$[n/(7-n)]$ for the water–methanol system, and a factor of $\sim$4 for the water–ethanol system, the data do not demand much of the theory.

The trend in values of Q_n with increase in n for the alcohol–water systems is the opposite of that observed in the dimethyl sulfoxide–water system,[6] for which Q_n(cor) increases slightly as n increases. This does not necessarily weaken the argument that the trend in Q_n with n for the alcohol–water systems is caused by steric interactions of alcohol molecules. The coordination of dimethyl sulfoxide with chromium(III) is through the oxygen atom[13] and the methyl group is, therefore, not bonded to the atom to which the chromium is bonded.

Medium effects upon the equilibrium quotients are not appreciable in the water–methanol system, they cause Q_n to increase with Z for the water–ethanol system, and they cause Q_n to decrease with Z for the water–dimethyl sulfoxide system. Where such effects exist, they may be rationalized in terms of preferential outer-sphere interaction between solvated chromium(III) ions and one or the other of the solvent components, as was illustrated in the water–dimethyl sulfoxide system.[6] It is reasonable that preferential outer-sphere interaction would be minimal in the water–methanol system. It seems clear, however, that the magnitude of such medium effects cannot be predicted. Their demonstrated existence in some systems[4,6] does cause concern regarding the conventional treatment of $\bar{n}$ data in which one must assume the absence of such effects.

The value of Q_2 obtained in the present study does not confirm the abnormal value derived in the earlier study based upon $\bar{n}$ data.[3] Values of $\bar{n}$ obtained in the earlier study agree reasonably well with values based upon the equilibrium quotients derived in the present study (see Table I). The disagreement is greatest in the range of $\bar{n} = 0.6$–1.9, with the previously determined values being higher. It is primarily due to this difference that the Q_2 from the earlier study is too high.

[13] C. V. Berney and J. H. Weber, *Inorg. Chem.*, 7, 283 (1968).

Anomalous Temperature Dependence of Isotropic Proton Nuclear Magnetic Resonance Shifts in Paramagnetic Chromium(II) and Cobalt(II) Complexes

Gerd N. La Mar and Gerald R. Van Hecke

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Received November 3, 1969

Abstract: The anomalous temperature dependence of the isotropic shifts of tris Cr(II) and Co(II) complexes with unsymmetrically methyl-substituted *o*-phenanthrolines has been investigated. These complexes exist in solution as statistical mixtures of *cis* and *trans* isomers, which produce four equally intense proton peaks per ligand position. The extent of deviation from Curie behavior is found to depend markedly on ligand position, and also to differ for each of the four peaks from certain ligand protons in the isomer mixture. For the Cr(II) complexes, the anomalous contact shifts appears to result from a temperature-dependent redistribution of unpaired spin between two d orbitals which interact differently with the three nonequivalent ligands in the *trans* isomer. This analysis leads to the assignment of the electronic ground state of the tris chelates as ^{3}E. The applicability of this nmr technique for determining ground states in tris bidentate complexes is discussed. The analysis of the isotropic shifts for the Co(II) complexes reveals that the extent of deviation from Curie behavior for the observed shifts at any ligand position correlates very well with the magnitude of the dipolar contribution to the observed shift. The significantly greater deviation from Curie behavior of the dipolar contribution relative to the contact contribution to the observed shifts is interpreted as arising from a sizable difference in the magnetic anisotropy between the various populated Kramer doublets.

A characteristic of isotropic nmr shifts for paramagnetic transition metal complexes is their strong temperature dependence, which results from the temperature dependence of the spin magnetization on the metal.[1–3] Although all isotropic shifts must approach zero as $T \rightarrow \infty$, the form of the temperature dependence may differ with the origin of the isotropic shift and the particular complex.

The contact shift for a complex possessing an essentially spin-only magnetic moment has been shown to exhibit Curie behavior according to eq 1 where all

$$\left(\frac{\Delta H}{H}\right) = -A\,\frac{\gamma_e}{\gamma_H}\,\frac{g\beta S(S+1)}{3kT} \qquad (1)$$

notations are standard.[1] For complexes with degenerate ground states which possess sizable orbital contributions to the magnetic moments, the net spin magnetization on the metal, as well as on all ligand nuclei, will deviate[2] from simple Curie behavior, usually in the form of a slight curvature to the $(\Delta H/H)$ *vs.* T^{-1} plot. The deviation from Curie behavior must be the same for all ligand contact shifts.[4]

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[1] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 29, 1361 (1958).

[2] R. M. Golding, *Mol. Phys.*, 8, 563 (1964).

[3] J. P. Jesson, *J. Chem. Phys.*, 47, 579 (1967).

[4] R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and A. H. White, *ibid.*, 45, 2688 (1966).

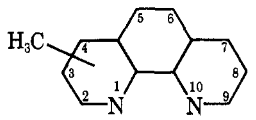
For complexes exhibiting either a fast structural isomerization between a paramagnetic and diamagnetic form (such as some four-coordinate nickel(II) complexes[5]) or a spin equilibrium for a given structure (such as for some octahedral iron(II) systems[4,6]), the contact shifts deviate from Curie behavior owing to the change with temperature of the relative populations of the two (or more) contributing species. The deviations from Curie behavior are again necessarily identical for all ligand contact shifts. In general, it has been concluded that the observed *contact* shifts for a distinct complex are proportional to its magnetic susceptibility,[7] independent of the mechanism which places the unpaired spin into the ligand.

Distorted octahedral complexes with T ground states usually exhibit sizable magnetic anisotropy,[8] so that in addition to contact shifts, the ligand protons experience significant dipolar shifts.[1,3] For a complex with an odd number of unpaired electrons, such as d^7 Co(II), the combination of spin-orbit coupling and an axial distortion splits the 12-fold degenerate $^4T_2$ ground state into six well-separated Kramer doublets. The contact and dipolar shifts for such a system are given by

$$\left(\frac{\Delta H}{H}\right)_i = \sum_{i=1}^{6}[K_i(g_{\parallel} + g_{\perp})(g_{\parallel} - g_{\perp}) + L(g_{\parallel}A_{\parallel}{}^i + 2g_{\perp}A_{\perp}{}^i)] \exp(-E_i/kT)/\sum_i \exp(-E_i/kT) \quad (2)$$

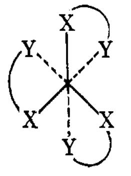
where $L = \beta S'(S' + 1)/(9kT\hbar)$, $K_i = (-\beta^2S'(S' + 1)/9kT)(3 \cos^2 \chi_i - 1)r_i^{-3}$, using standard notation.[3,9] A system which obeys eq 2 will exhibit temperature dependence for its isotropic shifts which results from a Curie behavior of K_i and L for any one Kramer doublet, on which is superimposed the temperature dependence of the relative populations of the six Kramer doublets. For separations of a few hundred reciprocal centimeters between Kramer doublets, as often observed in Co(II) complexes,[3] both the dipolar and contact shifts can deviate from Curie behavior if the g tensors for the various populated doublets differ appreciably.

