The p_z orbital on chlorine is considered to form the Cl–C σ bond. The low value of the ^{35}Cl resonance frequency means that either the Cl–C bond is relatively ionic in the complex, which causes a large N_{p_z} value for chlorine, or that Cl → C π bonding is occurring, which causes N_{p_x} and N_{p_y} to be less than two electrons apiece, or both. If σ-bond ionicity were responsible, then the $CCo_3(CO)_9$ group would have to be a rather strong σ donor. The ^{35}Cl resonance frequency is in the range of that found for $(CH_3)_2CHCl$ and $(CH_3)_3CCl$.[34] Evidence is available which indicates that the $CCo_3(CO)_9$ group is electron withdrawing, however. Therefore, a considerable amount of Cl→C π bonding must be occurring. This π bonding tendency between the R group and the apical carbon is consistent with the fact that the C–R bond is often found to be shorter than a single bond[2] and the fact that ν(C–Cl) in $ClCCo_3(CO)_9$ occurs at a rather high frequency in the infrared spectra (906 cm^{-1}).[35] The NQR data when coupled with the other data available are consistent with a significant amount of π character in the C–Cl bond. A highly ionic σ bond is less consistent with the data available.

The triethylsilyl derivative behaves as more of an electron-withdrawing agent than might be anticipated from its substituent parameter.[28] It was not included as a data point in Figures 2 and 3. More work is needed with substituents having low-lying unfilled energy states before detailed comments can be made about their electronic participation with the cobalt atoms.

In summary, NQR data at both ends of the $RCCo_3(CO)_9$ complex (^{59}Co and ^{35}Cl) indicate a significant amount of delocalization of electron density in the region of the apical carbon atom. This delocalization is responsible for extensive π transmission of electron density between the Co atoms and the substituent group, R.

Registry No. $CH_3OCCo_3(CO)_9$, 41751-68-2; $CH_3C(O)OCCo_3(CO)_9$, 13682-05-8; $CH_3CCo_3(CO)_9$, 13682-04-7; $HCCo_3(CO)_9$, 15664-75-2; $ClCCo_3(CO)_9$, 13682-02-5; $C_6H_5CCo_3(CO)_9$, 13682-03-6; $C_2H_5OC(O)CCo_3(CO)_9$, 19425-32-2; $CF_3CCo_3(CO)_9$, 18433-88-0; $(C_2H_5)_3SiCCo_3(CO)_9$, 64115-67-9; $C_6H_5C(O)CCo_3(CO)_9$, 40730-01-6.

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Proton Chemical Shifts and Diamagnetic Anisotropy in Cobalt(III) Pentaammine Complexes

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Measurements of the diamagnetic susceptibility anisotropy of a single crystal of $[Co(NH_3)_5Cl]Cl_2$ are reported. From these, the susceptibility anisotropy of the $[Co(NH_3)_5Cl]^{2+}$ ions is calculated and correlated with the chemical shift difference between cis and trans protons in aqueous solution. If the point-dipole approximated anisotropic magnetization of the cobalt d electrons is regarded as the origin of the chemical shift difference, then the chemical shift difference calculated from the measured anisotropy is larger than the observed difference by 1.0 ppm. The predicted sign is correct. Even though the calculated and observed shift differences differ, the angular part $(1-3\cos^2\theta)$ of the point-dipole approximation holds well, as shown by proton chemical shift measurements on 12 pentaammines and the hexaammine. This extended series also shows the inadequacy of the correlation of chemical shifts with wavelength of the lowest energy absorption in the optical spectra. It is suggested that the effects which may be responsible for the discrepancy of 1.0 ppm are electric field effects, moments higher than dipoles, significant amplitudes of low-frequency bending vibrations, and uncertainty about the point at which the point dipole should be placed.

