constants in eq 8 and 10. The quadrupolar effect turns out to be *ca.* 10 times greater. It follows that for this model, *i.e.*, tumbling of the loosely coordinated water molecules only through the tumbling of the whole vanadyl aquo complex, the observed additional relaxation at low temperature would occur primarily through quadrupolar coupling interrupted by chemical exchange with a lifetime of *ca.* 10^{-11} sec.

The interpretation of the O^{17} relaxation in VO^{2+} solutions in terms of interactions with water molecules in two different kinds of coordination sites receives support from a comparison with the temperature dependence of the proton nmr relaxation in aqueous $VOSO_4$ solutions: The data by Hausser and Laukien[22] can be explained by an analogous interpretation which assumes that at higher temperature the relaxation is controlled by the exchange of protons from the first coordination sphere, while at lower temperature the contributions from protons of water molecules coordinated to VO^{2+}, with a much shorter lifetime than those in the first coordination sphere, become important.

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Complexes of Cobalt(II). V. A Model for Anomalous Magnetic Behavior

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A strong-field approximation incorporating spin–orbit effects has been used to calculate paramagnetic susceptibilities as a function of temperature and crystal-field strength of cobalt(II) ions in an octahedral environment and in the vicinity of the "crossover" from a high-spin to a low-spin ground level. These calculations predict that the room-temperature magnetic moment should decrease smoothly from high-spin values (>4 BM) to low-spin values (*ca.* 1.7 BM) as the crystal-field splitting increases. A Boltzmann distribution over five levels (3 U′, E′, and E″) can be used to explain anomalous Curie–Weiss behavior reported previously for certain cobalt(II) complexes provided the crystal-field splitting is varied as a function of temperature.

Introduction

Most six-coordinated octahedral cobalt(II) complexes fall into two classes: those with magnetic moments which lie in the range 4.8–5.6 BM and are referred to as "high-spin" and those with moments in the range 1.73–2.0 BM which are referred to as "low-spin."[1] Recently, however, there have been found a number of six-coordinated cobalt(II) compounds which have room-temperature magnetic moments intermediate between these two classes.[2] Several of these "intermediate-moment" compounds have anomalous magnetic susceptibility curves; that is, they exhibit large deviations from normal Curie–Weiss behavior. In part I of this series,[3] Stoufer, Smith, Clevenger, and Norris listed five such complexes and presented curves of reciprocal susceptibility *vs.* temperature for each. Other cobalt(II) complexes exhibiting similar behavior have subsequently been found by Ramirez[4] and Fisher.[5] A tabulation of most of these compounds and their room-temperature magnetic moments is given in Table I, and plots of $1/\chi$ *vs.* T are shown in Figures 1 and 2 where χ is the molar paramagnetic susceptibility.

Of various possible qualitative explanations for this "anomalous" magnetic behavior, Stoufer, *et al.*,[3] concluded that the only one consistent with the experimental data involves a model in which there is a distribution of magnetic ions among two or more low-lying electronic levels. The specific idea of an equilibrium between two distinct electronic levels, each having different amounts of spin and orbital angular momenta, has been used in the past to explain unusual magnetic behavior.[6] However, in part I it was shown that, if spin–orbit coupling is introduced into the model, a d^7 ion such as Co(II) will have a total of five electronic levels arising from the two lowest terms (^2E and $^4T_1$), all five of which may be accessible at reasonable temperatures and at certain values of crystal-field strength near the point where the ^2E and $^4T_1$ terms cross (see Figure 3). It was postulated that a model based on a distribution over the five levels might lead to an explanation of the experimental results. The specific aim of this work is, then, to test this hypothesis in a quantitative fashion by actually calculating paramagnetic susceptibilities as a function of temperature in an attempt to produce theoretical curves similar to those shown in Figures 1 and 2.

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(1) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954).

(2) D. H. Busch, "Cobalt," R. S. Young, Ed., ACS Monograph Series, Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.

(3) R. C. Stoufer, D. W. Smith, E. A. Clevenger, and T. E. Norris, *Inorg. Chem.*, **5**, 1167 (1966).

(4) O. Ramirez, Ph.D. Dissertation, University of Florida, 1965.

(5) H. M. Fisher, Master's Thesis, University of Florida, 1965.

(6) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 4830 (1964), and references therein.

