The first excited state has a configuration [. . . $(b_{3g})(b_{1u})$] with symmetry B_{2u}.

Substituents on the chelate rings which remove electron density from the p_z orbitals of the bridging oxygen atoms decrease the b_{3g}–b_{1u} energy difference, give rise to molecules with destabilized singlet states, and consequently lower singlet–triplet splitting energies. Similarly, substituents which donate electron density increase the b_{3g}–b_{1u} splitting, stabilize the singlet state, and give rise to higher $|J|$ values.

Conclusions.—The following conclusions may be drawn from this study. The nature of the substituent and its relative position on the ligand greatly affect the magnetic properties of the dimeric compounds, and the effect is both electronic and steric in nature. Because of the complications, the data do not unambiguously support either mechanism of spin–spin coupling. However, the data for the [Cl, H, H] compound are very difficult to explain within the framework of the metal–metal bond model, since on the basis of this model, the singlet–triplet splitting energy should be equal to or lower than that observed for the unsubstituted compound with the same structure. That is not the case for [Cl, H, H]; the Néel temperature for the sample of this compound was approximately 80° higher than that of the unsubstituted compound.

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Complexes of Cobalt(II). I. On the Anomalous Magnetic Behavior of Some Six-Coordinate Cobalt(II) Complexes

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The average magnetic susceptibilities of ten related, six-coordinate microcrystalline cobalt (II) compounds have been determined between 100 and 500°K. One of these complexes is of the normal high-spin variety; nine exhibit room temperature magnetic moments lying below the range of values customarily found for high-spin, six-coordinate cobalt(II) systems but above that characterizing the low-spin systems. Six of the complexes having intermediate room temperature magnetic moments exhibit "anomalous" Curie–Weiss behavior. The observed behavior of the anomalous complexes is interpreted in terms of a Boltzmann distribution over thermally accessible levels characterized by different spin multiplicities. These six complexes provide the first examples of this type of behavior reported for cobalt(II) complexes.

Introduction

The six-coordinate complexes of cobalt(II) are usually high-spin with magnetic moments near 5 BM,[1,2] reflecting a large orbital contribution to the magnetic moment. The few six-coordinate, low-spin cobalt(II) complexes reported in the literature exhibit moments only slightly larger than the spin-only value of 1.7 BM, *viz.*, 1.9–2.0 BM.[1] Application of the crystal field theory leads one to expect that the octahedral complexes of a d^7 ion such as cobalt(II), formed by using an extended series of ligands having a sufficiently wide range of ligand field strengths, would be high-spin at the low-field limit and low-spin at the high-field limit. But, within a relatively small range of field strengths somewhere between the two extremes, the two states are expected to have comparable stabilities.[3]

Relevant data are rare, although there has been considerable speculation concerning the existence of a Boltzmann distribution of states characterized by more than one spin multiplicity in certain complexes with anomalous magnetic moments.[4–18]

A survey of values for the room-temperature magnetic moments of cobalt(II) complexes, presumably of coordination number six, reveals the existence of essentially no gaps in room temperature moment from about 1.8 to 5.2 BM,[16] and a number of those in the intermediate range must be considered unusual even when allowance is made for the partially quenched orbital angular momentum.

Intermediate room-temperature magnetic moments of cobalt(II) complexes could arise as a consequence of a combination of, or one of, the following: (1)

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(2) B. N. Figgis, *Nature*, **182**, 1569 (1958).

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(18) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Trans. Faraday Soc.*, **26**, 72 (1958).

an admixture of cobalt(III) complex with cobalt(II) complex; (2) a ferromagnetic impurity admixed with low-spin cobalt(II) complex; (3) an antiferromagnetic interaction in a high-spin complex; (4) a Boltzmann distribution over thermally accessible states of more than one spin multiplicity; and (5) a considerable amount of $^4T_1(^4F)$ character to the $^2E(^2G)$ level (or antithesis) permitted as a consequence of spin–orbit interaction. Each one of these possibilities will be considered in the light of the available experimental data.

The present authors have determined the magnetic susceptibility of a number of microcrystalline cobalt(II) complexes between 80 and 400°K. The ligands used to prepare these complexes contain unsaturated nitrogen donor atoms capable of forming π bonds with the metal ion.

