum different from that of Co(EDDS)$^-$ where the nitrogens must be cis.

Smaller splittings are expected for *cis*-Co(N)$_2$(O)$_4$ isomers,[12,13,15] and such splittings are observed for the remaining two isomers (Figure 2, Table I). The first absorption band for the isomer from the second eluate shows a small shoulder on the lower energy side. There is a distinct shoulder on the higher energy side of the first band of the isomer from the last eluate. These spectral features agree well with those for the two isomers of Co(L-asp)$_2^-$ which were isolated in an earlier study[4] but not identified.

Neal and Rose[11] compared the absorption spectrum of the Co(III) complex of EDDS with that of Co(EDTA)$^-$. EDDS contains two L-asp units joined by an ethylene linkage so that only cis(N) isomers are possible for complexes of EDDS. Assuming a tetragonal field related to that of Co(EDTA)$^-$, they calculated a higher Dq value for EDDS than for EDTA, although, within the limits of uncertainty, both values should be rounded to 2300 cm^{-1}. Using the same approach for the two cis isomers of Co(L-asp)$_2^-$, the Dq values are the same, 2400 cm^{-1}, and slightly higher than for EDTA or EDDS. Here the positions of the two components are taken from the CD peak maxima (Table I), since these should give a better indication of the energies than a gaussian analysis of the broad absorption bands. The position of the higher energy component for the isomer from the last eluate, assigned later the cis(N)trans(O_5) structure, is at slightly higher energy than that for the other cis isomer, indicating a slightly stronger equatorial-plane field for the former isomer or a stronger field for the oxygens of the six-membered rings. The smaller splitting for the isomer from the second eluate, assigned later the cis(N)trans(O_6) structure, indicates a smaller difference between the equatorial and axial fields and is consistent with a stronger field for the oxygens of the six-membered rings. These relative field strengths for five- and six-membered chelate rings do not correspond to those of simple bidentate amino acids[11,15,16] because of the constraints imposed by the fact that the rings are not joined at the terminus (N).

Circular Dichroism Spectra.—Optically active asp coordinates stereospecifically so that, for L-asp, looking along the methine bond from H to C, the ligand atoms must attach on one face of an ocetahedron in the clockwise sequence: NH_2, O_5, O_6. The mirror images of the structures in Figure 1 would have the opposite chirality of chelate rings and must contain D-asp. The three isomers isolated using D-asp gave CD curves which were enantiomeric to those of Figure 2.

The CD curve for the isomer from the first eluate (Figure 2, Table I) shows splittings consistent with the absorption spectrum and the effective tetragonal symmetry of a *trans*-Co(N)$_2$(O)$_4$ isomer. Similar results

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TABLE I

CHARACTERISTICS OF ABSORPTION AND CD SPECTRA OF Co(N)$_2$(O)$_4$ TYPE COMPLEXES

	First band				Second band			
	Absorption		Circular dichroism		Absorption		Circular dichroism	
Complex ion	$\tilde{\nu}_{max}$, cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}	$\tilde{\nu}_{max}$, cm^{-1}	$\Delta\epsilon_{max}$, M^{-1} cm^{-1}	$\tilde{\nu}_{max}$, cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}	$\tilde{\nu}_{max}$, cm^{-1}	$\Delta\epsilon_{max}$, M^{-1} cm^{-1}
trans-Co(gly)$_2$ox$^-$ [a]	$\sim$16,700	50.2	$\sim$16,670	−1.4	24,840	170	26,170	+0.69
	18,870	100	18,970	−2–07				
trans-Co(L-ala)$_2$ox$^-$ [a]	$\sim$16,700	50.2	$\sim$16,830	−1.1	25,970	174	25,990	+0.35
	18,940	102	19,680	−1.45			29,000	−0.13
Opposite isomer			$\sim$16,000	+0.4			26,350	−0.41
			18,500	+2.07				
trans-Co(L-ser)$_2$ox$^-$ [b]	$\sim$16,700	63.1	$\sim$16,070	−2.08	25,970	230	25,950	+0.45
(ser = serate ion)	19,050	135	19,350	−2.22			28,800	−0.22
Opposite isomer			$\sim$16,000	+0.51			26,350	−0.47
			18,670	+2.37				
trans-Co(β-ala)$_2$ox$^-$ [a]	16,000	57.6	15,700	−0.43	26,300	132	23,810	−0.13
	18,830	100	$\sim$16,070	−0.3			26,530	+0.71
			19,540	−0.57				
trans-Co(IDA)$_2^-$ [c]	16,670	11.5			27,770	56.3		
(IDA = iminodiacetate ion)	20,400	52.5						
trans(*N*)-Co(L-asp)$_2^-$	15,870	14.5	16,500	+0.35	26,460	79	25,100	+0.42
(first isomer eluted)	19,530	79.5	19,400	+1.42			28,400	−0.10
cis(*N*)*trans*(O_6)-Co(L-asp)$_2^-$	$\sim$16,700	79	17,900	−1.36	26,180	74.5	26,000	+0.62
(second isomer eluted)	19,230	180	20,300	+0.96				
cis(*N*)*trans*(O_5)-Co(L-asp)$_2^-$	17,240	124	17,300	+3.71	26,460	63.5	25,000	−0.54
(last isomer eluted)	$\sim$20,000	76	20,400	−1.72				
C_2-*cis*-Co(gly)$_2$ox$^-$ [d,e]	17,830	121			25,900	159		
C_1-*cis*-Co(gly)$_2$ox$^-$ [d,e]	18,350	141			26,320	174		
C_2-*cis*-Co(L-ser)$_2$ox$^-$ [b,e]	18,000	154.9	18,000	+3.70	25,900	199.6	26,100	−0.47
			22,450	−0.06				
Opposite isomer			18,150	−3.15			26,200	+0.48
C_1-*cis*-Co(L-ser)$_2$ox$^-$ [b,e]	18,480	154.9	17,970	+2.63	25,840	199.6	24,200	+0.05
			21,750	−0.06			26,200	−0.33
							29,070	−0.09
Opposite isomer			18,000	−3.18			24,000	−0.10
							26,350	+0.41
							29,200	−0.07
cis-Co(IDA)$_2^-$ [c,f]	17,800	151.4	17,100	−2.72	26,340	134.9	26,300	−0.79
			19,600	+2.94				
Co(EDTA)$^-$ [f]	18,600	347	17,300	−1.51	26,500	246	24,050	−0.29
			19,830	+0.76			27,900	−0.33
Co(EDDS)$^-$ [g]	19,400		$\sim$16,500	+	26,250			
			$\sim$18,000	− (more intense)				
			$\sim$21,000	+				