In the course of studies of the reactions of cobalt pentaammines, $[Co(NH_3)_5X]^{n+}$ where X is a monodentate ligand, we have accumulated a large number of nuclear magnetic resonance (NMR) data for ^{59}Co, ^{14}N, and ^{1}H nuclei in these complexes. We had noticed that the proton shifts bore no obvious relationship to the rate coefficients for proton exchange (see Table I) and that the shift data strongly implicated the magnetic anisotropy of the metal d electrons as the most

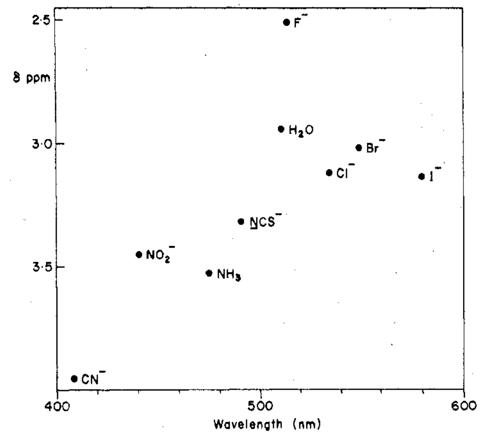

Figure 1. Chemical shift of the trans ammine protons vs. calculated or observed wavelength[13] of the lowest energy optical absorption band maximum ($^1E \leftarrow {}^1A_1$).

important factor determining the shifts. This latter hypothesis has been advanced and tested in a simple way recently by Yoneda and Nakashima.[1] Their model placed the protons at points along each of the five Co–N bond directions and at a distance equal to the Co–H distance, R. The protons were regarded as being sufficiently far removed from the cobalt d electrons that the inverse cubed distance of the kth d electron, r_k^{-3}, could be treated as a constant and removed from the matrix elements of Ramsey's equation[2] (1)

$$\sigma_{\mathrm{av}} = \frac{e^2}{3m}\langle 0|\sum_k r_k{}^{-1}|0\rangle - \frac{e^2}{6m^2}\sum_x^z\sum_n{}'(E_n - E_0)^{-1} \times$$
$$[\langle 0|_k \Sigma l_{xk}|n\rangle\langle n|\sum_k l_{xk} r_k{}^{-3}|0\rangle +$$
$$\langle 0|\sum_k l_{xk} r_k{}^{-3}|n\rangle\langle n|\sum_k l_{xk}|0\rangle] \quad (1)$$

and replaced by R^{-3}. For this idealized geometric model of the complex, this is equivalent to the point-dipole approximation for the d electron magnetization. They established the correlation of chemical shifts with d electron magnetic anisotropy by noting the similar dependence of the latter on the inverse absorption energies arising from one-electron excitations of the ground $t_{2g}{}^6$ configuration split by the tetragonal crystal field. The correlation of chemical shifts with the inverse energy of the absorption $^1E \leftarrow {}^1A_1$ is not nearly as good as those observed for ^{59}Co [3] and ^{17}O [4] and is even worse for the extended series of X ligands we have studied, which includes F^- and I^- (see Figure 1). In a more recent paper in their series, Nakashima, Sakaguchi, and Yoneda[5] consider the theory in greater detail and establish a connection between cobalt chemical shifts and the susceptibilities of the ions. With the assumption that susceptibility anisotropy and proton screening are correlated, they predict proton shifts and thus avoid the unsatisfactory optical correlation. Nakashima has summarized other hypotheses that have been advanced to account for the chemical shifts in such complexes.[6]

It is the purpose of this paper to present measurements of the anisotropic susceptibility of a cobalt pentaammine complex and thus to test the correlation between proton shifts and magnetic anisotropy directly, without using either optical data or cobalt chemical shifts. These last will be discussed in another paper.[7]

Experiments

A convenient direct route to the determination of the anisotropic susceptibility of these complex ions is a measurement of the magnetic anisotropy of a single crystal containing them. The crystal structure must be known, the ligand X and the counteranions should be isotropic, and, ideally, the fourfold axial symmetry of the cation should be preserved by the crystal symmetry. We found no pentaammine which met all these constraints and compromised with $[Co(NH_3)_5Cl]Cl_2$. This has virtually isotropic lattice anions and a coordinated chloride ion of small anisotropy (vide infra), and there is a recent crystal structure.[8] There are no fourfold axes in the crystal, but a valuable feature of the orthorhombic structure, space group *Pnma*, is that cobalt, its coordinated chloride, and three nitrogens lie in a mirror plane parallel to the *ac* plane. This means that the susceptibility tensor of the ion is strictly of rhombic symmetry with one principal axis parallel to the crystal *b* axis and the other two mutually perpendicular axes of indeterminate orientation in the *ac* plane.

