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 $\Delta\nu^{\text{iso}}$ in paramagnetic systems is the separation of such shifts into Fermi contact $\Delta\nu^{\text{con}}$ and dipolar $\Delta\nu^{\text{dip}}$ 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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generate ground state in idealized T_d geometry, becomes magnetically anisotropic only through second-order mixing of the ground level with the split components of the excited states (mainly T_2) *via* spin–orbit coupling, while, on the other hand, the ground state of $Ni(TPP)_2X_2$, an orbitally degenerate T_1 state in idealized T_d, might be expected to retain considerable magnetic anisotropy in its ground multiplet. This is exactly the situation found in octahedral complexes where nickel(II) complexes (A_{2g} ground state in O_h) are found to be nearly magnetically isotropic while cobalt(II) complexes (T_{1g} ground state in O_h) exhibit the highest anisotropies found in the first transition series.

Recently one of us has shown[4] that dipolar shifts may be evaluated directly from the principal molecular susceptibilities of a complex and a knowledge of certain geometric factors (*vide infra*). This approach has been substantiated by independent theoretical work.[5,6] It was of considerable interest, therefore, to obtain magnetic anisotropy data on complexes of the $M(TAP)_2X_2$ type in order to evaluate directly the dipolar shifts in these systems and to check the conclusions reached earlier[1] on the basis of pmr data alone. The triphenylphosphine complexes of the metal chlorides, $M(TPP)_2Cl_2$, were chosen since the cobalt and nickel complexes are isomorphous and the crystal structure of the latter compound is known.[7] Detailed single-crystal electronic spectral data on these complexes are also available.[8,9]

Experimental Section

Principal crystal magnetic anisotropies were measured at room temperature by the critical-torque (flip-angle) method of Krishnan and Bannerjee.[10] The technique, methodology, and apparatus of this method are described in detail elsewhere.[11] Measurements were made on single crystals of $Co(TPP)_2Cl_2$[12] and $Ni(TPP)_2Cl_2$[13] ranging in size from 10 to 42 mg. These crystals were grown by slow evaporation at 80° of 1-butanol solutions formed by mixing solutions containing stoichiometric quantities of metal chloride hexahydrate and triphenylphosphine. Polycrystalline samples were prepared by rapid cooling of such solutions. *Anal.* Calcd for $Co[(C_6H_5)_3P]_2Cl_2$: C, 66.07; H, 4.62. Found: C, 66.13; H, 4.54. Calcd for $Ni[(C_6H_5)_3P]_2Cl_2$: C, 66.09; H, 4.62. Found: C, 66.17; H, 4.61. The single crystals were mounted along the a^*, b, and c crystallographic axes of the monoclinic unit cell on one end of cylindrical Teflon sleeves using Duco cement. The sleeves had previously been treated with refluxing hydrochloric acid to remove ferromagnetic impurities. The crystal orientation was checked by X-ray oscillation photography and the alignment was found to be within 1.5° in every case. The crystals were mounted in the critical-torque apparatus by sliding the Teflon sleeve coaxially over the end of an 8-in. quartz rod (1-mm o.d.) suspended from a ~20-in. length of ~10–15 μ quartz torsion fiber. A Varian 4-in. electromagnet was then moved into place *via* a small railway so that the crystal hung between the pole pieces (pole faces tapered to 3 in., 2³/₈ in. gap). Measurements were made, as described in detail elsewhere,[11] with the field on by turning the torsion head, to which the upper end of the quartz fiber was attached, until "flipping" occurred. The critical angle α_{cr} through which the torsion head had to be turned is directly related to the anisotropy in the plane perpendicular to the suspension. In the present series of experiments α_{cr} ranged from 8.5 to 58.5 revolutions. For each mounting, measurements were made on two different crystals of each substance. The fiber was calibrated with two different crystals of tetragonal nickel sulfate hexahydrate which has a molar anisotropy (a or b axis mounting) of 80.8 VVk/mol at 27°[14] (1 Van Vleck (VVk) $\equiv 10^{-6}$ cgsu; see ref 11).