TABLE I
INTERMEDIATE MAGNETIC MOMENTS EXHIBITED BY ANOMALOUS COBALT(II) COMPLEXES[a]

No.	Compound	Room temp moments	Ref
I	$[Co(terpy)_2]Br_2 \cdot H_2O$	2.63	5
II	$[Co(PdAdH)_2]I_2$	2.85	3
III	$[Co(PBI)_2]I_2$	3.72	3
IV	$[Co(BMI)_3]I_2 \cdot H_2O$	2.91	3
V	$[Co(PMI)_3](BF_4)_2$	4.31	3
VI	$[Co(terpy)_2]Cl_2 \cdot 5H_2O$	2.51	5
VII	$[Co(GdH)_3]Br_2$	3.16	5
VIII	$[Co(PvdH)_3]Br_2$	4.23	5
IX	$[Co(DTPH)](ClO_4)_2$	2.36	3

[a] terpy, 2,2′,2″-terpyridine; PdAdH, 2,6-pyridindialdihydrazone; PBI, 2,6-pyridindialbis(benzylimine); BMI, biacetylbis(methylimine); PMI, 2-pyridinalmethylimine; GdH, glyoxaldihydrazone; PvdH, pyruvaldihydrazone; DTPH, 1,12-bis(2-pyridyl)-1,2,11,12-tetrakisaza-5,8-dithia-$\Delta^{2,10}$-dodecadiene.

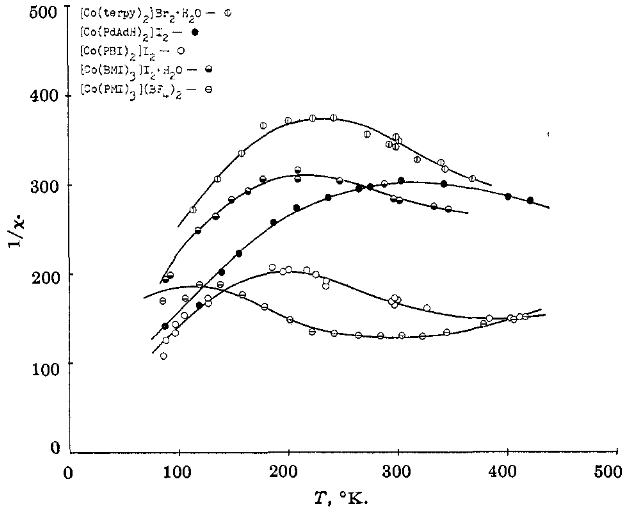

Figure 1.—Experimental curves of χ^{-1} *vs.* T.

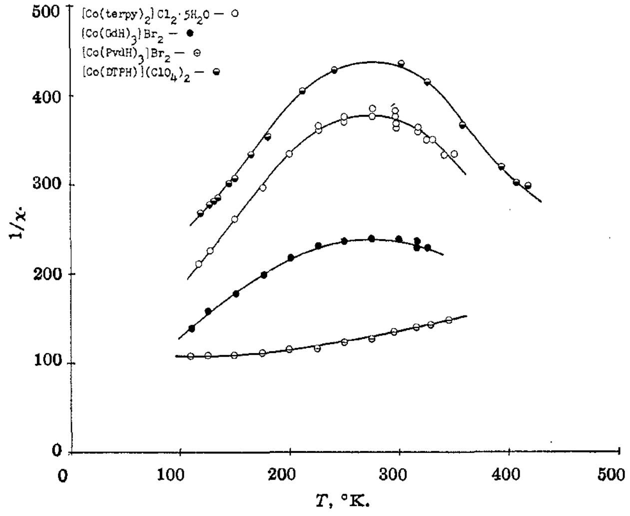

Figure 2.—Experimental curves of χ^{-1} *vs.* T.

Calculations

The energy of any one level can be expanded as a power series in H, the magnetic field strength

$$E = W_0 + HW_1 + H^2W_2 + \ldots \quad (1)$$

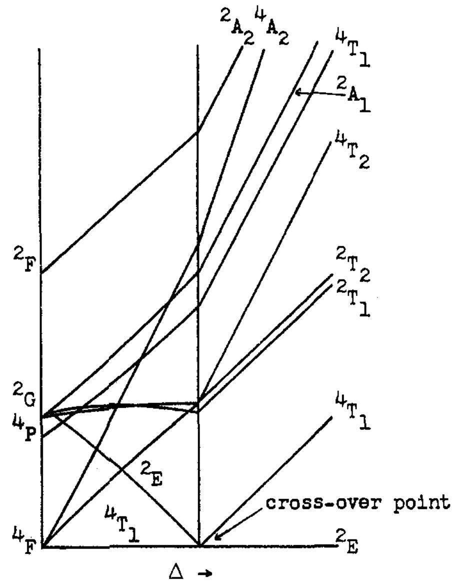

Figure 3.—Energy level diagram of a d^7 ion in an octahedral field.

so that W_0 corresponds to the zero-order energy of a level, W_1 to the first-order Zeeman energy, and W_2 to the second-order Zeeman energy. The susceptibility is then of the form[7]

$$\chi = N\frac{\Sigma(W_1^2/kT - 2W_2)e^{-W_0/kT}}{\Sigma e^{-W_0/kT}} \quad (2)$$

where N is Avogadro's number, and we have retained only that part of χ independent of H. The second-order Zeeman energy contributes what is sometimes called the "temperature-independent paramagnetism" or the "high-frequency contribution." By neglecting the second-order Zeeman effect and assuming only the ground level is occupied, eq 2 will be of the same form as Curie's law, $\chi = C/T$. Our model does not make these assumptions and so it is necessary to calculate the various values for W_0, W_1, and W_2.