It proved extremely difficult to grow good crystals large enough for accurate measurement of the susceptibilities. This was due to almost universal twinning produced by a new crystal seeding on the first and growing with it. This twinning was easily seen under the microscope as misoriented facets of one crystal protruding through one or more facets of an otherwise single crystal. Suspending these on fine quartz fibers parallel to crystal axes in a magnetic field confirmed the twinning; the crystals aligned themselves in the field but not with one axis along the field as required by crystal symmetry.

The method which successfully produced beautifully formed crystals made use of a gel.[9] To a stock solution (15 mL) of $Na_2SiO_3 \cdot 5H_2O$ (72.8 g) and water (225 mL), $HClO_4$ (~11 mL, 3.62 N) was added to adjust pH to ~5. This mixture was diluted to 110 mL, poured into U tubes 22 mm in diameter, and allowed to set overnight in a water bath at 40 °C. One branch of the U tube was filled with 2 N HCl and the other with a 0.2 M solution of $[Co(NH_3)_5H_2O]Cl_3$. The tube was stoppered and left in the water bath (40 °C) until crystals of $[Co(NH_3)_5Cl]Cl_2$ grew in the gel at the bottom. Some twinning was apparent in the largest crystals. A crystal weighing 9.175 mg was selected for detailed examination. Unit cell dimensions of this crystal were measured on a diffractometer and agreed with the published data[8] to within 0.01 Å.

The magnetic anisotropy was measured at 22 °C by the Kirshnan critical torque method[10] using apparatus described in detail elsewhere.[11] Large single crystals of 1,3,5-triphenylbenzene were used to calibrate torsion fibers. $\Delta\chi_b$ for these crystals was taken as 174×10^{-6} cm^3 mol^{-1}.[10]

NMR spectra were recorded on a Varian HA-100 spectrometer at 32 ± 1 °C. Chemical shifts are referred to sodium 3-(trimethylsilyl)propanesulfonate as internal reference.

The measured molar susceptibility anisotropies of the crystal are

$$\left.\begin{aligned} \chi_a - \chi_b &= -13.5 \pm 0.1 \\ \chi_b - \chi_c &= +6.4 \pm 0.1 \\ \chi_c - \chi_a &= +7.0 \pm 0.1 \end{aligned}\right\} \times 10^{-6}\ \mathrm{cm^3\ mol^{-1}} \quad \begin{aligned} (2) \\ (3) \\ (4) \end{aligned}$$

Since three independent measurements were made, the fact that the sum of the anisotropies is zero constitutes an excellent check on the experiment.

In principle, these results, together with a measurement of the average susceptibility, $^1/_3(\chi_a + \chi_b + \chi_c)$, allow the three principal susceptibility axes of $[Co(NH_3)_5Cl]Cl_2$ in the crystal to be determined, given the transformation which relates its susceptibility tensor axes to those of the crystal. However, because one principal axis of the molecule in the *ac* plane is not necessarily parallel to the Co–Cl bond, we do not know this transformation. But even if we assumed that the diamagnetic anisotropy of $[Co(NH_3)_5Cl]Cl_2$ was determined primarily by the intracation crystal field, so that the transformation angle, α, was close to the angle between the Co–Cl bond and the crystal *a* axis (40.4°[12]), then no reliability could be attached to the molecular anisotropy so calculated. This can be shown as follows. Let K_1 and K_3 be the molecular susceptibilities in the *ac* plane, K_2 that along the *b* axis, and let α be the angle between K_1 and the crystal *a* axis. Then

$$\chi_a = K_1 \cos^2\alpha + K_3 \sin^2\alpha \quad (5)$$

$$\chi_b = K_2 \quad (6)$$

$$\chi_c = K_1 \sin^2\alpha + K_3 \cos^2\alpha \quad (7)$$

Subtraction of eq 7 from eq 5 gives

$$\chi_c - \chi_a = (K_1 - K_3)(1 - 2\cos^2\alpha) \qquad (8)$$

Then, by partial differentiation, the error in the anisotropy, $\delta(K_1 - K_3)$, is related to the errors in α and $\delta\alpha$ and in the crystal anisotropy $\delta(\chi_c - \chi_a)$, according to eq 9:

$$\delta(K_1 - K_3) = -\frac{4\sin\alpha\cos\alpha}{(1 - 2\cos^2\alpha)^2}(\chi_c - \chi_a)\delta\alpha + \frac{1}{(1 - 2\cos^2\alpha)}\delta(\chi_c - \chi_a) \qquad (9)$$