The purpose of the present communication is threefold, *viz.*, (1) to present data pertaining to some magnetically anomalous crystalline complexes of cobalt(II), (2) to discuss the applicability to some of these systems of a model based on a Boltzmann distribution over thermally accessible levels of different spin multiplicities, and (3) to consider qualitatively the effect of spin–orbit coupling which may become very important in the vicinity of the crossover point between the $^4T_1(^4F)$ and $^2E(^2G)$ states.

Experimental Section

Magnetic Measurements.—The Gouy method was used to determine the magnetic susceptibilities of the complexes investigated. The magnetic field, calibrated with a standard solution of nickel chloride,[19] water,[19] and solid nickel ammonium sulfate hexahydrate,[20] was produced by means of a Varian Associates Model V 4004 4-in. electromagnet.

The transfer of certain samples to the Gouy sample tube was accomplished either under a stream of dry nitrogen or in a controlled atmosphere box to avoid the apparent degradation to unknown products which frequently occurred in air.

The temperature control apparatus and the cryostat employed in these measurements followed the basic design of Figgis and Nyholm.[21] The temperature of the sample could be controlled to within 0.1°K for an indefinite period of time over the range 80–500°K.

The precision with which the determination of magnetic moments of these samples was made is better than ±0.05 BM.

Sample Preparations and Analytical Data. Tris(biacetyldihydrazone)cobalt(II) Iodide.—This complex was prepared according to the method of Stoufer and Busch.[22] *Anal.* Calcd for $[Co(C_4H_{10}N_4)_3]I_2$: N, 25.65. Found: N, 25.95, 25.94.

Tris[biacetylbis(methylimine)]cobalt(II) Iodide Monohydrate.—This complex was prepared according to Figgins and Busch.[23] *Anal.* Calcd for $[Co(C_6H_{12}N_2)_3]I_2 \cdot H_2O$: C, 32.40; H, 5.74; N, 12.60. Found: C, 31.39; H, 4.27; N, 12.63.

Tris(2-pyridinalhydrazone)cobalt(II) Iodide.—The synthesis of this complex followed the method of Stoufer and Busch.[22] *Anal.* Calcd for $[Co(C_6H_7N_3]I_2$: C, 31.97; H, 3.13; N, 18.64. Found: C, 31.84; H, 3.40; N, 18.21.

Tris(2-pyridinalmethylimine)cobalt(II) Fluoroborate.—This complex was prepared according to the method of Figgins and Busch.[23] *Anal.* Calcd for $[Co(C_7H_8N_2)_3](BF_4)_2$: C, 42.52; H, 4.05; N, 14.18. Found: C, 42.36; H, 4.13; N, 14.16.

Bis(2,2′,2″-tripyridyl)cobalt(II) Perchlorate Monohydrate.—A sample of the complex was lent to us by Professor D. H. Busch of The Ohio State University. *Anal.* Calcd for $[Co(C_{15}H_{11}N_3)_2](ClO_4)_2 \cdot H_2O$: C, 48.53; H, 3.26; N, 11.32; Cl, 9.54. Found: C, 48.93; H, 3.50; N, 11.15; Cl, 9.50.

Bis(2,6-pyridindialdihydrazone)cobalt(II) Iodide.—The complex was prepared according to the manner of Stoufer and Busch.[22] *Anal.* Calcd for $[Co(C_7H_9N_5)_2]I_2$: C, 26.31; H, 2.84; N, 21.92. Found: C, 26.31; H, 2.64; N, 20.52.

Bis[2,6-pyridindialbis(benzylimine)]cobalt(II) Iodide.—The complex was prepared according to the manner of Lions and Martin[24] except that the crude product was dissolved in a minimum of water and a saturated solution of potassium iodide was added, causing the complex to crystallize from solution as the iodide salt. The dark brown needles were washed and dried in the manner described, mp 251°. *Anal.* Calcd for $[Co(C_{21}H_{19}N_3)_2]I_2$: C, 53.64; H, 4.03; N, 8.94. Found: C, 53.48; H, 3.19; N, 8.72.

Bis-1,3-bis(2-pyridyl)-2-azapropenecobalt(II) Perchlorate Monohydrate.—This complex was prepared according to the method of Lions and Martin.[24] *Anal.* Calcd for $[Co(C_{12}H_{11}N_3)_2(ClO_4)_2 \cdot H_2O$: C, 42.99; H, 3.58; N, 12.54. Found: C, 42.52; H, 3.48; N, 12.31.