Zero-Order Energy, W_0.—The calculation of the energy values for the pertinent levels of Co(II) follows the strong-field method outlined by Griffith.[8] A brief description is presented here.

For the strong-field coupling scheme, the crystal-field splitting energy is taken as being greater than the interelectronic interaction energy which in turn is taken to be greater than the spin–orbit coupling energy. A crystalline field of octahedral symmetry splits the five d orbitals into two sets—a triply degenerate set designated t_2 and lying lowest and a doubly degenerate e set at an energy Δ above the t_2 set. Cobalt(II) is a d^7 ion, and, for a strong crystalline field, the seven electrons will be in a ground-state configuration of t_2^6e or "low-spin" configuration. Promoting one electron from a t_2 orbital to an e orbital results in a "high-spin configuration, $t_2^5e^2$. By group theoretical methods, the various term states which can arise from these configurations are found to be

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(7) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961, p 131.

(8) See ref 7, Chapter 9.

$$\begin{aligned} t_2{}^6e &\longrightarrow {}^2E \\ t_2{}^5e^2 &\longrightarrow {}^4T_1 + 2{}^2T_1 + 2{}^2T_2 \end{aligned} \qquad (3)$$

The energy-level diagram for a d^7 system as calculated by Tanabe and Sugano[9] is shown in Figure 3, and the point at which the ^{2}E and ^{4}T$_1$ terms are of equal energy is labeled the "crossover point." The region of the crossover point is the area under investigation and it is thus the two terms ^{2}E and ^{4}T$_1$ that are of interest. All other terms are of sufficiently high energy that they may be neglected.

The next problem is to find how these two terms split under spin–orbit coupling and subsequently how they mix. Taking the direct product of the irreducible representation for the spin part and the irreducible representation for the space part, one finds that the ^{2}E term is not split by spin–orbit coupling, but transforms as a four-dimensional representation, U′, under the double group O*. The ^{4}T$_1$ term does split, however, into four levels designated E′, E″, $^3/_2$U′, and $^5/_2$U′. The E″ and $^5/_2$U′ levels are degenerate in the absence of interaction with other terms, in which case we have the situation as depicted in Figure 4. Here we have defined the energy difference between the ^{4}T$_1$ and ^{2}E terms by the arbitrary parameter δ which will be positive to the right of the crossover point and negative to the left.

No attempt has been made to relate δ to Δ, the crystal-field splitting energy, for two reasons: (1) Δ is not required for calculating magnetic susceptibilities; (2) in order to relate δ to Δ, the pairing energy must be known; however, there does not seem to be any general agreement on a value (see part II[10] and the discussion therein). The U′ level arising from ^{2}E has off-diagonal elements with the $^3/_2$U′ and $^5/_2$U′ levels of ^{4}T$_1$, and this interaction mixes the two terms. The matrix elements are calculated with the one-electron spin–orbit operator, $\zeta\sum_i l_i \cdot s_i$, which is usually assumed to hold. Griffith has done this and the results are given in Table II where the zero energy is taken as the unperturbed energy of the ^{2}E term. ζ is the one-electron spin–orbit coupling constant which we have taken as 450 cm^{-1} in agreement with Liehr.[11] Diagonalizing the matrix and plotting the energies of the five levels as a function of δ gives the diagram depicted in Figure 5, which differs from Figure 3 of part I in choice of energy axes. This diagram is consistent with that of Liehr,[11] who has presented the entire energy-level diagram for an octahedral d^7 ion.

First- and Second-Order Energies, W_1 and W_2.—We now actually have five levels, the wave functions for which are diagonal with respect to the spin–orbit coupling operator; two are the original E′ and E″ levels. The other three, however, are necessarily linear combinations of the wave functions belonging to the original three U′ levels. Hence

$$\psi_i = a_{1i}\phi_1 + a_{2i}\phi_2 + a_{3i}\phi_3 \qquad (4)$$

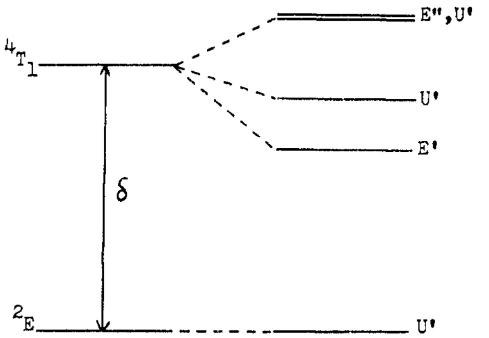

Figure 4.—Splitting of ^{4}T$_1$ and ^{2}E under spin–orbital coupling.