Since α is close to 45°, the denominators are small. In fact, the angular error dominates and an error in α of only 0.1° at $\alpha = 40°$ would contribute an error of $\pm 45 \times 10^{-6}$ cm^3 mol^{-1} to the anisotropy $(K_1 - K_3)$.

We therefore use the following procedure to get $(K_1 - K_3)$. If we assume that the $[Co(NH_3)_5Cl]Cl_2$ anisotropy is determined entirely by the *intra*cation crystal field and that the susceptibilities K_2 and K_3 are identical, then

$$K_1 - K_2 = K_1 - K_3 = (K_\parallel - K_\perp) = (\chi_a - \chi_b) - (\chi_b - \chi_c) = -(19.9 \pm 0.2) \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1} \qquad (10)$$

Retaining these assumptions, we can then calculate α from eq 8 to be 34.7 ± 0.2°. The difference between this angle and the Co–Cl direction is due to the absence of strict, fourfold cation symmetry, to crystal fields from neighboring ions, and to any anisotropy in the lattice chloride ions.

Before assigning the value of $-(19.9 \pm 0.2) \times 10^{-6}$ cm^3 mol^{-1} to be the value appropriate to the cation in aqueous solution, it remains to investigate possible contamination by paramagnetic Co(II) species and to ask whether the crystal field in the liquid state is significantly different from that in the solid, for it is this crystal field which determines the anisotropy in the susceptibility. On this question, we note that the cis Co–N distances in the *ac* plane are 1.960 ± 0.006 and 1.981 ± 0.007 Å compared with 1.962 ± 0.004 Å along the *b* axis. For this difference to be a significant cause of anisotropy in the cis ammonia plane, it would have to induce a splitting of the C_{4v} ^1E term which was a significant fraction of the $^1A_2$, ^1E splitting of about 2600 cm^{-1}.[13] We know of no theoretical or experimental evidence for this in the strong field d^6 configuration, although such small splittings would be difficult to resolve experimentally. In support we note that the $^1A_2 \leftarrow {}^1A_1$ and $^1E \leftarrow {}^1A_1$ absorption energies for *trans*-$[Co(en)_2Cl_2]ClO_4$ in the solid state[14] are similar to those observed in aqueous solution.[13]

Cobalt(III) is thermodynamically unstable with respect to cobalt(II) under the crystal growing conditions used and only the irreversibility of the cobalt(II), cobalt(III) couple prevents gross contamination of the crystals with such strongly anisotropic species. We nevertheless checked this by low-temperature EPR. At 4.2 K, the crystal for which the anisotropy in the susceptibility was measured had weak signals with the characteristic $^{59}Co^{2+}$ nuclear hyperfine structure. We estimated the ratio of Co(II) to Co(III) to be 5 ppm by comparison of signal strengths from a known amount of Co^{2+} in a single crystal of MgO placed next to the $[Co(NH_3)_5Cl]Cl_2$ crystal in the cavity. The signals from the $[Co(NH_3)_5Cl]Cl_2$ crystal were too weak for analysis of the spin Hamiltonian; however, maximum anisotropy was found in the *ac* plane and corresponded to minimum and maximum *g* values of 3.1 and 4.8, occurring respectively at 26 and 64° on either side of the crystal *a* axis. Combining these figures with the concentration estimate and assuming a value for the second-order contribution of the other Kramers doublets to the susceptibility anisotropy to be as large as the calculated, first-order, Zeeman contribution, we get a maximum contribution to the anisotropy in the *ac* plane of 0.02×10^{-6} cm^3 mol^{-1}. At room temperature, the upper Kramers doublet may be populated, but necessarily at the expense of the ground doublet. Even if the anisotropy from such populated upper doublets was double that from the ground doublet, it is clear that the low level of Co(II) ensures that anisotropy from such species can be ignored.