Bulk powder susceptibilities were determined by the Gouy method at four different field strengths. These measurements were calibrated with mercuric tetrathiocyanatocobaltate[15] and checked with tris(ethylenediamine)nickel(II) thiosulfate.[16] All reported measurements are corrected to 25°. The results for the principal susceptibilities are believed to be accurate to within ±4%.

Results

The principal crystal anisotropies, average susceptibilities, and derived principal molecular susceptibilities at 25° are listed in Table I. The relationship between the crystal and molecular axes obtained from the crystal structure[7,17] is given in Figure 1. The metal atoms occupy special positions of C_2 site symmetry with the b axis of the monoclinic cell coincident with the C_2 axis of the complex, here designated z. The metal and

TABLE I
PRINCIPAL CRYSTAL ANISOTROPIES AND MOLECULAR SUSCEPTIBILITIES AT 25°[a,b]

	$\Delta\chi_b$	$\Delta\chi_c$	$\Delta\chi_{a^*}$	$\bar{\chi}^c$	χ_x	χ_y	χ_z
$Co(TPP)_2Cl_2$	1872 (c)[d]	105 (b)	1753 (c)	8357	9568	7696	7807
$Ni(TPP)_2Cl_2$	490 (a^*)	71 (a^*)	412 (b)	4650	4348	4838	4767

[a] In VVk/mol (1 VVk = 10^{-6} cgsu). [b] The subscripts a^*, b, and c refer to the vertical crystallographic axes of suspension; the subscripts x, y, and z refer to the molecular coordinate axes (see Figure 2). [c] Includes a diamagnetic correction of −428 VVk/mol. [d] The crystallographic axis most nearly parallel to the magnetic field in the absence of any fiber torque is given in parentheses.

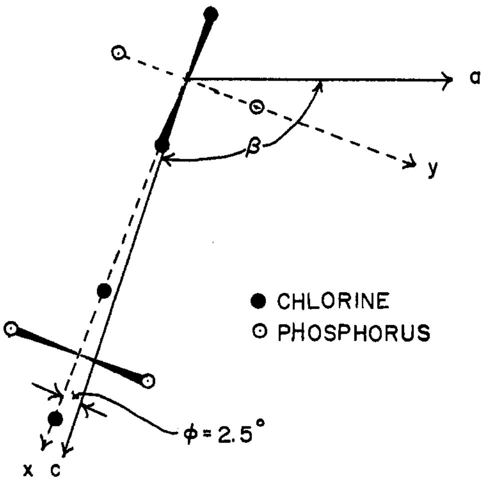

Figure 1.—Relationship between the crystallographic and molecular axes showing the two molecules of $M(TPP)_2Cl_2$ in the unit cell. The view is down the b axis of the monoclinic cell which is coincident with the $C_2 = z$ axis of the complex.

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[17] An $h0l$ Weissenberg photograph showed the β angle to be in agreement with that given in ref 7 rather than the slightly different value quoted in ref 9.

coordinated ligand atoms form units of very nearly C_{2v} symmetry (the P–M–P and Cl–M–Cl planes make an angle of 89.1°). This idealized symmetry will be assumed here with the molecular x axis lying in the Cl–M–Cl plane and perpendicular to the z axis. The x axis makes an angle φ of 2.5° with the c axis. The molecular y axis completes the orthogonal coordinate system and very nearly lies in the P–M–P plane. This coordinate system conforms to that used by Fereday, *et al.*,[9] but differs from that used by LaMar, *et al.*,[1] in that the x and y axes are interchanged. The principal molecular susceptibilities χ_x, χ_y, χ_z were determined by solving eq 1 simultaneously employing (1a), (1d), and either

$$|\chi_x - \chi_y| = \Delta\chi_b \tag{1a}$$

$$|\chi_y \sin^2 \varphi + \chi_x \cos^2 \varphi - \chi_z| = \Delta\chi_{a^*} \tag{1b}$$

$$|\chi_y \cos^2 \varphi + \chi_x \sin^2 \varphi - \chi_z| = \Delta\chi_c \tag{1c}$$

$${}^1/_3(\chi_x + \chi_y + \chi_z) = \bar{\chi} \tag{1d}$$

(1b) or (1c). The results for the two solutions in each case were in virtually perfect agreement. Some confidence can be assigned to the anisotropy measurements since only two are linearly independent and the third provides a check.