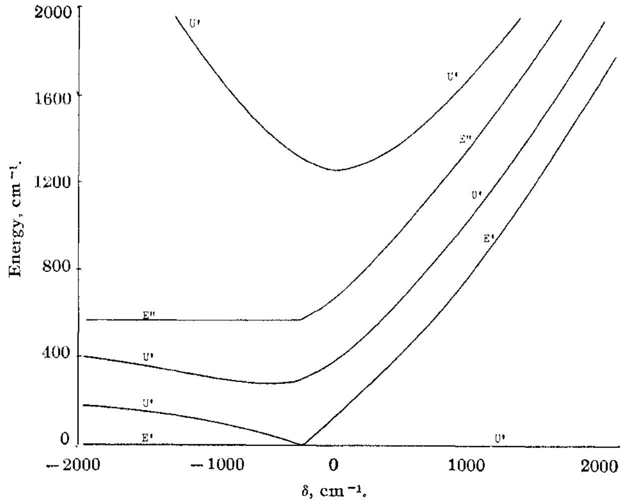

Figure 5.—Energy level diagram for a d^7 system at the crossover point in an octahedral field, spin–orbit coupling included.

Table II

Spin–Orbit Coupling Matrices for d^7 in Units of ζ

	U′ (^{2}E)	$^3/_2$U′ (^{4}T$_1$)	$^5/_2$U′ (^{4}T$_1$)	E′ (^{4}T$_1$)	E″ (^{4}T$_1$)
U′ (^{2}E)	0	$1/\sqrt{5}$	$3/\sqrt{5}$	0	0
$^3/_2$U′	$1/\sqrt{5}$	$\delta - {}^1/_3$	0	0	0
$^5/_2$U′	$3/\sqrt{5}$	0	$\delta + {}^1/_2$	0	0
E′	0	0	0	$\delta - {}^5/_6$	0
E″	0	0	0	0	$\delta + {}^1/_2$

where the ψ_i's are the diagonalized functions and the ϕ's are those belonging to the U′ levels before interaction. The calculation of the first- and second-order Zeeman energies involves matrix elements of the form

$$H_{ij} = \langle \psi_i{}^M | \mathcal{H}_1 | \psi_j{}^M \rangle \qquad (5)$$

where $\mathcal{H}_1$ is the contribution to the over-all Hamiltonian due to the perturbation of an external magnetic field, and M is the quantum number representing the different rows of the representation of ψ in that field. It can be shown that $\mathcal{H}_1$ is diagonal in M and is given by[8]

$$\mathcal{H}_1 = h^{-1}\beta H(L + 2S) \qquad (6)$$

Since x, y, and z are equivalent for an octahedral crystalline field, we can take the magnetic field to be along the z axis. The Hamiltonian is then written as $h^{-1}\beta H_z\sum_i(l_{zi} + 2s_{zi})$, a one-electron operator.

First-order Zeeman splitting involves the removal of the degeneracy of each individual level and so we

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[9] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).
[10] H. M. Fisher and R. C. Stoufer, *Inorg. Chem.*, **5**, 1172 (1966).
[11] A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

need only the diagonal elements. Second-order Zeeman energies arise because the field causes interaction between different levels. Second-order perturbation theory gives us the expression

$$E_i^{(2)} = \sum_{j \neq i} \frac{H_{ij}H_{ji}}{W_{0i} - W_{0j}} \qquad (7)$$

for the necessary energies. W_2 is then $E_i^{(2)}/H^2$.

Results and Discussion

The susceptibility, as calculated from eq 2, is dependent on three variables, ζ, δ, and T, these not necessarily being independent of each other. The W's are functions of ζ and δ.

The one-electron spin–orbit coupling parameter, ζ, having a free-ion value[12] of 515 cm^{-1} for Co(II), is expected to be smaller for ions in a crystalline field.[13] Several test computations were made using a range of values for ζ; however, the susceptibilities were found to be relatively insensitive to these variations and the general shapes of the χ^{-1} *vs.* T curves were not affected at all. Liehr[11] used a value of 450 cm^{-1} which we have adopted for our calculations.