Discussion

How does this diamagnetic anisotropy compare with that predicted from the proton chemical shifts for ammonia cis and trans to bound chloride ion in $[Co(NH_3)_5Cl]Cl_2$? McConnell[15] has quantitatively developed Ramsey's equation to facilitate the calculation of nuclear screening (particularly of protons) caused by anisotropic magnetization in remote groups. His theory requires, inter alios, that the electrons in the group "move in molecular orbitals which have essentially zero amplitude within, say, one bond length of" the proton. For the electrons in the group, which consists of the six d electrons in our case, r_k^{-3} is expanded as a series in increasing powers of r_k/R, where R is the cobalt proton distance and the first nonzero terms are retained. These are terms in R^{-3} which, when averaged for an axially symmetric group in a molecule tumbling in solution, reduce to the familiar point-dipole expression

$$\sigma = (K_\parallel - K_\perp)\langle 1 - 3\cos^2\theta\rangle_{av}/3R^3N \qquad (11)$$

where θ is the polar angle of the proton measured from the cobalt nucleus as origin. It is necessary to retain the additional average to allow for the internal molecular motion, e.g., of the cis ammonia ligands, which throughout this work we assume to be rotating freely about the Co–N bond. The free rotation of the trans ammonia can be ignored since this rotation axis corresponds with the fourfold axis. Taking the distances and angles from the crystal structure,[8] the Co–N–H angle to be 110° and a nitrogen to proton distance of 1.02 Å,[16] we get

$$\delta_{cis}{}^{H} - \delta_{trans}{}^{H} = -0.78(K_\parallel - K_\perp) \times 10^6/NR^3 \quad \text{ppm} \qquad (12)$$

Substitution for the experimentally observed $(K_\parallel - K_\perp)$ gives a chemical shift difference *which is 1.0 ppm larger than that observed.* We now consider other effects which might contribute to this discrepancy of 1.0 ppm.

Electric Field Effects.[17] Electric field effect discrimination of cis and trans ammonia protons could contribute to the chemical shift difference. Because of the similar geometric relationship of the cobalt to the cis and trans protons, any electric charge on the cobalt atom would not discriminate between them. However, charge on the bound Cl$^-$ might. Using the field effect coefficient given in ref 18 and the known cation geometry, we calculate that for half a negative charge placed at the bound Cl$^-$ position the cis proton resonance is moved to high field by 0.45 ppm and the trans resonance to high field by 0.25 ppm. The half charge is a rough estimate based on the Pauling electroneutrality principle[19] as demonstrated by diffraction studies of $[Co(NH_3)_6][Co(CN)_6]$[20] and on the electric field gradient at the coordinated Cl$^-$ nucleus in *trans*-$[Co(en)_2Cl_2]Cl\cdot HCl\cdot 4H_2O$[21] which indicates substantial departure from ionic toward covalent character. These electric field effect shifts are therefore in such a sense to account for part of the discrepancy, reducing it to 0.8 ppm. Against this argument in favor of electric field effects, we note that the weighted chemical shift $({}^2/_3\delta_{cis} + {}^1/_3\delta_{trans}$, vide infra) for neutral ligand complexes should be to low field of those for anionic ligands. The figures in the table show no such discrimination.

Chloride Ion Magnetic Anisotropy. The electron density of the bound Cl$^-$ ion is axially symmetric and could therefore contribute to the cis–trans shielding difference by magnetic anisotropy effects. The anisotropy of the Cl$^-$ electron density is difficult to estimate; even for the better characterized C–Cl bond, literature values for its anisotropy vary considerably. If for the complex we overestimate it to be -7×10^{-6} cm^3 mol^{-1}, that is, one-third of the average susceptibility of a chlorine atom,[23] then using a point-dipole model, we calculate a discrimination of 0.05 ppm between cis and trans protons. There is strong evidence that this is an overestimate and that electric field effects are more important than magnetic anisotropy effects for chlorine.[24] This effect is again too small to explain away the discrepancy, although it is in the sense required to account for a small part of it. The lattice chloride