[a] Reference 13. [b] Reference 15. [c] J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Jap.*, **35,** 567 (1962). [d] Reference 14. [e] C_1 and C_2 refer to the symmetry of the isomer. [f] C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **8,** 1145 (1969). [g] Reference 11.

from CD and absorption curves have been reported for *trans*(N)-Co(aa)$_2$ox$^-$ complexes[15] (aa refers to a glycinate, L-alaninate, β-alaninate, or L-serinate ion). The CD spectrum in the first band region for the isomer in the first eluate is most similar to those of the (−)-*trans*-(*N*)-Co(α-aa)$_2$ox$^-$ isomers.

The chirality of a metal chelate has been described in terms of the spiral patterns of the chelate rings ignoring differences among the chelate rings or differences of ligand atoms.[17,18] For the trans(N) isomer (Figure 1) the connection of each N is a half-bond from the center of the O–C–C–C–C–O chain, or the arrangement differs by only this slight extent from possessing a plane of symmetry. The slight deviation from a symmetrical arrangement is consistent with the relatively low intensity of the CD peaks (Figure 2) for the isomer from the first eluate. There are, of course, contributions to the optical activity from the presence of asymmetric centers in the ligands and from chiral ring conformations.

The CD curves for the cis isomers (Figure 2) are of similar form, but their sign patterns are opposite, suggesting an antipodal relationship between the isomers. It can be seen that these isomers, as drawn in Figure 1, are quasiantipodal in overall form; they differ in the interchange of the five- and six-membered rings. Each has two "in-plane" or G rings, and the "out-of-plane," R, or trans(O) rings describe a right spiral about the C_2 axis (as for (+)$_{546}$-Co(EDTA)$^-$) for the cis(N)-trans(O$_6$) isomer and a left spiral about the C_2 axis (as for (−)$_{546}$-Co(EDTA)$^-$) for the cis(N)trans(O$_5$) isomer. The CD peak intensities are much greater for the isomer from the third eluate. As the cis(N)trans(O$_6$) isomer is drawn in Figure 1, it can be seen that the six-membered rings connect to the nearly planar five-membered amino acid chelate rings only a half-bond from their centers. Thus this structure, like that of the trans(N) isomer, deviates only slightly from an arrangement which would possess a plane of symmetry (through both O$_6$ and bisecting the N–O$_5$ ring) if one considered the chelate rings as symmetrical connectors. The lower intensity of the CD peaks for the isomer from the second eluate would be consistent with a lower effective chirality of the cis(N)trans(O$_6$) structure. The cis(N)trans-(O$_5$) structure is less symmetric because of O$_5$ ring is connected one full bond from the center of the N–O$_6$ ring and the latter is puckered significantly.