Initial susceptibility calculations were made holding δ constant and curves of the form shown in Figure 6 resulted. For a δ value of $+4000$ cm^{-1}, corresponding to a very strong crystalline field (sufficiently far from the crossover point that the system can be considered essentially low-spin), we find the χ^{-1} *vs.* T plot to be linear from 0°K to well above room temperature. As the value of δ is reduced from large positive values, through the crossover point and to large negative values, the curves show a continuous decrease in slope. Concomitantly, there is a small degree of curvature incipient at high temperatures. The appearance of this curvature occurs at lower and lower temperatures as the over-all slope decreases (with decreasing δ), the high-temperature portion reverting to straight-line behavior. At a δ value of approximately -600 cm^{-1}, the plot is essentially a straight line over the entire temperature range. With a further decrease in δ, the general slope continues to decrease but the curvature reverses; that is, it turns away from the temperature axis and its point of appearance begins to shift back toward higher temperatures.

The curvature is caused by two factors operating in eq 2: (1) the second-order Zeeman energies, W_2, which tend to decrease the slope as the temperature increases since W_2 is always negative for the ground level, and (2) the influence of the Boltzmann factor which will tend to decrease the slope with increasing temperature to the right of the crossover point where contributions from excited levels will increase the value of χ (decrease $1/\chi$) and increase the slope with increasing temperature to the left of the crossover point where the contributions from excited levels decrease the value of χ. With either one or both effects operating, there is significant deviation from the normal Curie–Weiss behavior and evaluation of a Weiss constant is meaningless.

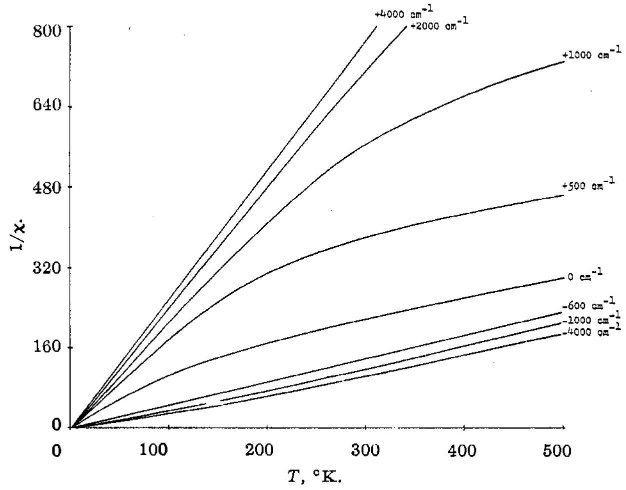

Figure 6.—χ^{-1} *vs.* T for various values of constant δ.

Recently, Barraclough[14] performed calculations similar to those described herein and derived curves analogous to those of Figure 6. His results differ significantly from the present ones only in the vicinity of $\delta = 0$. He takes into account the contribution to χ only from the ground electronic level, neglecting the contributions from the other four levels (see Figure 4).

Using the standard formula

$$\mu_{\text{eff}} = 2.828\sqrt{\chi T} \qquad (8)$$

at a δ value of -4000 cm^{-1}, we calculate a room-temperature magnetic moment of 4.64 BM which lies toward the lower limit of the range customarily quoted (4.8–5.6 BM) for pure high-spin complexes.[1] This lower value may be attributed in part to the fact that our model does not take into account mixing of high-energy terms other than ^2E with the ground term $^4\text{T}_1$, a reasonable omission in the vicinity of the crossover point, but a less and less valid approximation as one proceeds to weaker and weaker fields. Presumably then, if one were to include matrix elements of interaction with higher energy terms, sufficient additional orbital angular momentum would be introduced into the resultant ground level at large negative values of δ to produce the moments more frequently encountered experimentally. At a δ value of $+4000$ cm^{-1} we calculate a room-temperature magnetic moment of 1.76 BM, in excellent agreement with the spin-only moment of low-spin octahedral d^7 complexes. Thus, increasing δ, which corresponds to increasing the crystalline field, causes the effective magnetic moment to decrease in the fashion shown in Figure 7. The important point to be noted is that a smooth decrease in room-temperature magnetic moments from high-spin to low-spin values for Co(II) complexes, concomitant with increasing crystal-field strength, should be regarded as an expected phenomenon.

A very interesting and apparently unreported phenomenon has resulted from the calculations of the sepa-

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[12] T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).

[13] J. Owen, *Proc. Roy. Soc.* (London), **A227**, 183 (1955).

[14] C. G. Barraclough, *Trans. Faraday Soc.*, **62**, 1033 (1966).