Analysis and Discussion

Dipolar Shift Equations.—Equations, valid for ligand fields of axial symmetry, have been given[4] for dipolar shifts in terms of susceptibility anisotropy. For the present case of rhombic symmetry, one has

$$\frac{\Delta\nu^{\text{dip}}}{\mu} = -DG(\theta,r) - D'G'(\theta,\Omega,r) \tag{2}$$

where for $1/\tau_{\text{m}} \ll$ ZAE (Jesson's case a[18])

$$D = \frac{1}{3N}\left[\chi_z - \frac{\chi_x}{2} - \frac{\chi_y}{2}\right]; \; D' = \frac{1}{2N}[\chi_x - \chi_y] \tag{3}$$

while for $1/\tau_{\text{m}} \gg$ ZAE (Jesson's case c[18])

$$D = \frac{1}{30N}[6\chi_z - 3\chi_x - 3\chi_y + (\chi_z\chi_x)^{1/2} + (\chi_z\chi_y)^{1/2} - 2(\chi_x\chi_y)^{1/2}]$$

$$D' = \frac{1}{10N}[3\chi_x - 3\chi_y + (\chi_z\chi_x)^{1/2} - (\chi_z\chi_y)^{1/2}] \tag{4}$$

where τ_{m} is the correlation time for tumbling in solution, ZAE is the Zeemann anisotropy energy, and N is Avogadro's number. $G(\theta,r)$ and $G'(\theta,\Omega, r)$ are the geometric factors defined as

$$G(\theta,r) = \left\langle\frac{3\cos^2\theta - 1}{r^3}\right\rangle_{\text{av}} \tag{5}$$

and

$$G'(\theta,\Omega,r) = \left\langle\frac{\sin^2\theta \cos 2\Omega}{r^3}\right\rangle_{\text{av}} \tag{6}$$

where the variables are defined as in Figure 2 and the average is taken over motions rapid on the pmr time scale. For cases in which the ground-state manifold is well separated from all excited levels and the susceptibilities are describable by $\chi_\alpha = Ng_\alpha^2 \beta^2 S(S+1)/3kT$ ($\alpha = x$, y, or z), eq 2 and 3 reduce to the expression[1] for the dipolar shift in terms of g values appropriate to the averaging conditions. Equations 2 and 4, arrived at inductively, also reduce to the appropriate expression in terms of g values.[19]

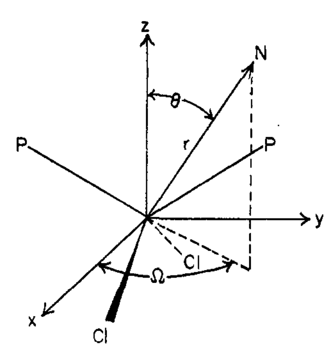

Figure 2.—Relationship between the molecular coordinate axes and the spherical polar coordinates r, θ, and Ω defining the positions of a nucleus N.

Evaluation of Geometric Factors.—In order to calculate dipolar shifts from eq 2–4, it is necessary to have knowledge of the geometric factors. The molecules under consideration are less than ideal in this regard since the position of a given phenyl proton with respect to the metal and the magnetic axes of the complex is dependent upon internal rotations about both the M–P and P–C bonds. In their original study LaMar, *et al.*,[1] employed the "free rotation" model wherein $G(\theta,r)$ and $G'(\theta,\Omega,r)$ were calculated as converged averages of 1° increments of both rotations. Accurate structural parameters were unavailable at that time and only the ratios of the geometric factors for the various protons were of interest in the absence of magnetic anisotropy data.