Table I. Proton Chemical Shifts of $[Co(NH_3)_5X]^{n+}$ Ions in 0.01 M DCl or $DClO_4$ Solutions at 32 ± 1 °C in Parts per Million from Internal Sodium (3-Trimethylsilyl)propanesulfonate and Rate Coefficients for Proton Exchange[22] at 34 °C

$[Co(NH_3)_5X]^{n+}$ X (anion/acid)	Chemical shifts		$^1/_3(\delta_{trans} + 2\delta_{cis})$	Rate coeff, $M^{-1}\,s^{-1}$	
	δ_{trans}	δ_{cis}		Trans	Cis
CN^- ($CH_3SO_3^-$/DCl)	3.96	3.05	3.35	4.9×10^3	8.1×10^4
SCN^- (Cl^-/DCl)	3.64	3.54	3.57		
NH_3 ($CH_3SO_3^-$/$DClO_4$)	3.53	3.53	3.53		
NO_2^- ($CH_3SO_3^-$/DCl)	3.45	3.45	3.45	1.2×10^5	1.2×10^5
NCS^- ($CH_3SO_3^-$/$DClO_4$)	3.32	3.77	3.62	2.0×10^6	9.2×10^4
N_3^- (ClO_4^-/$DClO_4$)	3.26	3.41	3.36		
I^- (ClO_4^-/DCl)	3.13	3.50	3.38		
Cl^- (ClO_4^-/$DClO_4$)	3.12	3.75	3.57	$\sim 9 \times 10^5$	1.9×10^4
Br^- (ClO_4^-/DCl)	3.02	3.62	3.42		
OH_2 (ClO_4^-/DCl)	2.93	3.93	3.60		
$O_2CNH_2^-$ (ClO_4^-/$DClO_4$)	2.88	3.87	3.54	4.0×10^5	2.6×10^4
$O_2CCH_3^-$ (Cl^-/$DClO_4$)	2.77	3.87	3.50	3.5×10^5	1.3×10^4
F^- (NO_3^-/$DClO_4$)	2.51	3.90	3.44	1.5×10^6	3.2×10^4

ions are not necessarily isotropic and the assumption that the whole of the diamagnetic anisotropy measured for the molecular unit in the crystal is due to the cation alone may be in error. Whether any such lattice anion anisotropy should be added to or subtracted from the cation anisotropy has not been determined. We have been unable to detect any nuclear quadrupole resonances for ^{35}Cl in these crystals. Such studies in the presence of a small magnetic field could elucidate this point. Even though there are two lattice anions per cation, this effect can be expected to be small since the electric field gradient evidence[21] from *trans*-$[Co(en)_2Cl_2]Cl\cdot HCl\cdot 4H_2O$ shows that lattice Cl^- ions have considerably less anisotropic electron distributions than coordinated chloride ion.

Medium Effects. There is no doubt that medium effects also contribute. The spectra of the bromo- and chloropentaammine perchlorates in dimethyl sulfoxide show the chemical shift difference between cis and trans protons to be enhanced by 0.14 and 0.09 ppm, respectively, over the differences in aqueous solution. Further, our chemical shift differences in Me_2SO are greater than those published for these two compounds[1] by 0.09 and 0.12 ppm, respectively. These different values are probably a reflection of other medium effects such as concentration, counteranions, or temperature. They are still not large enough effects in the present context.

Molecular Vibrations. Finally, the geometry of the cation taken from the structure data[8,12] is an idealization. The atomic coordinates we have used are the centers of the thermal ellipsoids in the solid. In solution, the amplitudes of the low-frequency N–Co–N and N–Co–Cl bending vibrations will be larger and will tend to place the protons more away from $\theta = 0$ and 90°, thus reducing the effect of the anisotropy. The average in eq 11 should consider these internal motions as well as ammonia rotations. If the low-frequency bending vibrations are significant, we would expect to see the cis–trans chemical shift difference increase with decreasing temperature.