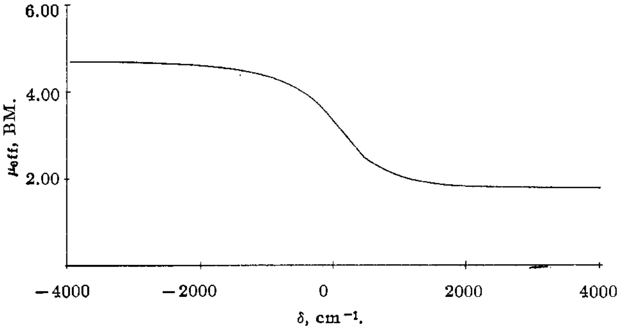

Figure 7.—Room-temperature magnetic moment *vs.* δ.

rate contributions to the over-all susceptibility from each of the five levels of Figure 6, namely, the existence of negative contributions to χ from excited (thermally accessible) levels. Individual percentage contributions of the levels at various values of δ and T, as calculated from eq 2, are reported in Table III. The unexpected negative contributions are the direct result of the inclusion of the *second-order* Zeeman energy, W_2, in our computation. Examination of eq 2 reveals that a large positive value for W_2 can give rise to a negative contribution to χ for a particular level should $2W_2$ be larger than W_1^2/kT. The increasing size and frequency of occurrence of negative contributions with increasing T, as a result of the inverse temperature dependence of the latter term, is apparent in Table III. Positive values of W_2 arise for certain excited levels because of the form of eq 7. If the shift in energy due to the second-order Zeeman effect for a particular level is primarily the result of mixing of magnetic states from a level of lower energy, then the denominator of the term on the right of eq 7 determines that $E^{(2)}$, and hence W_2, will be positive.

It is evident from Table III that the contributions to χ from excited energy levels due to a Boltzmann distribution are significant, at least in the vicinity of the crossover point. For example, at a δ value of zero and a temperature of 300°K, the E′ level, lying approximately 190 cm^{-1} above the U′ ground level, contributes 39.5% to the over-all susceptibility. At a δ value of +1000 cm^{-1} where the energy separation is about 900 cm^{-1}, the contribution from E′ has dropped to 5.7%.

Although the mathematical model thus far presented affords an explanation of the existence of intermediate magnetic moments, it does not lead to susceptibility curves containing maxima and minima as are observed experimentally (Figures 1 and 2). In order to extend the theory further in the hope of resolving the problem while remaining within the formalism already developed, it is necessary to examine some of the assumptions inherent in the calculations.

The curves of Figure 6 were calculated for constant values of δ. However, it is unreasonable to presume that δ remains constant over a large temperature range, and in fact it is much more logical to expect the crystal-field potential to be a function of temperature.[15] As the temperature of the sample increases, the populations of the various excited vibrational levels are increased, thereby increasing the average ligand–metal distance, and hence decreasing the potential around the metal ion. Such shifts in Δ (and thus δ) should be observable in the vibrational spectra of transition metal complexes, and this has apparently been observed for some ions.[16] Also, in an epr study of Co(II) complexes presented in part IV,[17] data are presented which strongly indicate that δ is very temperature dependent.

Table III

Individual Percentage Contributions of the Five Levels to χ

	δ, cm⁻¹								
	4000	3000	2000	1000	0	−1000	−2000	−3000	−4000
					T = 100°[a]				
E′	...	...	...	...	8.6	95.5	97.7	98.2	98.3
U′	100.0	100.0	100.0	100.0	91.4	4.7	2.3	1.8	1.7
U′	...	...	...	...	...	−0.2	...	...	...
					T = 300°[b]				
E′	...	...	...	5.7	39.5	102.6	98.9	98.8	98.7
U′	100.0	100.0	100.0	94.5	61.4	2.3	4.3	2.9	2.3
U′	...	...	...	...	...	−3.5	−0.9	1.2	2.6
E″	...	...	...	...	...	−1.4	−2.3	−2.9	−3.6
					T = 500°				
E′	...	0.1	4.4	32.9	53.8	122.0	112.0	111.0	110.0
U′	100.0	99.9	96.0	70.5	54.8	−5.0	0.7	−1.8	−2.8
U′	...	...	−0.3	−2.5	−5.2	−10.5	−3.4	3.0	7.3
E″	...	...	−0.1	−0.6	−3.4	−6.5	−9.3	−12.2	−14.9
U′	...	...	...	−0.3	...	...	...	...	...

[a] Zero contribution from E″ and U′. [b] Zero contribution from U′.