The G ("in-plane") rings of Co(EDTA)$^-$ are more

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strained than the R rings.[19] This strain is relieved by enlarging the chelate rings or removing the N–N linkage as in *cis*-Co(IDA)$_2^-$. The five-membered ring of asp is more constrained, with respect to conformational change, than in the case of IDA because the rings are not joined at the terminal atom in asp. The cis(N)-trans(O$_6$) isomer has the constrained O$_5$ rings as G rings and the CD curve for the second eluate is very similar in intensities and sign pattern to that of $(+)_{546}$-Co(EDTA)$^-$ which has the same absolute configuration as the cis(N)trans(O$_6$) isomer in Figure 1. In the case of cis(N)trans(O$_5$) the G rings have six members and should be strain free. The CD curve for the third eluate is closely related to that of the isomer of *cis*-Co(IDA)$_2$ which has been assigned the absolute configuration[20] of $(-)$-$_{546}$Co(EDTA)$^-$ and this is the same as that of the cis(N)trans(O$_5$) isomer in Figure 1.

The stereospecific ligand EDDS[11] could give two isomeric complexes with Co(III), corresponding to the cis(N)trans(O$_6$) and cis(N)trans(O$_5$) isomers in Figure 1. The results reported favored the cis(N)trans(O$_5$) structure. The CD curve of Co(EDDS)$^-$ has the same sign pattern in the first band region as for model compounds related to $(-)_{546}$-Co(EDTA)$^-$ and for the isomer from the third eluate, to which we have assigned the cis(N)trans(O$_5$) structure. Their reservation[11] about using CD data for their assignment was based upon intensity considerations, not sign patterns. Relative intensities have been shown[20] to vary greatly within a series of model compounds of Co(EDTA)$^-$.

All results are consistent with the assignments of the isomer from the first eluate to the trans(N) structure, that from the second eluate to the cis(N)trans(O$_6$) structure with the absolute configuration corresponding to $(+)_{546}$-Co(EDTA)$^-$, and that from the third eluate to the cis(N)trans(O$_5$) structure with the absolute configuration corresponding to $(-)_{546}$-Co(EDTA)$^-$.

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Direct Evaluation of Dipolar Nuclear Magnetic Resonance Shifts from Single-Crystal Magnetic Susceptibilities. Paramagnetic Anisotropy of Dichlorobis(triphenylphosphine)cobalt(II) and -nickel(II)

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The principal molecular susceptibilities of the pseudotetrahedral dichlorobis(triphenylphosphine)cobalt(II) and -nickel(II) complexes were determined from single-crystal magnetic anisotropy measurements (Krishnan's critical torque method) and bulk susceptibility measurements (Gouy method) at room temperature. The cobalt compound was found to be considerably more anisotropic than the nickel complex with the anisotropy in the opposite sense. The results were used to evaluate the dipolar contributions to the isotropic pmr shifts of the phenyl protons. Large upfield dipolar shifts (2.1–0.5 ppm) are predicted for the cobalt compound and small downfield shifts (0.6–0.1 ppm) are calculated for the nickel complex. These results are consistent with an earlier evaluation of dipolar shifts in analogous systems based on pmr data alone.

Introduction

Fundamental to the study of isotropic nuclear magnetic resonance shifts $\Delta\nu^{\rm iso}$ in paramagnetic systems is the separation of such shifts into Fermi contact $\Delta\nu^{\rm con}$ and dipolar $\Delta\nu^{\rm dip}$ contributions. Contact shifts provide a measure of the unpaired electron spin density at the resonating nucleus, whereas dipolar shifts arise from a through-space dipolar interaction between the electronic magnetic moment and the nuclear spin moment which does not vanish in magnetically anisotopic systems. One of the earliest attempts to separate contact and dipolar shifts was made by LaMar, Horrocks, and Allen,[1] who studied the proton magnetic resonance (pmr) spectra of the pseudotetrahedral dihalobis(triarylphosphine)cobalt(II) and -nickel(II) complexes: M(TAP)$_2$X$_2$; M = Co, Ni; X = Br, I. In these systems, the ortho and para phenyl proton resonances are shifted upfield and the meta is shifted downfield. Replacement of a proton by a methyl group results in a resonance shift for the methyl protons opposite in sign to that of the replaced proton. This behavior was attributed to the dominance of the contact interaction owing to the delocalization of unpaired electron spin density in the π systems of the phenyl rings. Significant differences in the shift ratios between the cobalt and nickel systems were, however, observed. It was postulated[1] that this difference in ratios was due to a difference in the dipolar interaction between the two systems. On the basis of the similarity of the shift ratios of the Ni(TPP)$_2$X$_2$ systems (TPP = triphenylphosphine) to those of phenyl rings of nickel complexes of aminotroponeimineates[2,3] where dipolar shifts were not expected, it was suggested[1] that no significant dipolar interaction occurred in the Ni(TAP)$_2$X$_2$ complexes. The shift ratio differences were then accounted for quantitatively in terms of a dipolar shift being present in the Co(TPP)$_2$X$_2$ complexes. This conclusion was somewhat surprising since tetrahedral cobalt(II), with an orbitally nonde-

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