Concluding Remarks

In spite of the fact that the magnitude part of the point-dipole approximation appears to have failed, the evidence is strong that the angular part $(1 - 3\cos^2\theta)$ still holds. It will be noted from the table that $(\delta_{trans} + 2\delta_{cis})/3$ is a constant to good approximation. (That the relative coefficients of δ_{trans} and δ_{cis} are 1 and 2 in spite of the protons being off the parallel and perpendicular axes is a fortuitous consequence of the assumption of free NH_3 rotation and of the fact that $\langle\cos^2\theta\rangle$ is half.) Alternatively, the trans protons are chemically shifted twice as far from the weighted mean and in the opposite sense to the cis protons as noted by Nakashima.[6] This would be expected to follow from the point-dipole approximation. The sign is as expected from the measured susceptibility anisotropy. Thus the angular part of the approximation holds, at least at θ near 22.5° (trans) and near 90 ± 22.5° (cis), and near these angles, it is only the magnitude that is in error.

We conclude that the proton chemical shifts in these complexes reflect the anisotropic magnetization of the cobalt d electrons at least in sign and in dependence on the angular term but that the magnitude of the effect has not been satisfactorily accounted for. In these complexes, the protons are distant 2.5 Å from the metal. It is generally felt that at such distances, breakdown of the point-dipole approximation occurs.[25] In the rare earth shift reagents, the approximation works well,[26] but substrate nuclei in this case are usually at least 3 Å distant from the anisotropic center, and the 4f electron radial averages indicate a more compact distribution than for 3d electrons in cobalt.[27] Part of the magnitude difference between calculated and observed shifts may be explained by electric field effects, part by large bending vibrational amplitudes in solution and part by uncertainty in choosing the point at which the anisotropy should be placed —it is not necessarily coincident with the Co nucleus. We have not considered higher moments[28] in the expansion of the anisotropy since there are only two proton positions in these complexes at which the shielding can be measured.

We note as a corollary of this work that if one wants to discuss the proton chemical shifts in terms of aspects of electronic structure other than diamagnetic anisotropy, one should remove the effects of the latter by taking the weighted sum $(2\delta_{cis} + \delta_{trans})$ and not $(4\delta_{cis} + \delta_{trans})$ as has been used before.[29] An informative extension of this work would be a study of susceptibility anisotropy and chemical shift correlations in stereochemically rigid protonated cage-like ligands surrounding (apart from a variable monodentate ligand X) Pd, Pt, Rh, or Ir, where the incidence of spin paramagnetism is very low. The angular variation could be explored away from the two positions in the pentaammines.

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Registry No. $[Co(NH_3)_5Cl]Cl_2$, 13859-51-3; $[Co(NH_3)_5CN]^{2+}$, 19529-81-8; $[Co(NH_3)_5SCN]^{2+}$, 15005-69-3; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(NH_3)_5NO_2]^{2+}$, 14482-68-9; $[Co(NH_3)_5NCS]^{2+}$, 14970-18-4; $[Co(NH_3)_5N_3]^{2+}$, 14403-83-9; $[Co(NH_3)_5I]^{2+}$, 15392-08-2; $[Co(NH_3)_5Cl]^{2+}$, 14970-14-0; $[Co(NH_3)_5Br]^{2+}$, 14970-15-1; $[Co(NH_3)_5OH_2]^{3+}$, 14403-82-8; $[Co(NH_3)_5O_2CNH_2]^{2+}$, 19173-65-0; $[Co(NH_3)_5O_2CCH_3]^{2+}$, 16632-78-3; $[Co(NH_3)_5F]^{2+}$, 15392-06-0.

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Dipolar Magnetic Anisotropy and Anomalous Susceptibility Behavior in $[(CH_3)_3NH]_3Mn_2Br_7$, a Heisenberg Linear-Chain Antiferromagnet

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Magnetic susceptibility measurements between 1.5 and 30 K are reported for a single crystal of $[(CH_3)_3NH]_3Mn_2Br_7$. The results are quite similar to those previously reported for the chloride analogue which was shown to be composed of two different types of Heisenberg linear chains. At the lowest temperatures the present compound, however, exhibits different behavior and appears to lose its one-dimensional character and order antiferromagnetically. A model which includes the effect of dipolar intrachain interactions has been successfully used to describe the anisotropy observed in the paramagnetic state with the resulting intrachain exchange parameters of $J_1/k = -4.5 \pm 0.8$ K and $J_2/k = -0.206 \pm 0.007$ K.