We will be concerned here with the temperature dependence of the isotropic proton shifts in the Cr(II) and Co(II) tris chelates with unsymmetrically methyl-substituted *o*-phenanthrolines (I). The observed room-temperature isotropic shifts for these chelates have been reported previously,[10] as have the shifts for the complexes with the related symmetric ligands.[11,12]

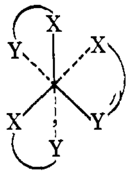

I

In the Cr(II) complexes, the isotropic shifts are primarily contact in origin,[10,11] with π-type spin density dominant at the 3,4,7,8 positions. The 2,9-H shifts probably arise from a combination of some moderate dipolar shifts and negative spin density in the σ system due to exchange polarization between the t_{2g} metal and lone-pair nitrogen electrons.[13] The Co(II) chelates displayed isotropic shifts resulting[10] from both direct σ delocalization and sizable dipolar shifts, with $g_{\parallel} > g_{\perp}$, with the 4,7 positions also experiencing some π spin density.

Complexes with unsymmetrically methyl-substituted ligands displayed[10] four equally intense peaks for some ligand protons, indicating that the *cis* (II) and *trans* (III) isomers are present[14] in statistical amounts. For Cr(II), the π-dominated 4,7 contact shifts were found to be the most sensitive to the reduced molecular symmetry.[10] Significant dipolar contributions to the sizable differences in observed shifts for the 4-CH_3 peaks, for example, can be discounted since this position shows by far the largest spread in the four resonances, while the geometric factor[11] for this position is the smallest in these complexes. Thus for Cr(II) chelates, the sizable difference in contact shifts between the *cis* and *trans* isomers or between the nonequivalent ligands within the *trans* isomer must arise from differences in the *π contact interaction.*



II (*cis*)



III (*trans*)

For the Co(II) compounds with unsymmetrical ligands, the sizable magnetic dissymmetry experienced by all ligand protons was concluded[10] to arise from differences in the *dipolar interaction.*[3] Thus in the *trans* isomer, each of the three nonequivalent ligands experiences different dipolar shifts, which are again different from the dipolar shifts for the three equivalent ligands in the trigonally symmetric *cis* isomer.

Our primary interest here will be the fact that the contact shifts for the Cr(II) complexes and the isotropic shifts for the Co(II) exhibit large deviations from Curie behavior for some ligand protons, though not for others. Furthermore, the isotropic shifts for the four peaks for certain ligand protons show widely differing extents of deviation from Curie behavior.

Experimental Section

The complexes and solutions used in this study are those reported previously.[11] CD_3OD was used for the Cr(II) and Co(II) complexes. The methyl-substituted ligands will be abbreviated by deleting the name of the substituent, using the numbering as shown in I. Thus 4,6-dimethyl-*o*-phenanthroline is designated at 4,6-phen.

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[5] D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Amer. Chem. Soc.*, **85**, 397 (1963); J. E. Parks and R. H. Holm, *Inorg. Chem.*, **7**, 1408 (1968).

[6] J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Amer. Chem. Soc.*, **89**, 3158 (1967).

[7] D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

[8] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

[9] The ~200-Hz (at 100 MHz) 2,9-H line widths for the complexes of interest indicate $T_{1e} \ll \tau_e$, where T_{1e} and τ_c are the electron relaxation time (~10^{-13}) and the molecular tumbling time (10^{-10}), respectively. Thus either case a or c in ref 3 is applicable. Because of the very large dipolar shifts, we feel that case a is much more likely. However, any qualitative use we will make of eq 2 will *not* depend on whether case a or b is in fact applicable.

[10] G. N. La Mar and G. R. Van Hecke, *Inorg Chem.*, in press.

[11] G. N. La Mar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, **91**, 3442 (1969).

[12] D. W. Larsen and A. C. Wahl, *J. Chem. Phys.*, **41**, 908 (1964).

[13] L. E. Orgel, *Discuss. Faraday Soc.*, **26**, 93 (1958); A. D. Levy and L. E. Orgel, *Mol. Phys.*, **3**, 583 (1960).

[14] F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967).

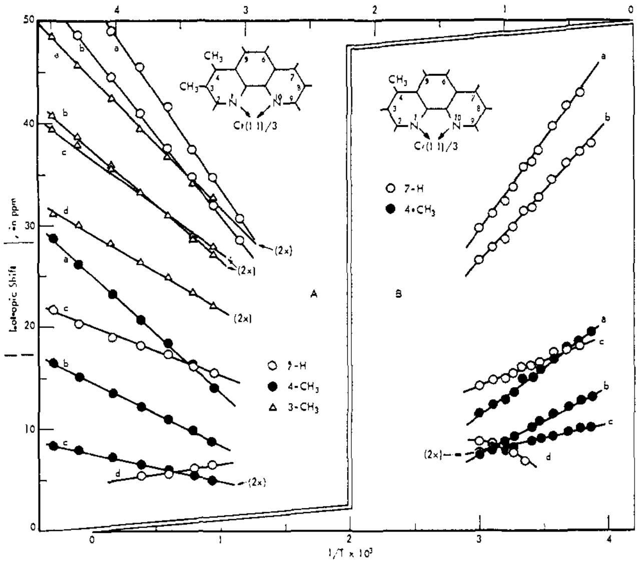

Figure 1. Curie plot for (A) (3,4-phen)$_3$CrCl$_2$ and (B) (4-phen)$_3$-CrCl$_2$ in methanol.