Evidence that the "free-rotation" model may not provide an entirely realistic assessment of geometric factors is supplied by the numerous X-ray structures of TPP complexes which are now in the literature. The free-rotation model weights equally all angles of "pitch" of the phenyl rings with respect to the "C_3" axis of TPP. This pitch is described by the parameter Γ for rotation about the P–C bond axes with $\Gamma = 0°$ corresponding to the phenyl plane being parallel to the C_3 axis and $\Gamma = 90°$ corresponding to an "inverted-umbrella" conformation. Figure 3 shows a bar graph of the number of phenyl groups exhibiting particular pitch angles, taken in 5° intervals, obtained from 26 structures in the literature.[7,20] There is a clear bias toward inter-

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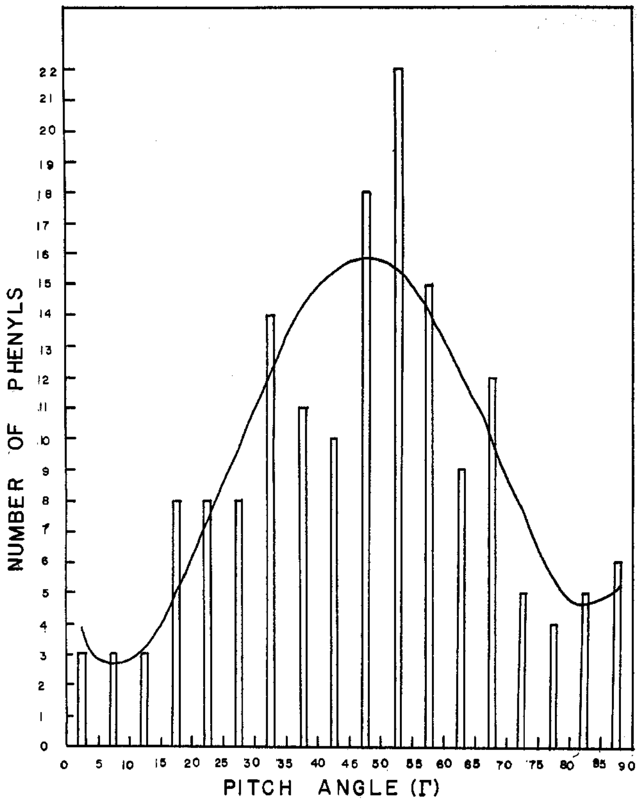

Figure 3.—Bar graph showing the number of phenyl groups in TPP complexes having pitch angles Γ in 5° intervals, taken from solid-state X-ray structural data; see text. The solid curve represents a least-squares fit to a fourth-order polynomial.

TABLE II

CALCULATED GEOMETRIC FACTORS (Å^{-3})[a]

	Ortho		Meta		Para	
	10^4G (θ,r)	$10^3G'$ (θ,Ω,r)	10^5G (θ,r)	$10^4G'$ (θ,Ω,r)	10^5G (θ,r)	$10^4G'$ (θ,Ω,r)
Weighted model	−2.06	−1.43	−5.30	−3.60	−4.44	−3.53
Free-rotation model	−1.24	−1.02	−3.85	−2.99	−3.31	−3.07

[a] The structural parameters used in the calculation, taken from ref 20b, were as follows: bond distances: M–P, 2.333 Å; P–C, 1.824 Å; C–C, 1.40 Å; C–H, 1.08 Å; bond angles: P–M–P, 110.4°; M–P–C, 113.7°; all phenyl angles, 120.0°.