Compounds which display lower dimensional characteristics in their magnetic behavior have attracted much interest of late,[1] primarily because of the availability of model solutions applicable to such systems. In particular, Mn(II) compounds are of special interest since that ion usually exhibits low anisotropy thus leading to magnetic behavior which is Heisenberg-like in nature. To a large extent, recent work has involved three relatively different Mn(II) linear chain compounds: $CsMnCl_3{\cdot}2H_2O$,[2-8] $[(CH_3)_3NH]MnCl_3{\cdot}2H_2O$,[9-11] and $[(CH_3)_4N]MnCl_3$ (TMMC).[12-21] These materials, as well as some of their analogues, consist of infinite chains of mono-, di-, and trihalide-bridged Mn(II) ions, respectively. More recent work[22,23] has resulted in the discovery of a compound, $[(CH_3)_3NH]_3Mn_2Cl_7$ (TTMMC), which has been characterized as containing two different types of magnetically independent linear chains of Mn(II) ions. The structure analysis[23] of this material shows it consists of infinite chains of trihalide-bridged Mn(II) ions (very similar to those found in TMMC) separated by $[(CH_3)_3NH]^+$ cations and $(MnCl_4)^{2-}$ anions. A view of its structure down the chain axis is shown in Figure 1. The magnetic results[22] clearly imply that the $(MnCl_4)^{2-}$ ions interact in linear chains, consistent with the structure which shows close Cl–Cl contacts between the otherwise isolated tetrahedra. The separation of the Mn(II) ions in the chains formed by the tetrahedra is twice the separation of the halide-bridged ions.

The magnitude of the exchange associated with the chains of tetrahedra is roughly 50 times smaller than that found for the TMMC-like chains. Thus, since the contribution to the susceptibility from the TMMC-like chains is quite small, the primary source of the magnetic behavior in the temperature region above 1 K is the magnetic exchange in the chains of tetrahedra, and therefore TTMMC offers an excellent opportunity for studying magnetic effects in a Heisenberg linear-chain system over a temperature region which is large compared to the exchange involved. In particular, TTMMC may provide the first opportunity to study the magnetic heat capacity of a high-spin Heisenberg linear-chain system without having to make large corrections for lattice contributions. However, such measurements would be considerably easier if the intrachain exchange in the chains of tetrahedra were somewhat larger. It is with this idea in mind that the present study, in which the bromide analogue of TTMMC was prepared, was undertaken, since bromide isomorphs of chloride compounds often exhibit greater magnetic exchange.[9] As it turns out, the intrachain exchange in $[(CH_3)_3NH]_3Mn_2Br_7$ (TTMMB) is not significantly different from that of TTMMC, but the magnetic behavior at lowest temperatures is.

Experimental Section

Single crystals of TTMMB were obtained in a manner similar to that used to obtain the TTMMC crystals: an absolute methanolic solution of $(CH_3)_3N{\cdot}HBr$ and $MnBr_2$ was slowly evaporated in a sealed container over a period of 2 years. The needles obtained tend to grow long and thin and become thick only over an extended period of time. They are orange-red and very similar in habit to those of TTMMC, being six-sided in general, although the side faces are not always equally developed. Use of a polarizing microscope showed the needle axis to be a uniaxial axis, as was the case for TTMMC. Thus, although it is possible that TTMMB and TTMMC may not be strictly isomorphic, their gross physical features indicate a degree of similarity sufficient to allow interpretation of the present results in terms of the TTMMC structure. Anal. Calcd for $[(CH_3)_3NH]_3Mn_2Br_7$: C, 12.72; H, 3.56; N, 4.94; Mn, 12.93; Br, 65.84. Found (by Galbraith Laboratories, Inc.): C, 12.54; H, 3.89; N, 4.86; Mn, 12.78; Br 65.74. The agreement is quite satisfactory.

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