The proton nmr spectra were recorded on a Varian HR-100 spectrometer, employing conventional audio side bands for calibration. The internal reference employed was TMS for the methanol solutions. The temperature was controlled by a Varian V 4343 temperature control unit, which was precalibrated with methanol.

The proton spectra for the 4,7-phen, 5-phen, 4-phen, 3,4-phen, and 4,6-phen complexes with Cr(II) and Co(II) were obtained over a temperature range, ~−50 to +50°, though some Co(II) samples were run to −75°. The nmr traces for the Fe(III) chelates in D$_2$O with 4-phen and 3,4-phen between 0 and 40° were also recorded.

The isotropic shifts are defined as the difference in resonance position between the paramagnetic complex and the diamagnetic iron(II) complex such that an upfield shift is considered positive.

Results and Discussion

Cr(II) Complexes. Previous work has shown[11] that the contact shifts for (phen)$_3$CrCl$_2$ follow the Curie law approximately, this being consistent with its "spin-only" magnetic moment,[15] which has been shown to be constant over the temperature range of our nmr experiments. For unsymmetrically 4-CH$_3$-substituted complexes, the four π-dominated 4-CH$_3$ and 7-H contact shifts do not all follow the Curie law, although they do give approximately straight lines, as illustrated in Figure 1 for (3,4-phen)$_3$Cr^{2+} and (4-phen)$_3$Cr^{2+}. For both these chelates, as well as for (4,6-phen)$_3$CrCl$_2$, of the four widely spaced 7-H peaks, one follows the Curie law approximately (7-H(c)), two contact shifts decrease much *faster* with increasing temperature (7-H(a) and (b)), and one decreases much *slower* with increasing temperature (7-H(d)) than predicted by simple Curie behavior. For the 7-H(d) peak in each of the three chelates, the shift actually *increases* with increasing temperature over the short temperature range that it is resolvable. For the 4-CH$_3$ peaks, one shift again approximated Curie behavior, (4-CH$_3$(c)), two decreased faster than Curie behavior, (4-CH$_3$(a) and (b)), and the fourth resonance possessed too small a shift to determine the temperature dependence with any confidence. The error of the observed position, (±10 Hz), plus the ambiguity of the diamagnetic resonance (±10 Hz), does not yield a slope which deviates from Curie behavior within experimental error. The 3,5,6,8 peaks generally overlapped with the 4-CH$_3$ or with each other over most of the accessible temperature range, so that accurate temperature dependences could not be obtained. However, the shifts for these positions definitely deviated considerably less from Curie behavior than the 4,7 shifts, as exemplified by the 3-CH$_3$ shifts for the 3,4-phen complex, illustrated in Figure 1A. The fact that the 4,7-CH$_3$ shifts follow the Curie law approximately for the symmetric chelate, (4,7-phen)$_3$Cr^{2+} (Figure 2A), indicates that the reduced symmetry of the ligands may be responsible for the anomalous behavior. Thus the different temperature dependences of the four 7-H and 4-CH$_3$ shifts must reflect some differences in the metal–ligand spin delocalization mechanism between the two isomers and even among the three ligands in the *trans* isomer.

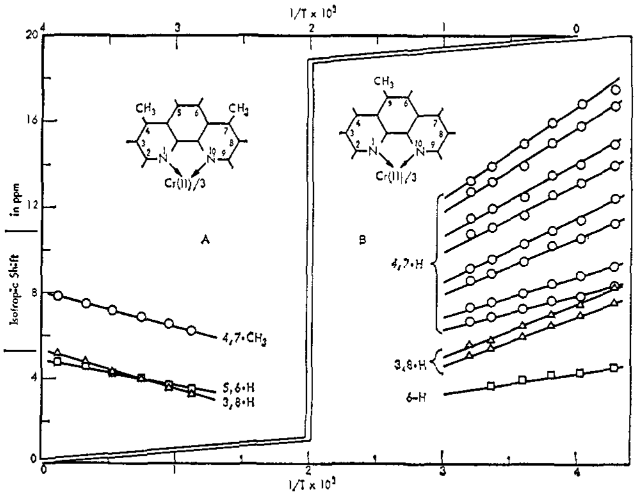

Figure 2. Curie plot for (A) (4-7-phen)$_3$CrCl$_2$ and (B) (5-phen)$_3$-CrCl$_2$ in methanol.

It is possible to account for this anomalous behavior by considering the symmetry properties of the metal d orbitals and the ligand π molecular orbitals of the symmetric ligands, and later evaluate the effect of unsymmetrical substitution. This will be an oversimplified view inasmuch as we should be dealing with the accessible states rather than just the molecular orbitals, but such an analysis should still be valid qualitatively. A more detailed and necessarily tedious analysis does not appear warranted at this time. The π MO's for a symmetric bidentate ligand will be designated φ or ψ, depending whether they remain unchanged or change sign on rotation about the ligand C$_2$ axis. The occupied d orbitals, which in octrahedral symmetry are designated t$_{2g}$, split into e and a$_1$ in trigonal symmetry. The φ MO's may interact with e and a$_1$ metal d orbitals, while the ψ MO's can interact only with metal e orbitals. Based on the coordinate system in Figure 3, the ligand and metal basis orbitals for D$_3$ symmetry have been shown[16] to be those listed in Table I. On each line are listed the proper linear combinations of the d orbitals and the combination of

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[15] A. Earnshaw, L. R. Larkworthy, K. C. Patel, K. S. Patel, R. L. Carlin, and E. G. Terezakis, *J. Chem. Soc.*, *A*, 511 (1966); Y. M. Udachin and M. E. Dyatkina, *J. Struct Chem.* (*USSR*), **8**, 325 (1967) [*Zh. Strukt. Khim.*, **8**, 368 (1967)].

[16] L. E. Orgel, *J. Chem. Soc.*, 3683 (1961).