mediate values with the peak in the 50–55° range. The falloff near 0° occurs owing to interference of the ortho protons with the moiety to which TPP is coordinated. The decrease in frequency of values near 90° represents interphenyl interactions. The free-rotation model considers neither of these effects. In order to account for these biases which can be expected to operate in the present $M(TPP)_2Cl_2$ complexes, geometric factors were calculated for each proton at every 5° in Γ, averaging over a 360° rotation about the M–P bond axis (ψ rotation) until convergence of the individual geometric factors representing a particular Γ value was achieved ($\Delta\psi = 5°$). Then, for each Γ value, the geometric factors for the two ortho and two meta protons were averaged. These resulting averages were then weighted according to the curve obtained from a least-squares fit of the distribution in Figure 3 to a fourth-order polynomial as shown. These final "weighted-model" geometric factors are listed in Table II along with those obtained from the free-rotation model for comparison. The structural parameters used in the calculations were taken from the crystal structure[20b] of $Ni(TPP)_2Br_2$ and are indicated in the footnote to Table II. Several features are evident. The $G'(\theta,\Omega,r)$ averages are roughly an order of magnitude larger than the $G(\theta,r)$ values. The geometric factors calculated from the free-rotation model are in every case slightly less in absolute magnitude than those computed from the weighted model. For the weighted model the ratios ortho:meta:para are, for $G(\theta,r)$, 1.00:0.26:0.22 and, for $G'(\theta,\Omega,r)$, 1.00:0.25:0.25, while for the free-rotation model the corresponding ratios are, for $G(\theta,r)$, 1.00:0.31:0.27 and, for $G'(\theta,\Omega,r)$, 1.00:0.29:0.30. The para:ortho ratios differ considerably from those found earlier[1] using the free-rotation model and somewhat different structural parameters. In the present case, geometric factors represent fairly slowly converging averages of numbers rapidly changing in both magnitude and sign as a function of internal rotations. For instance, at a pitch angle of $\Gamma = 50°$, $G'(\theta,\Omega,r)$ for the ortho protons varies between -2.12×10^{-2} and $+1.38 \times 10^{-2}$ as a function of rotation about the M–P bond axis. Thus the final averages are quite sensitive to any biases or preferred conformations built into the model. At this point an elaborate calculation was performed in which certain orientations were excluded owing to the expected repulsive van der Waals interactions between the ortho protons and the other phosphorus and the two chlorine atoms coordinated to the metal. This had the effect of significantly increasing the absolute magnitudes of the calculated averages. Owing to the additional unknown parameters involved and the problem of determining an appropriate weighting scheme, further efforts along these lines were dropped. One must conclude that while the geometric factors are considerably uncertain, they are probably good to within a factor of 2 with the likelihood that the calculated averages (weighted model) are less in absolute magnitude than the true values.

Evaluation of Dipolar Shifts.—Inspection of eq 2–4 reveals that the dipolar shifts will be roughly proportional to the sum of the products of the axial anisotropy, $\Delta\chi_{ax} = \chi_z - {}^1/_2(\chi_x + \chi_y)$, with $G(\theta,r)$ and the equatorial anisotropy, $\Delta\chi_{eq} = \chi_x - \chi_y$, with $G'(\theta, \Omega, r)$. For the compounds of interest one has the following data: $Co(TPP)_2Cl_2$, $\Delta\chi_{ax} = -825$, $\Delta\chi_{eq} = +1872$ VVk/mol; $Ni(TPP)_2Cl_2$, $\Delta\chi_{ax} = +174$, $\Delta\chi_{eq} = -490$ VVk/mol (see Table I). Qualitatively, since $|\Delta\chi_{eq}|$ exceeds $|\Delta\chi_{ax}|$ by more than a factor of 2 and $G'(\theta,\Omega,r)$ dominates $G(\theta,r)$ by an even greater factor (see Table II), the equatorial anisotropy is seen to determine the dipolar shifts. Furthermore the shifts are expected to be greater for $Co(TPP)_2Cl_2$ than for $Ni(TPP)_2Cl_2$ and of opposite sign. A quantitative evaluation of dipolar shifts using eq 2–4 is given in Table III. The qualitative expectations discussed above are borne out by the calculations. The dipolar shifts are opposite in sign for the cobalt and nickel complexes and the absolute magnitudes in the former case are approximately 4 times those of the latter. The only significant shifts arise from the term involving $\Delta\chi_{eq}$ and $G'(\theta,\Omega,r)$, the shifts from the term involving $\Delta\chi_{ax}$ and $G(\theta,r)$ being almost negligible and of opposite sign. This possibility was considered but thought to be less likely in the earlier study.[1]