1,12-Bis(2-pyridyl)-1,2,11,12-tetrakisaza-5,8-dithia-$\Delta^{2,10}$-dodecadienecobalt(II) Perchlorate.—This complex was prepared according to the method of Lions and Martin.[25] *Anal.* Calcd for $[Co(C_{16}H_{20}N_6S_2)](ClO_4)_2$: C, 31.07; H, 3.26; N, 13.59. Found: C, 30.83; H, 3.46; N, 13.40.

Analytical measurements were made by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Results

A summary of the magnetic moments of several crystalline cobalt(II) complexes investigated is given in Table I together with the corresponding Weiss constants when applicable.[26]

Table I

Magnetic Moments and θ Values for the Co(II) Compounds Studied

Complexes[a]	Reported μ_{eff} 300°K	Our obsd μ_{eff} 300°K	Our obsd μ_{eff} 100°K	θ (for normal complexes), deg
$[Co(BdH)_3]I_2$	4.17[22]	4.20	3.35	142
$[Co(BMI)_3]I_2 \cdot H_2O$	2.91[23]	2.91	1.91	Anomalous
$[Co(PAH)_3]I_2$	4.63[22]	4.71	4.06	19
$[Co(PMI)_3](BF_4)_2$	4.37[23]	4.31	2.16	Anomalous
$[Co(terpy)_2](ClO_4)_2 \cdot H_2O$		3.74	3.23	65
$[Co(terpy)_2](ClO_4)_2$	4.3[13]	...	...	...
$[Co(terpy)_2]Cl_2 \cdot H_2O$	2.1[13]	...	...	...
$[Co(terpy)_2]Br_2 \cdot H_2O$	2.7[13]	...	...	Anomalous[13]
$[Co(PdAdH)_2]I_2$	2.9[22]	2.85	2.22	Anomalous
$[Co(PBI)_2]I_2$	3.8[24]	3.72	2.38	Anomalous
$[Co(PPMI)_2(ClO_4)_2 \cdot H_2O$	4.3[24]	3.64	3.31	38
$[Co(DTPH)](ClO_4)_2$	2.50[25]	2.36	1.90	Anomalous

[a] The following abbreviations are used in Table I and throughout the remainder of the text: BdH, biacetyldihydrazone; BMI, biacetylbis(methylimine); PdAdH, 2,6-pyridindialdihydrazone; PMI, 2-pyridinalmethylimine; PBI, 2,6-pyridindialbis(benzylimine); terpy, 2,2′,2″-terpyridine; PAH, 2-pyridinalhydrazone; DTPH, 1,12-bis(2-pyridyl)-1,2,11,12-tetrakisaza-5,8-dithia-$\Delta^{2,10}$-dodecadiene; PPMI, 1,3-bis(2-pyridyl)-2-azapropene.

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[21] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

[22] R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc.*, **78**, 6016 (1956).

[23] P. E. Figgins and D. H. Busch, *ibid.*, **82**, 820 (1960).

[24] F. Lions and K. Martin, *ibid.*, **79**, 2736 (1957).

[25] F. Lions and K. Martin, *ibid.*, **80**, 3858 (1958).

[26] A tabulation of molar susceptibilities, magnetic moments, and corresponding temperatures has been deposited as Document No. 8821 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $2.50 for photoprints or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

The inverse of the corrected molar susceptibility *vs.* temperature curves ($1/X_c = T/C + \theta/C$) for these nine compounds are presented in Figures 1 and 2. Examination of these figures reveals that only one of the complexes investigated exhibiting intermediate magnetic moments, *viz.*, $[Co(terpy)_2](ClO_4)_2 \cdot H_2O$, follows the normal Curie–Weiss behavior. The remaining complexes characterized by intermediate room-temperature moments exhibit anomalous Curie–Weiss behavior, Figure 2.

Discussion

Possible Explanations.—The magnetic susceptibilities of cobalt(II) complexes containing the structural group $-N{=}\overset{|}{C}{-}\overset{|}{C}{=}N-$ have been reported customarily at room temperature only although complexes of this type have been investigated extensively.[1,13,22–25,27–35] However, by comparison with relevant data, the magnetic behavior of some of the complexes discussed herein is unique (Table I and Figures 1 and 2). Therefore, the applicability of the several factors presented in the Introduction as possible causes of intermediate room-temperature magnetic moments will be examined in the light of these data.