Table I. Symmetry Orbitals for D_3 Complexes

d orbitals			Ligand π MO's[a]	
			φ's (LAO)	ψ's (HBO)
e	$\frac{1}{\sqrt{2}}(d_{xz} - d_{yz})$	d_1	$\frac{1}{\sqrt{2}}(\varphi_B - \varphi_C)$	$\frac{1}{\sqrt{6}}(2\psi_A - \psi_B - \psi_C)$
	$\frac{1}{\sqrt{6}}(2d_{xy} - d_{xz} - d_{yz})$	d_2	$\frac{1}{\sqrt{6}}(2\varphi_A - \varphi_B - \varphi_C)$	$\frac{1}{\sqrt{2}}(\psi_B - \psi_C)$
a_1	$\frac{1}{\sqrt{3}}(d_{xy} + d_{xz} + d_{yz})$	d_3		$\frac{1}{\sqrt{3}}(\psi_A + \psi_B + \psi_C)$

[a] $\varphi_n = (1/\sqrt{2})(\pi_{n1} - \pi_{n2})$, $\psi_n = (1/\sqrt{2})(\pi_{n1} + \pi_{n2})$, where n = A, B, C in Figure 3. The phen highest bonding (HBO) π MO is ψ; the lowest antibonding (LAO) π MO is φ.

φ and/or ψ ligand MO's which may interact. Metal unpaired spins in the a_1 d orbital will interact equally with each of the three ligands. However, for the e orbitals, one basis function, d_1, interacts twice as much with ligand A as with ligands B and C, while basis orbital d_2 interacts equally with only ligands B and C.[17]

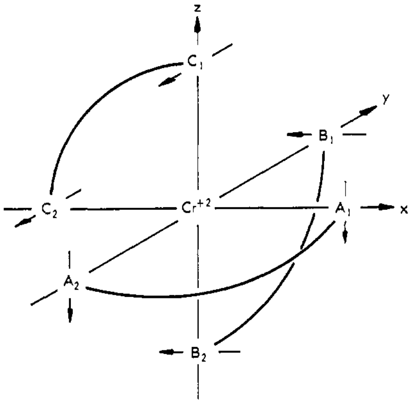

Figure 3. Coordinate system for $(phen)_3Cr^{2+}$.

As long as d_1 and d_2 remain degenerate, a single unpaired spin in the e orbitals will interact equally with all three ligands. Table I illustrates that this is true whether we are considering either the φ or ψ ligand π MO's.

In Figure 4 we follow the metal t_{2g} orbitals as they are subjected first to a trigonal (D_3) distortion from symmetric ligands, and then to a very small rhombic distortion (*trans* isomer for the unsymmetrical ligand). The "spin-only" magnetic moments[16] for these complexes have suggested[11] that the trigonal splitting, δ, in Figure 4 is quite large. On the other hand, the rhombic splitting, ϵ, of the e orbitals in the *trans* isomer is expected to be very slight. In the following discussion, we make the simplifying, though not restrictive, assumption that lowering the D_3 symmetry to C_1 in the *trans* isomer affects primarily the energies of the metal d orbitals, causing them to be slightly split, but leaving the molecular structure and metal–ligand bonds essentially unaltered.

In case (a) in Figure 4, level a_1 is more stable than e in the trigonal field, leading to an $^3A_1$ ground state. Thus in C_1 symmetry, the two components of the split e set, d_1 and d_2, will each contain an unpaired electron over the temperature ranges accessible in our nmr experiments. Thus a simple Curie behavior is predicted for all contact shifts in both *cis* and *trans* isomers for this ground state. This conclusion is independent of the above assumption.

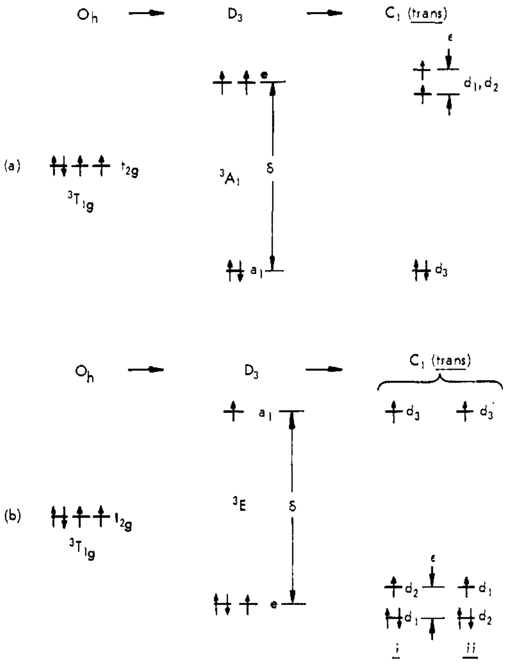

Figure 4. Possible electron occupation of d orbitals in low-spin Cr(II).

Alternatively, if the e level is lower than a_1, as shown in case (b) in Figure 4, the ground state is ^3E. In this configuration, reducing the symmetry to C_1 in the *trans* isomer produces a singly occupied d_3 orbital over all accessible temperatures, while the two split components of e, d_1 and d_2, contain three electrons between them. If $0 < \epsilon \sim kT$, the odd e electron will in fact not reside wholly in the lower energy orbital, but will be found in both d_1 and d_2 in proportions determined by Boltzmann statistics. However, since d_1 and d_2 interact differently[17] with the three ligands in the *trans* isomer, a variation in temperature will produce not only a change in the net spin magnetization on the metal according to the Curie law, but superimpose on this Curie behavior the effect of a redistribution of the unpaired electron spin between d_1 and d_2.

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(17) Since the rhombic distortion in the *trans* isomer is only a very small perturbation on the D_3 symmetry, the d_1 and d_2 basis functions under D_3 should serve as reasonable approximations to the basis orbitals for the *trans* isomer. However, any linear combination of d_1 and d_2 will produce basis functions each of which will interact differently with the three ligands.