Since the original[1] separation of contact and dipolar contributions was based on shift *ratios*, these will now

TABLE III

ISOTROPIC, DIPOLAR, AND CONTACT SHIFTS AT 25°[a]

		$G(\theta,r)$[b]	$G'(\theta,\Omega,r)$[b]	$\Delta\nu^{\mathrm{dip}}$ [c]	$\Delta\nu^{\mathrm{iso}}$ [d]	$\Delta\nu^{\mathrm{con}}$ [e]
			$Co(TPP)_2Cl_2$			
Eq 3[f]	Ortho	−0.09	+2.22	+2.13	+10.35[h]	+8.22
	Meta	−0.02	+0.56	+0.54	−8.08[h]	−8.62
	Para	−0.02	+0.55	+0.53	+11.51[h]	+10.98
Eq 4[g]	Ortho	−0.07	+1.54	+1.47		+8.88
	Meta	−0.02	+0.39	+0.37		−8.45
	Para	−0.01	+0.38	+0.37		+11.14
			$Ni(TPP)_2Cl_2$			
Eq 3[f]	Ortho	+0.02	−0.58	−0.56	+6.38[i]	+6.94
	Meta	+0.01	−0.15	−0.14	−8.03[i]	−7.89
	Para	0.00	−0.14	−0.14	+11.16[i]	+11.30
Eq 4[g]	Ortho	+0.01	−0.41	−0.40		+6.78
	Meta	+0.00	−0.10	−0.10		−7.93
	Para	+0.00	−0.10	−0.10		+11.26

[a] In ppm. [b] Contribution to the dipolar shift from the term involving the geometric factor indicated. [c] Dipolar shift calculated from susceptibility anisotropy data using the weighted-model geometric factors. [d] Observed isotropic shifts. [e] Contact shifts obtained from the relation $\Delta\nu^{\mathrm{iso}} = \Delta\nu^{\mathrm{con}} + \Delta\nu^{\mathrm{dip}}$. [f] Averaging conditions: $1/\tau \ll$ ZAE. [g] Averaging conditions: $1/\tau \gg$ ZAE. [h] G. N. LaMar, Ph.D. Thesis, Princeton University, 1964. [i] E. A. LaLancette and D. R. Eaton, *J. Amer. Chem. Soc.*, **86**, 5145 (1964).

TABLE IV

SHIFT RATIOS FOR PROTONS OF $M(TPP)_2Cl_2$ COMPLEXES

	Obsd isotropic shifts		Contact shifts (eq 3)		Contact shifts (eq 4)	
	Ni	Co	Ni	Co	Ni	Co
$\Delta\nu_{\mathrm{para}}/\Delta\nu_{\mathrm{ortho}}$	1.75	1.11	1.63	1.34	1.66	1.26
$\Delta\nu_{\mathrm{meta}}/\Delta\nu_{\mathrm{ortho}}$	−1.26	−0.78	−1.14	−1.05	−1.17	−0.95

be considered. It is seen from Table IV that the ratios of the *observed* isotropic shifts are considerably different for the cobalt and nickel systems. If the mechanism of spin delocalization is the same for the two systems, then the *ratios* of the *contact* shifts are expected to be identical. This will be the case if the spin delocalization is determined by the electronic structure of the ligand independent of whether it is coordinated to cobalt(II) or nickel(II). Using the *contact* shifts of Table III, obtained by correction of the observed shifts for the calculated dipolar components, the *contact* shift ratios of Table IV were derived for the two averaging conditions. It is seen that the ratios are brought more closely into agreement, particularly for the conditions appropriate to eq 3. Were the dipolar shifts slightly larger in absolute magnitude, even better agreement would be achieved. Since it is likely that the geometric factors have been underestimated (*vide supra*), the present agreement between the cobalt and nickel contact shift ratios can be considered satisfactory.