To determine the dependence of δ on T from the first principles would require an intimate knowledge of both inter- and intramolecular interactions as well as their interdependence, internuclear separations, and, in general, detailed information which is not presently available. It was therefore decided to assume a general equation for δ as a function of temperature of the form

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[15] T. M. Dunn, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

[16] O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

[17] J. G. Schmidt, W. S. Brey, Jr., and R. C. Stoufer, *Inorg. Chem.*, **6**, 268 (1967).

$$\delta = \delta_0 + aT + bT^2 + cT^3 \qquad (9)$$

The coefficients were chosen such that the over-all shift in δ over a 400°K temperature range would be on the order of 1200 cm^{-1} at a maximum. Shifts in the optical spectra of some crystalline hydrated transition metal ions have been observed to be 200–500 cm^{-1} over a 200°tK emperature range.[16] The cobalt(II) salt studied was $CoSO_4 \cdot 7H_2O$, for which a rather large shift of the absorption assigned to a superposition of $T_1(^4F) \rightarrow T_1(^4P)$ and $T_1(^4F) \rightarrow A_2(^4F)$ transitions was observed. A shift of 500 cm^{-1} for this band would correspond to a change of crystal-field potential of approximately 600 cm^{-1} (maximum). Over a 400°K range, one might therefore expect a shift upward of 1200 cm^{-1}.

With the above criterion in mind, various values for the coefficients a, b, and c were selected. By varying δ_0, the value of δ at 0°K, and embodying eq 9 into the computation of χ, curves such as those shown in Figure 8 were produced. The values of δ_0 and the coefficients for each curve of Figure 8 are given in Table IV. In general, reducing the value of a, b, or c results in a broadening of the curves and a shift of the maximum toward higher reciprocal susceptibility and higher temperatures. Also, as would be expected, the lower the value of δ_0, the lower the temperature at which the maximum appears. There are innumerable values and combinations of values which can be used for δ_0 and the coefficients. The curves depicted in Figure 8 are intended only to indicate that it is possible to explain the general structure of the experimental χ^{-1} *vs.* T curves by allowing the crystal-field potential to be a function of temperature. A reasonable fit for all experimental curves can be obtained by varying the four parameters.

Ewald, Martin, Ross, and White[18] have attempted to explain anomalous χ^{-1} *vs.* T behavior found in certain iron(III) complexes using arguments not too different from those used herein for cobalt(II) complexes. In order to achieve reasonable fit between their theoretical and experimental curves, they weighted the contribution to the magnetic susceptibility from the high-spin term by a constant equal to the ratio of the vibrational partition functions for a complex in its high-spin and low-spin forms. However, they have not given the value of this constant, which must be used to obtain a fit, or justified the magnitude required.

The difference in vibrational partition functions between any two terms or levels is dependent on the difference in shapes for the potential energy curves of the two terms. Because the best available potential energy curves for these types of systems are still highly qualitative, it is impossible to derive even semiquantitative results from this approach. To avoid this problem, Ewald, *et al.*, make several simplifying assumptions in calculating their curves, *e.g.*, that the vibrational partition functions are independent of temperature, that Δ is independent of temperature, and that mixing of levels under spin–orbit coupling is negligible. With regard to the latter point, of the two terms of d^5 which Ewald, *et al.*, take into consideration, the $^2T_2$ term splits into two levels, an E$''$ and a U$'$, while, although the $^6A_1$ does not split, it does transform as degenerate E$''$ and U$'$ levels under octahedral symmetry. Thus, there should be considerable mixing of levels in the vicinity of the crossover point of the d^5 system.

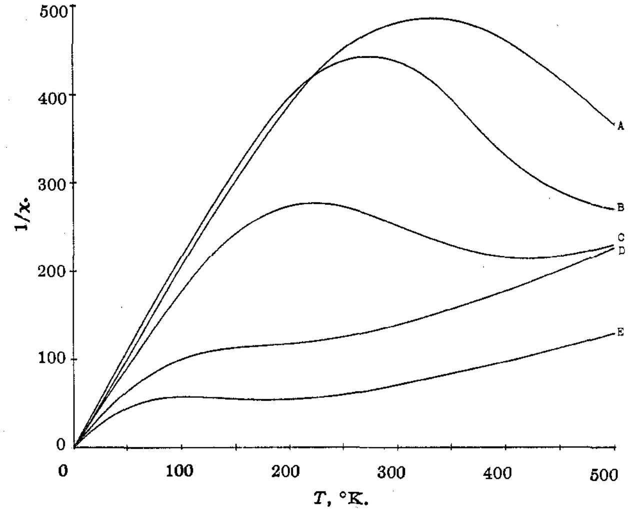

Figure 8.—χ^{-1} *vs.* T with δ = f(T). Parameters for curves given in Table IV.