We will first consider the situation where the unpaired spin resides in the ligand lowest antibonding π MO (ψ type). For the case where d_1 is lower than d_2 (i in Figure 4b), only d_2 will contain *unpaired* spin in the limit $T \rightarrow 0$, predicting that only ligands B and C will receive equal amounts of spin density, as shown in Table I. In the limit $T \rightarrow \infty$, the *unpaired* spin population of d_1 and d_2 will be equal, and ligands A, B, and C will receive equal amounts of spin density, as in the complexes with symmetric ligands. This energy level scheme therefore predicts that for the three resonances from the *trans* isomer two contact shifts (B and C) will decrease *faster* and one shift (A) will decrease *slower* with increasing temperature than predicted by Curie behavior, in exact agreement with observation in Figure 1. Furthermore, it is also predicted that the three *trans* 4-CH_3 and 7-H shifts should converge with increasing T, due to equalizing the d_1 and d_2 spin population, which is qualitatively observed in Figure 1. In the situation where d_2 is lower than d_1 (ii in Figure 4b), two contact shifts should decrease slower and one faster with increasing T than Curie behavior, contrary to observation. The fourth peak, which must arise from the *cis* isomer, is predicted to exhibit simple Curie behavior for both case a and b in Figure 4, as observed, since the *cis* isomer retains the degeneracy of d_1 and d_2. Our analysis here is similar to that proposed by Lin and Orgel[18] for the mixed four-coordinated Ni(II) chelates. However, the predictions[18] of the temperature dependence of the contact shifts in the Ni(II) chelates were not borne out by experiment.[19]

In the situation where the unpaired spin resides in the highest bonding π MO (φ type), the observed deviations from Curie behavior arise only if d_2 is lower than d_1. Because the spin-containing MO cannot be specified,[10] it is not possible to determine the relative energies of d_1 and d_2 in the *trans* isomer. However, only case b in Figure 4 is capable of accounting for the anomalous temperature dependence of the contact shifts, whether the spin is in the highest bonding or lowest antibonding MO.

It is therefore possible to differentiate between the *cis* and *trans* resonances for 4-CH_3 and 7-H on the basis of their temperature dependence. Previous assignment of the resonances to the individual isomers was possible only when they were present in nonstatistical amounts.[14] Thus for both 4-CH_3 and 7-H, peaks labeled a, b, and d in Figure 1 belong to the *trans* isomer, while c belongs to the *cis* isomer. This is in agreement with the previous speculative assignment based on the expectation[11] that the shifts of the *cis* isomer should resemble those of the complexes with symmetric ligands more than the shifts of the less symmetric *trans* isomer.

Inasmuch as the π spin density at the 4 and 7 positions depends on the availability of unpaired spin in the d orbital with proper π-bonding symmetry, some π spin density arrives on the ligand by direct delocalization. However, the fact that the 4-CH_3 shifts differ in sign within the *trans* isomer, and that the 3-CH_3 π shifts are essentially insensitive to the dissymmetry of the *trans* isomer, suggests that some π spin density also originates from σ–π polarization within the ligand, as has been postulated to be the case in related nickel(II) complexes.[11]

The difference in the three 4-CH_3 or 7-H contact shifts does not arise solely from the effect of spin redistribution between d_1 and d_2, as evidenced by the fact that the average of the three shifts for the *trans* isomer differs significantly from the shift for that position in either the *cis* isomer or the chelates with symmetric ligands. In addition, Figure 4b alone cannot account for the difference in shift direction for the 4-CH_3 peaks in the *trans* isomer. Therefore the metal–ligand bond for the three ligands in the *trans* isomer must differ slightly, though this difference is unlikely to be the source of the anomalous temperature dependence by itself.

In principle, the extent of the deviation from Curie behavior for the three *trans* peaks could allow the determination of the energy separation of d_1 and d_2, if we knew the difference in the three 4-CH_3 or 7-H shifts in the limit where the spin populations of d_1 and d_2 are equal. Unfortunately, our temperature range is too limited to achieve this situation for the 4-CH_3 substituted complexes. For $(5\text{-phen})_3Cr^{2+}$, the 4,7-H π contact shifts appear to follow the Curie law approximately, as shown in Figure 2B, indicating that d_1 and d_2 do not differ much in electron population, and that the relative populations are not altered sufficiently over the accessible temperature range.

We therefore suggest that the ground state for the Cr(II) chelates with phen ligands is ^3E. Because of the great similarity of the structure and bonding properties of phen and bipyridine (bipy), it is very likely that $(bipy)_3Cr^{2+}$ also possesses a ^3E ground state. Analyses of the magnetic moments of these phen and bipy chelates have shed little light on the nature of the ground state, and polarized crystal spectra have not yet been reported, so that direct confirmation of our assignment is not feasible at this time. However, our postulated ^3E ground state is consistent with the observation[20] that the isoelectronic d^4 complex $Ti(bipy)_3$ is *diamagnetic*, which can be rationalized only by case b in Figure 4.

For the analogous Fe(III)–phen chelates,[10,11] it can be easily shown by similar arguments as for Cr(II) that only for case a in Figure 4 will a low-spin d^5 complex give rise to anomalous temperature dependence for ligand π contact shifts. However, for each of the 4-CH_3-substituted Fe(III) complexes, the 4-CH_3 shifts, which are at least partially π in origin,[10] obey the Curie law quite accurately, as shown for $(4\text{-phen})_3Fe^{3+}$ in Figure 5. We therefore conclude that these Fe(III) chelates are also examples of case b and possess an $^2A_2$ ground state, which is in complete agreement with the results of an analysis of the temperature dependence of the solid-state magnetic moment of $(phen)_3Fe(ClO_4)_3$.[21]

The value of a similar analysis of the temperature dependence for the Co(II) chelates is questionable because of the presence of very large dipolar shifts, which are also capable of producing anomalous temperature dependence of the observed shifts (*vide infra*). However, the fact that the two accurately obtainable 4-CH_3 shifts in both $(4\text{-phen})_3Co^{2+}$ and

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(18) W. C. Lin and L. E. Orgel, *Mol. Phys.*, 7, 131 (1963).

(19) D. R. Eaton and W. D. Phillips, *J. Chem. Phys.*, 43, 392 (1965); A. Chakravorty and R. H. Holm, *J. Amer. Chem. Soc.*, 86, 3999 (1964).

(20) S. Herzog and R. Taube, *Angew. Chem.*, 70, 469 (1958).

(21) B. N. Figgis, *Trans. Faraday Soc.*, 57, 204 (1961).

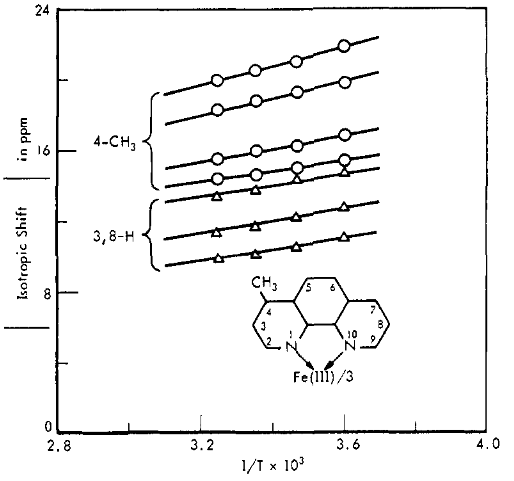

Figure 5. Curie plot for $(4\text{-phen})_3FeCl_3$ in D_2O.