The admixing of cobalt(III) complex with high-spin cobalt(II) complex (arising as a consequence of air oxidation) would cause the observed magnetic moment, calculated on the basis of cobalt(II) complex, to lie considerably below the range of high-spin values encountered most frequently, for any admixed cobalt(III) complex would certainly be of the low-spin variety; however, such a mixture would be detected by routine chemical analysis in most instances as well as by means of other physical measurements. For example, such a mixture should exhibit normal Curie–Weiss behavior. Thus, because of the care taken to prevent atmospheric oxidation during the preparation and handling of these complexes, and on the basis of the analytical data included in this paper and the deviation from Curie–Weiss behavior exhibited by all but two of the complexes having intermediate room-temperature moments, the existence of a mixture of cobalt(III) complex with cobalt(II) complex is precluded.

The presence of *ferromagnetic impurity* in a complex renders the observed magnetic susceptibility dependent upon the field strength used to make the determination. The magnetic moments of the complexes listed in Table I are uniformly independent of field strength and, therefore, the possibility of ferromagnetic interaction is excluded.

Antiferromagnetic interactions would cause deviations from the normal Curie–Weiss behavior only below the transition temperature (Neel point) of the sample. Thus, below the transition temperature the magnetic susceptibility should increase as the temperature increases, *i.e.*, the reciprocal of the magnetic susceptibility should decrease with increasing temperature. Clearly, the curves presented in Figure 3 do not bear these general features; therefore, one can conclude that antiferromagnetism is not the cause of the peculiar magnetic behavior of these cobalt(II) complexes.

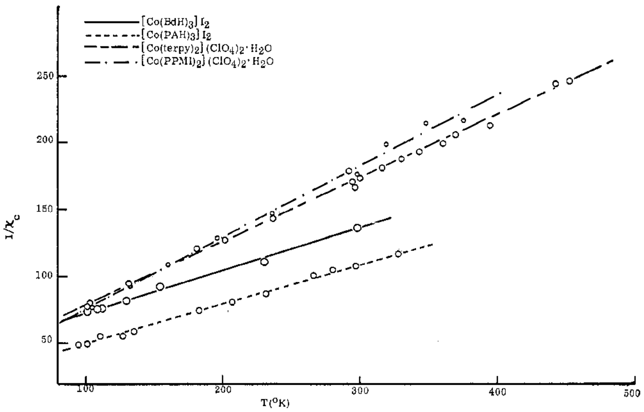

Figure 1. Inverse of corrected molar susceptibility *vs.* temperature.

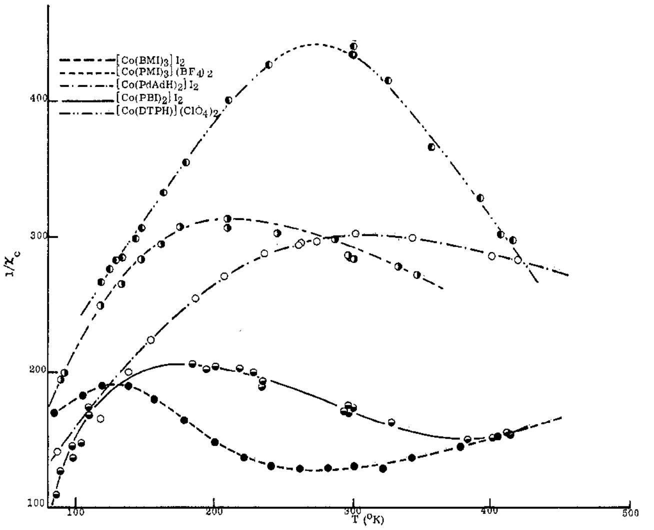

Figure 2.—Inverse of corrected molar susceptibility *vs.* temperature.

The remaining possibilities, *viz.*, *a Boltzmann distribution over different spin states and a mixing of* $^4T_1(^4F)$ *and* $^2E(^2G)$ *states*, both factors arising from spin–orbit interaction, merit careful consideration.

Two-Level Model.—A very simple model for these anomalous systems, based on an equilibrium mixture of two spin states (quartet and doublet) and ignoring the effects of spin–orbit coupling, leads to rather gratifying results.[15,36] By assuming a low-spin magnetic moment between 1.8 and 2.0 BM and a high-spin magnetic moment between 4.8 and 5.2 BM, the mole fraction of each of the two states was calculated for each temperature at which a determination was made.