Thus it has been demonstrated that the postulate of LaMar, *et al.*,[1] that the difference in observed shift ratios between the cobalt and nickel systems is due to a difference in dipolar shifts between the two systems is entirely consistent with the magnetic anisotropy data for these systems. The major difference from the conclusions arrived at earlier,[1] on the basis of pmr data alone, is that the nickel complex does exhibit *some* dipolar contribution to its isotropic shifts. The lesser magnitude and opposite sign of this contribution accounts for the success of the original analysis.[1]

Magnetic Anisotropy.—Finally, it is appropriate to consider briefly the susceptibility tensors of these molecules. Inspection of Table I reveals that the susceptibility tensors are roughly axial in that $\chi_y \cong \chi_z \neq \chi_x$ for both $Co(TPP)_2Cl_2$ and $Ni(TPP)_2Cl_2$. In this sense it is the x axis which is unique rather than the $C_2 = z$ axis of the C_{2v} complex. The x axis lies in the Cl–M–Cl plane (see Figure 2). Taking, for the moment, $\chi_{\parallel} = \chi_x$ and $\chi_{\perp} = {}^1/_2(\chi_y + \chi_z)$, one has, for $Co(TPP)_2Cl_2$, $\chi_{\parallel} - \chi_{\perp} = +1817$ VVk/mol while, for $Ni(TPP)_2Cl_2$, $\chi_{\parallel} - \chi_{\perp} = -454$ VVk/mol. In terms of a percentage of the average susceptibility $\bar{\chi}$, these anisotropies represent 21.7 and 9.8% for the cobalt and nickel complexes, respectively. These values may be compared to the percentage anisotropies found for the $CoCl_4^{2-}$ anion in Cs_3CoCl_5 (7.8%)[21] and Cs_2CoCl_4 (7.6%)[21] and for $NiCl_4^{2-}$ of $[(C_2H_5)_4N][NiCl_4]$ (15.9%).[22] In the tetrahalometalate anions the lowering of the ligand field symmetry is due only to angular distortions. Much larger low-symmetry components are to be expected in the present $M(TPP)_2Cl_2$ complexes owing to the presence of two dissimilar ligands. Under the small distortions present in the MCl_4^{2-} species, the anisotropies conform to the expectation discussed in the Introduction with $NiCl_4^{2-}$ having the larger anisotropy. As the ligand field distortion is increased, the anisotropy of pseudotetrahedral cobalt(II) complexes is expected to continue to rise since it is proportional to the magnitude of the splitting of the excited T_2 level of T_d. On the other hand, increasing distortion in the nickel(II) case will cause orbitally nondegenerate $^3A_2$, $^3B_1$, and $^3B_2$ levels, arising from the lifting of the degeneracy of the T_1 ground state by the C_{2v} ligand field, to separate to a greater extent. The magnetic properties will then tend to resemble those of a complex with orbitally nondegenerate ground state. The above discussion suggests that, in a phenomenological sense, the major contribution to the ligand field distortion in $M(TPP)_2Cl_2$ complexes is the dissimilarity of the ligands rather than angular distortions. Further discussion of the electronic structures of these complexes will be deferred until completion of ligand field calculations on the ^4F,^4P and ^3F,^3P states in fields of C_{2v} symmetry including spin–orbit coupling.

While magnetic anisotropy data are unavailable for the $M(TPP)_2X_2$ (X = Br, I) compounds which were studied by LaMar, *et al.*,[1] it is quite likely that their magnetic properties will be similar to those of the X = Cl compounds studied here. Considering the relative positions of the ligands in the spectrochemical series,[12] I < Br < Cl ≪ TPP, it is expected that the anisotropy of the cobalt complexes will increase in the order Cl < Br < I, while those of the nickel complexes, which are small to begin with, might decrease slightly in the same order. Thus the present estimate of a net difference in dipolar shift for the ortho protons between the nickel and cobalt complexes of +2.7 ppm (using eq 2 and 3; see Table III), with the latter upfield, is quite consistent with the earlier[1] evaluation of upfield shifts for these resonances in the cobalt systems of +3.5 ppm for X = Br and +4.1 ppm for X = I.

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