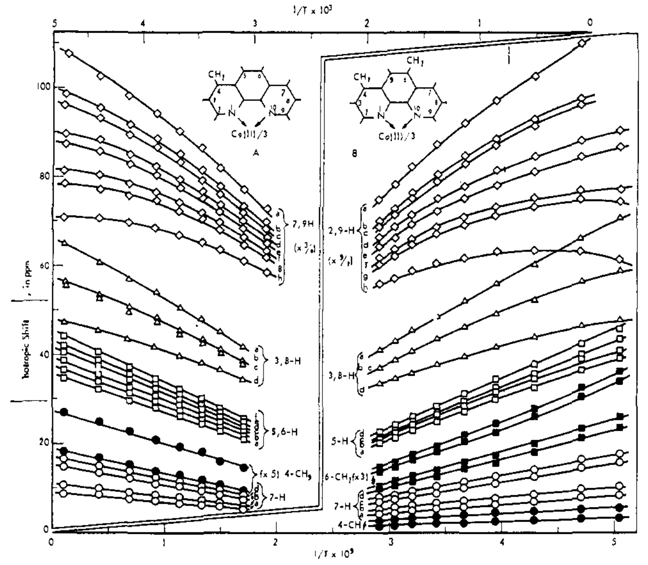

Figure 6. Curie plot for (A) $(4\text{-phen})_3CoCl_2$ and (B) $(4,6\text{-phen})_3CoCl_2$ in methanol.

$(4,6\text{-phen})_3Co^{2+}$ do not deviate significantly from Curie behavior (Figure 6) we suggests that these complexes probably possess a $^4A_2$ ground state. To our knowledge, no other data have been reported which can support this assignment. The one consistency noted is that for each of the three metal ions studied here, we conclude that the e level is more stable than the a level.

We therefore suggest that this technique may well have a more general applicability for determining the orbital ground-state symmetry of tris chelates with bidentate ligands. Analysis of the unpaired electron configurations of the transition metal ions reveals that octahedral complexes with T ground states will exhibit this spin redistribution in the π system, while for those complexes with E ground states this anomalous Curie behavior may show up in the delocalized σ spin density. A number of first-row transition metal ions with T (V(III), low-spin Cr(II) and Fe(III), and Co(II)), and E (Mn(III) and high-spin Cr(II)) ground states can be expected to possess the relatively short electronic spin relaxation time necessary for successful nmr studies.

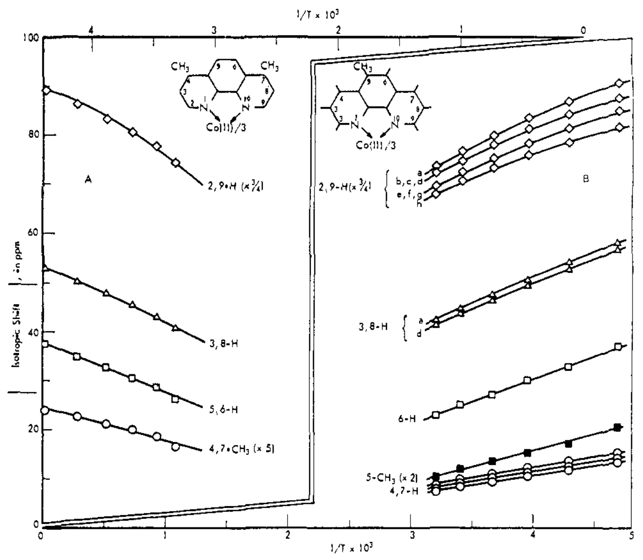

Figure 7. Curie plot for (A) $(4,7\text{-phen})_3CoCl_2$ and (B) $(5\text{-phen})_3CoCl_2$ in methanol.

The contact shifts for tris chelates of V(III) with both symmetric and unsymmetric acetylacetonate-type ligands have been reported.[14] The complexes with unsymmetrically methyl-substituted ligands have produced the well-spaced, four equally intense peaks per ligand position indicative of the statistical isomer mixture. However, each of the four lines displays essentially Curie behavior,[22] which leads us to conclude that the ground state of tris(acetylacetonate)vanadium(III) must be $^3A_2$. This conclusion is in complete agreement with results from both the polarized crystal spectra and the magnetic susceptibility.[23,24]

One general conclusion that becomes obvious from the anomalous temperature dependence of the contact shifts in these Cr(II) complexes is the fact that ligand contact shifts are *not* necessarily proportional to magnetic susceptibility. In fact, the delocalization mechanism may have to be carefully considered in relating ligand contact shifts to the net spin magnetization on the metal.

Co(II) Complexes. Figure 6 illustrates the anomalous temperature dependence of the isotropic shifts for $(4\text{-phen})_3Co^{2+}$ and $(4,6\text{-phen})_3Co^{2+}$. The π-dominated 4-CH_3 contact shifts approach Curie behavior, in contrast to the Cr(II) chelates. On the other hand, the 2,9-H shifts deviate appreciably from Curie behavior, increasing much more slowly with decreasing temperature than predicted by the Curie law. Furthermore, the extent of this deviation is different for each of the eight 2,9-H peaks of the complexes shown in Figure 6, as well as for all other unsymmetrically substituted complexes. The 3,8-H shifts show deviations in the same direction as 2,9-H, though much smaller, while the 5,6-H shifts deviate in the *opposite* direction, so that the shifts increase faster than expected as the temperature is lowered.

Inasmuch as the deviations from Curie behavior differ significantly for the eight 2,9-H shifts, the magnetic anomaly must arise in the proton–electron interaction which causes the differences in the eight isotropic shifts. However, as the data for $(4,7\text{-phen})_3CoCl_2$ in Figure 7A indicate, this anomalous temperature

[22] R. H. Holm, private communication.
[23] T. S. Piper and R. L. Carlin, *Inorg. Chem.*, 2, 260 (1963).
[24] B. N. Figgis, J. Lewis, and E. Mabbs, *J. Chem. Soc.*, 2480 (1960).

behavior is present for 2,9-H even in complexes with symmetric ligands, so that its origin cannot depend *solely* on the dissymmetry of the *trans* isomer, as was the case for Cr(II).