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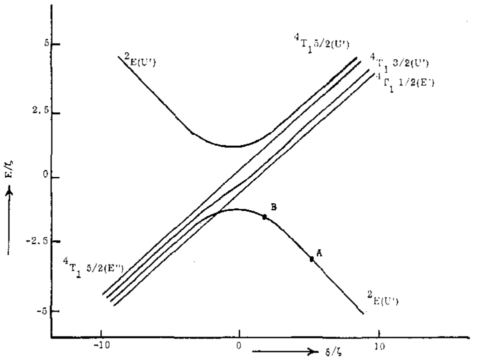

Figure 3.—Behavior of multiplets as Δ passes through crossing points. δ is the energy difference between $^4T_1$ and ^2E in the absence of spin–orbit coupling, and ζ is the one-electron spin–orbit coupling parameter.

A plot of ln K as a function of $1/T$ for the reaction

$$\text{high spin } (^4T_1) \rightleftarrows \text{low spin } (^2E)$$

results in curves which, in some instances, are linear over a temperature range of more than 150°K. For each plot, however, there exists a temperature region in which severe curvature is noted; the plots are linear above and below this region. The values of $\Delta H°$ calculated from the slope of the linear portions of these curves for the non-Curie–Weiss complexes are within the range -0.2 to -5 kcal/mole (negative in every instance), indicating that the $^2E(^2G)$ state is the one of lower energy. It will be noted from Table I that the low-temperature magnetic moments of the anomalous complexes lie close to the spin-only value for $S = {}^1/_2$. The $\Delta S°$ values are, in most instances, negative (from -1 to -9 eu), which is consistent with the decrease in multiplicity of states accompanying the transition from the high-spin levels to the low-spin level and the possible decrease in ionic volume. Nonetheless, this model is, at best, very inaccurate. Certainly little quantitative significance can be attached to it. The observed behavior is too complex to account for on the basis of this simple model. It would appear that the susceptibility of either the high-spin state and/or the low-spin state must be temperature dependent;[2,13] but inclusion of spin–orbit coupling, insofar as it splits the $^4T_1(^4F)$ state,[3] rendering the reference moment of the quartet state temperature dependent, does not greatly alter the fit of the data above 80°K.[36]

Spin–Orbit Coupling Effects.—Spin–orbit coupling in cobalt(II) complexes has been discussed by Abragam and Pryce,[37] who consider the mixing of $^4T_1(^4F)$ with $^4T_1(^4P)$. In the vicinity of the crossover point between $^4T_1(^4F)$ and $^2E(^2G)$, the mixing of these levels becomes the dominant feature of the energy level diagram.[38] This situation is represented in Figure 3, where the effects of low-symmetry components of the field have been neglected as a first approximation. Thus, in the vicinity of the crossover point there may exist a distribution over five levels characterized by different spin multiplicities. The resulting magnetic behavior would not be a simple function of temperature as is predicted by the two-level model.

It is interesting to note that anharmonic vibrations may also contribute to deviations from normal paramagnetic behavior. Thus, with an increase in temperature, an anharmonicity of the potential surface would tend to increase the average metal–donor distance and thereby decrease Δ. As a consequence, the electronic ground level at low temperatures may correspond to point A in Figure 3, while as the temperature is raised, the corresponding point would move toward B, thereby increasing the quartet character of the level.

Ligand Basicity.—The effectiveness of the α-dimine type ligands is attributable, in part, to their ability to participate in dπ–pπ bonding with the metal ion. In the case of the dipositive ions of the group VIII elements, this involves the delocalization of metal electrons toward the π system of the ligands. It has been suggested that it is just this type of interaction which tips the scales in favor of the formation of low-spin octahedral iron(II) complexes.[11] The analogous nickel(II) complexes are high spin.[1,13,22–25,27–35] This observation is consistent with the fact that the pairing energy increases in the series iron(II), cobalt(II), nickel(II). The pairing energy for iron(II) in complexes involving the ligands of the dimethine type has been estimated by Busch, *et al.*,[34] to lie between 13,000 and 13,740 cm^{-1}, whereas that of cobalt(II) is expected to lie some 2000–3000 cm^{-1} higher.[39]