TABLE IV

PARAMETERS OF EQ 9 USED TO CALCULATE THE CURVES OF FIGURE 8

Curve	δ_0	a	b	c
A	1000	−2.0	+8.0 × 10^{-3}	−1.4 × 10^{-5}
B	1000	0	−3.0 × 10^{-3}	−4 × 10^{-6}
C	500	0	−3.0 × 10^{-3}	−4 × 10^{-6}
D	100	−2.0	0	0
E	500	−6.0	0	+1.0 × 10^{-5}

From an examination of the curves of Figure 6, it is evident that, from a mathematical point of view, any factor which increases the proportion or importance of high-spin levels mixed into the ground level as the temperature increases will accentuate the curvature already present, even to the point of developing maxima and minima. This is essentially what reducing δ with increasing temperature accomplished for the d^7 model presented herein and what weighting the high-spin term with a ratio of partition functions accomplished for the d^5 model presented by Ewald, *et al.*

It is the authors' opinion that, at the present level of knowledge, the criterion that the crystal-field potential is a function of temperature stands out as an important factor causing the specific anomalous behavior of the cobalt(II) complexes. It is not unreasonable to suspect that this also applies to the anomalous iron(III) complexes and possibly other anomalous transition metal compounds. However, it is undoubtedly true that there are many contributing factors, some major and some minor, which could play a role in determining magnetic behavior. Ewald, *et al.*, investigated one of these; other possibilities include the effect of the electronic state on the metal–ligand distance, the effect of covalency, and the effect of distortions from octahedral symmetry.

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[18] A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.* (London), **A280**, 235 (1964).

In a transition from a low-spin to a high-spin term, it has been postulated that there will be an increase in the metal–ligand internuclear distance caused by an electron jumping from a t_2 orbital to an e orbital.[19] As a result, Δ will be different for different levels. However, a recent paper[20] investigating cobalt bond lengths has concluded that the spin state probably has only a very small effect on the metal ion radius. It is therefore concluded that, if differences in radii between the various levels is a factor at all, it is probably a minor one.

All the calculations presented in this work have been based on a simple crystal-field model which does not take into account any covalency which may be present. Evidence has been presented by Fisher and Stoufer[10] which indicates that the strong crystalline field present in these anomalous cobalt(II) compounds is the result of extensive π interaction. This implies a significant amount of covalent bonding. Since magnetic moments arise from orbital and spin angular momenta, it is the effect of covalency on these properties which could limit the usefulness of the calculations. However, a partial covalency due to an admixture of ligand orbitals into the metal ion wave functions will not change the number of unpaired electrons of a particular level, and hence will not alter the spin angular momentum. Additional orbital angular momentum will not be added, and so the total effect can only be further quenching of the orbital angular momentum associated with the metal ion. This has been partially taken into account by using a value for the spin–orbit coupling constant lower than its free-ion value. Furthermore, the actual magnitude of the crystal-field splitting, which is seriously affected by covalency, does not directly enter the calculations. Hence, although covalency is certainly present in these compounds, it is unlikely that it plays a significant role in determining their specific magnetic behavior.

Another very possible factor which must be considered is distortions from cubic symmetry. For the model presented herein, pure octahedral symmetry has been assumed, although some Jahn–Teller distortion might be expected. However, a study of the structure of the low-spin cobalt(II) compound $K_2Ba[Co(NO_2)_6]$ by Bertrand and Carpenter[21] reveals that the cobalt ion is surrounded by six nitrogens undistorted from octahedral geometry. The epr study of part IV[17] revealed an experimental g value around 2.1 for this compound and also for several of the anomalous compounds listed in Table I. In addition, Van Vleck[22] has shown that, if the low-symmetry matrix elements are small compared with kT, the average calculated susceptibility will not be very different if such low-symmetry elements are neglected entirely. The experimental values of the susceptibilities of the compounds listed in Table I were all taken from solid, microcrystalline materials; no single-crystal measurements have yet been made. Therefore, from an experimental point of view, any anisotropy present has been averaged. Thus, until single-crystal studies are made, the degree to which distortion from octahedral symmetry influences the magnetic behavior remains indeterminate. There is the possibility that such distortions are temperature dependent; this factor has been implicitly allowed for by assuming δ to be a function of temperature.

Thus, our basic model of an equilibrium mixture of several low-lying electronic levels, with the additional requirement that δ be a function of temperature, affords reasonable agreement with the experimental results. The exact nature and importance of this factor, as well as the other possible factors discussed herein and by Ewald, *et al.*, cannot be determined at this time. It remains for more detailed experimental data to give more explicit direction to an expanded theoretical treatment.

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[19] J. H. van Santen and J. S. van Wieringen, *Rec. Trav. Chim.*, **71**, 420 (1952).

[20] M. T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Commun.*, 307 (1966).

[21] J. A. Bertrand and D. A. Carpenter, *Inorg. Chem.*, **5**, 514 (1966).

[22] J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, Chapter 7.