Analysis of the isotropic shifts of Co(II) complexes with both symmetric and unsymmetric phen ligands has shown[11] that, except for possibly the 4,7 position, the observed isotropic shifts arise both from downfield σ contact shifts, in the order 2,9-H > 3,8-H $\sim$ 5,6-H, and upfield dipolar shifts with 2,9-H > 3,8-H, and downfield dipolar shifts for 5,6-H. For (phen)$_3$CoCl$_2$, the calculated σ contact contributions are −157, −48, −3, and −13 ppm, while the dipolar contributions are +60, +8, −4, and −10 ppm for 2,9-H, 3,8-H, 4,7-H, and 5,6-H, respectively.[11] It has been proposed that the difference in isotropic shifts for the eight 2,9-H peaks, as well as for the 3,8-H or 5,6-H peaks, in unsymmetric ligands arises primarily from a difference in the *dipolar* shifts for the nonequivalent protons in the isomer mixture, with the *contact* contributions to each of the eight peaks essentially identical. This conclusion was based on the observation[11] that for analogous, magnetically isotropic Ni(II) complexes, where similar direct σ contact shifts are present, only a single peak per ligand position appears for the unsymmetrical ligand. This proposed difference in dipolar shifts in the *trans* isomer has been shown to be consistent with either a small shift of the magnetic axis from the trigonal axis or, more likely, with the dipolar shifts arising from the decrease to a rhombic *g* tensor. Also, the relative magnetic dissymmetries for the various ligand protons were found to be proportional to their geometric factors, 2,9-H > 3,8-H $\sim$ 5,6-H.[11]

Since the contact contribution for the eight 2,9-H, 3,8-H, or 5,6-H shifts in Figure 6, for example, should be approximately equal, we must conclude that the observed 2,9-H and 3,8-H shifts will have increasing dipolar contributions as the magnitude of the observed shift *decreases*, while the 5,6-H shifts must have increasing dipolar contributions as the observed shift *increases*. Assuming that the 2,9-H *contact* shifts are approximately equal in phen and in both isomers of 4,6-phen complexes, the *dipolar* contributions to peaks a through h in Figure 6 are calculated as approximately +45, 54, 57, 60, 63, 68, 70, and 77 ppm, respectively, at *RT*. Thus peaks labeled a for all ligand positions in Figures 6 and 7 should each have the smallest dipolar contributions, while peaks labeled h for 2,9-H, d for 3,8-H and 5-H, and f for 5,6-H should have the largest dipolar contributions. If we calculate the dipolar contributions for all ligand protons on the assumption[25] of equal contact shifts in the phen, 4-phen, and 4,6-phen chelates, we obtain the calculated relative ratio of dipolar/contact shifts listed in Table II under $\Delta H_d/\Delta H_c$.

The deviation from Curie behavior for a given peak can be expressed numerically as the percentage change in the product ΔHT, which should be constant for all shifts in the limit of Curie behavior.[1] These percentage changes have been calculated from the data in Figure 6, and are also listed in Table II. The data in this table clearly show that there is a very direct correlation between the extent of deviation from Curie behavior and the relative magnitude of the dipolar and the contact contributions to the observed isotropic shift, $\Delta H_d/\Delta H_c$. A similar correlation is found for the 5-phen complex, which experiences only small magnetic dissymmetry for the 2,9-H protons, as shown in Figure 7B. For any set of protons, the magnitude of the percentage change in ΔHT parallels the increase in the dipolar contribution. In addition, for a given complex, the relative directions or signs of the percentage changes in $\Delta H \cdot T$ and the sign of the dipolar shift for the different ligand positions are identical. The fact that the percentage change in ΔHT is largest for 7-H, even though this ligand position experiences the smallest dipolar shift, results from the fact that 7-H dipolar shift represents a much larger fraction of the observed shift than for any other proton.

Table II. Percentage Change in ΔHT from +70 to −60°

Position		4-phen		4,6-phen	
		$\delta(\Delta HT)$[a]	$\Delta H_d/\Delta H_c$[b]	$\delta(\Delta HT)$	$\Delta H_d/\Delta H_c$
2,9-H	a	−8	−0.32	−9	−0.30
	b	−12	−0.36	−13	−0.36
	c	−13	−0.37	−13	−0.37
	d	−16	−0.40	−17	−0.41
	e	−17	−0.41	−18	−0.42
	f	−20	−0.44	−22	−0.47
	g	−22	−0.45	−23	−0.48
	h	−26	−0.90	−30	−0.53
3,8-H	a	−1	−0.06	$\sim$0	−0.00
	b	−3	−0.15	−3	−0.14
	c	−4	−0.16		
	d	−11	−0.26		
				−13	−0.26
5,6-H	a	+18	+1.21	+17	+1.14
	b	+17	+1.13	+15	+1.05
	c	+16	+1.06	+14	+0.98
	d	+15	+0.96	+12	+0.88
	e	+15	+0.90		
	f	+14	+0.81		
7-H	a	+35	+2.4	+31	+2.4
	b	+34	+2.0	+32	+2.0
	c	+21	+1.3	+18	+1.1
	d	+16	+1.0	+15	+0.8

[a] Percentage change in the product of observed shift and absolute temperature from +70 to −60°. Lettering as shown in Figure 6. [b] Ratio of calculated dipolar shift over contact shift, at 0°.

We therefore conclude that the deviations from Curie behavior of the observed shifts for both symmetric and unsymmetric phen chelates of Co(II) must result primarily from non-Curie behavior of the *dipolar* shifts. It is not possible to determine if the contact shifts follow the Curie law exactly, so that we will restrict ourselves to the conclusion that the dipolar shifts deviate from Curie behavior significantly more than the *contact* shifts.

A qualitative understanding of the different temperature dependences of the contact and dipolar contributions to the isotropic shifts can be gleaned from an inspection of eq 2. Since this equation predicts[3] an identical Curie behavior for both contact and dipolar shifts for a *single* Kramer doublet, the anomalous behavior must arise from the change with temperature of the relative populations of the various Kramer

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(25) This assumption is only very approximate, since the 2,9-H shifts in (phen)$_3$Co^{2+} and (4,7-phen)$_3$Co^{2+} differ by $\sim$8%, while the 3,8-H and 5,6-H shifts are essentially identical (M. Wicholas and R. S. Drago, paper presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 8–13, 1968). However, this assumption does *not* affect the estimates to the relative dipolar contributions to 2,9-H shifts. As long as we do not compare $\Delta H_d/\Delta H_c$ between different complexes, our analysis remains valid.

doublets, which are usually separated by a few hundred reciprocal centimeters in Co(II) complexes. Thus if the g tensors for the various Kramer doublets differ, both the contact and dipolar shifts will deviate from Curie behavior. The contact shift is always proportional to some "average" g value for each level, while the dipolar shift is proportional to some function of the difference in $g_{\parallel}$ and $g_{\perp}$, $(g_{\parallel} + g_{\perp})(g_{\parallel} - g_{\perp})$ in our case.[3,9] Thus if the *average* g values for the accessible Kramer doublets differ significantly less than their relative g-tensor anisotropies, the extent of deviation from Curie behavior is predicted to be much greater for the dipolar than the contact shifts. It could be stated that, in general, eq 2 predicts *different* temperature dependences for contact and dipolar shifts in such Co(II) systems.

Because of the lack of any experimental esr data, a detailed check of this postulate is not possible for our system at this time. However, a complete esr study[26] of the trigonally distorted six-coordinated bis Co(II) complexes of poly(pyrazolyl)borates has shown that $(g_{\parallel} + g_{\perp})(g_{\parallel} - g_{\perp})$ differs by a factor of ~ 4 for the two lowest lying Kramer doublets, which are $\sim 90\%$ populated at room temperature, while $(g_{\parallel} + 2g_{\perp})$ differs by only <2 for the same levels. Therefore this system should show larger deviations from Curie behavior for its dipolar than contact shifts.

We therefore suggest that for the present Co(II) complexes, the magnetic anisotropies must differ more than the average g values for the accessible Kramer doublets. Furthermore, since the dipolar shifts increase faster than Curie behavior as the temperature is lowered, the lowest Kramers doublet must possess the greater magnetic anisotropy.

The observed correlation between the extents of deviation from Curie behavior and the dipolar contribution to the observed isotropic shift (in both relative signs and magnitudes), calculated by assuming similar σ spin density distributions in the Co(II) and magnetically isotropic Ni(II) chelates,[10] can be taken as evidence that, except for the 4,7 positions, similar spin delocalization mechanisms are operative in these Co(II) and Ni(II) chelates. Thus the previous contention[27] that this method of qualitatively separating contact and dipolar shifts in these Co(II) chelates is totally invalid is erroneous. Their[27] conclusions depended on comparing the isotropic shifts of sets of protons which obviously experienced different types of spin density, and thus put the method in its most unfavorable light.

Similar, though slightly more complicated, non-Curie behavior has been observed for other distorted octahedral complexes which are expected to exhibit sizable magnetic anisotropy,[28] suggesting that such anomalous behavior is more common than previously considered.[29]

(26) J. P. Jesson, *J. Chem. Phys.*, **45**, 1049 (1966); **47**, 582 (1967).

(27) M. Wickolas and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 2196 (1968).

(28) G. N. La Mar, *ibid.*, **92**, 1806 (1970).

(29) NOTE ADDED IN PROOF. B. R. McGarvey (private communication) has recently rederived the equations for the contact and dipolar shift (ref 3) for trigonally distorted Co(II) complexes, including the contributions from the second order Zeeman interaction. His equations predict essentially Curie behavior for the contact shifts, and a strong deviation from Curie behavior for the dipolar shifts, which serves to confirm our present qualitative experimental findings. Furthermore, McGarvey's specific predictions of non-Curie behavior for the dipolar shifts in the bis(pyrazolyl borate)cobalt(II) complexes have been experimentally observed (G. N. La Mar and J. P. Jesson, to be published).

Kinetic Study of the Oxidation of Thallium(I) by Neptunium(VII)[1]

R. C. Thompson[2] and J. C. Sullivan

Contributions from Argonne National Laboratory, Argonne, Illinois 60439, and the University of Missouri, Columbia, Missouri 65201.

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Abstract: The empirical form of the rate law for the reaction between Np(VII) and Tl(I) in acid perchlorate media is $-d[\mathrm{Np(VII)}]/dt = k'[\mathrm{Np(VII)}][\mathrm{Tl(I)}]$, where $\ln k' = \ln k + n \ln [\mathrm{H^+}]$. At 25° in 1 M perchloric acid $k = 4.46 \pm 0.04\ M^{-1}\ \mathrm{sec}^{-1}$ and $n = 0.901 \pm 0.008$. The apparent activation energy is 7.73 ± 0.42 kcal/mol. Results of ^{18}O tracer studies are presented.

When Tl(I) is oxidized by the reagents Co(III),[3] Ce(IV),[4] and Ag(II),[5] evidence has been presented for the existence of Tl(II) as an important kinetic intermediate oxidation state. It is of interest to ascertain if the production of this intermediate is independent of the oxidant. This work presents such an attempt by the kinetic study of the reaction

$$2\mathrm{Np(VII)} + \mathrm{Tl(I)} = 2\mathrm{Np(VI)} + \mathrm{Tl(III)} \qquad (1)$$

In addition, the results to be presented extend the limited information available on the reaction characteristics of Np(VII) in acid media.[6]

Experimental Section

Reagents. The Np(VII) stock solutions in 1 M NaOH were prepared electrolytically as previously described.[6] Thallium(I)

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Argonne National Laboratory summer staff member.

(3) K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, 343 (1956).

(4) J. W. Gryder and M. C. Dorfman, *J. Amer. Chem. Soc.*, **83**, 1254 (1961).

(5) R. W. Dundon and J. W. Gryder, *Inorg. Chem.*, **5**, 986 (1966).

(6) J. C. Sullivan and A. J. Zielen, *Inorg. Nucl. Chem. Lett.*, **5**, 927 (1969).