The magnitude of the crystal field splitting produced by ligands containing the dimethine group in cobalt(II) complexes has been reported in only a few instances; however, it is possible to obtain an estimate of the splitting from consideration of analogous nickel(II) complexes in which, with surprising uniformity, the magnitude of Δ is usually found to lie between 12,500 and 12,700 cm^{-1}.[33] All large deviations from this range can be attributed to steric effects. By considering these data and the relative magnitudes of the splitting in analogous nickel(II) and cobalt(II) complexes[40–42] we conclude that the splitting for cobalt(II) complexes will be no smaller than that for the nickel(II) analogs and perhaps as much as 10% greater, *i.e.*, a reasonable upper limit for Δ might be fixed at 14,000 cm^{-1}. Thus, it appears that the maximum expected splitting for cobalt(II) complexes involving unsaturated nitrogen atoms is insufficient to cause pairing of spins in a *regular* octahedral environment. There is some indication, however, that on the basis of qualitative arguments this apparent discrepancy can be resolved by a tetragonal distortion of the octahedral geometry.[30]

Pseudo-Tetragonal Distortion.—The limiting case

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[37] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.* (London), **A206**, 173 (1951).

[38] A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

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[41] D. H. Busch, private communication.

[42] Unpublished results.

of a tetragonal distortion in which the ligand donor atoms are drawn away from the metal atom along the z axis is the square plane. Although there have been reported a few high-spin planar complexes of cobalt(II) (involving either four oxygen or four sulfur donor atoms), the majority of the cobalt(II) complexes which are believed to be square-planar are of the low-spin variety.[43,44] On this basis, it is reasonable to expect that as the tetragonal distortion increases in the sense of decreasing effective basicity along the unique axis, the possibility of electron pairing is enhanced.

There are two factors which should contribute to a pseudo-tetragonal distortion of these complexes, *viz.*, the Jahn-Teller effect and the symmetry of the ligands used in preparation of the complexes. The Jahn-Teller distortion is expected to be greater for the low-spin complex than for the high-spin complex because in the former case the degeneracy occurs in antibonding orbitals, whereas in the latter case it occurs in "nonbonding" orbitals. In fact, as a consequence of this difference in the pseudo-tetragonal distortion of the high-spin complex and the low-spin complex it may be impossible to produce a smooth transition from high-spin complex to low-spin complex by increasing ligand basicity.

A comparison of the ligands which form the magnetically normal complexes with those which form the magnetically abnormal ones reveals that, with one exception, the ligands of the latter group are either tridentate or hexadentate.[30] In the case of the planar tridentate ligands, the acyclic imine nitrogen atoms lie in a plane about the metal ion, while the heterocyclic amine (pyridine) nitrogen atoms lie above and below the plane defining a unique axis. A similar situation exists in the case of the one hexafunctional ligand (DTPH) containing two sulfur and four unsaturated nitrogen donor atoms. It is significant to note that one of the few six-coordinate cobalt(II) complexes that is reported to be low spin contains the planar tridentate ligand 2,6-pyridindialbis(methylimine).[30] This ligand molecule is very similar to the ligands 2,6-pyridindialdihydrazone, 2,2′,2′′-terpyridine, etc., studied during the course of this investigation.

Solid-State Effects.—Other important factors operative in these systems influencing the observed behavior are related to crystal geometry, *i.e.*, mismatch of ion size, imbalance of attractive power, etc. These factors have been discussed by Liehr.[38] Relevant examples are found within the present series of complexes. Wilkins, *et al.*, have reported that the magnetic susceptibility of bis(terpyridine)cobalt(II) bromide monohydrate is anomalous; this observation has been confirmed in our laboratory.[42] Furthermore, we have found the chloride salt pentahydrate (3.22 BM at 300°K) to be magnetically anomalous.[42] Additional environmental effects produced by near neighbors of the coordination polyhedra in the crystalline state are illustrated by the fact that the room-temperature magnetic moment of the perchlorate salt monohydrate is different from that reported for the anhydrous salt (3.74 and 4.3 BM, respectively). The perchlorate salt monohydrate exhibits normal Curie-Weiss behavior although it is characterized by a rather low room-temperature magnetic moment and a rather large Weiss constant (Table I).

Summary

Three of the nine complexes of cobalt(II) investigated and characterized by intermediate room-temperature magnetic moments, *viz.*, $[Co(BdH)_3]I_2$, $[Co(terpy)_2](ClO_4)_2 \cdot H_2O$, and $[Co(PPMI)_2](ClO_4)_2 \cdot H_2O$, exhibit normal Curie-Weiss behavior. Of these, $[Co(terpy)_2](ClO_4)_2 \cdot H_2O$ is characterized by a room-temperature magnetic moment slightly below the spin-only value for a high-spin d^7 ion. The other two complexes have larger Weiss constants than usually encountered for magnetically simple octahedral cobalt(II) complexes[1] (Table I), represented within this series by $[Co(PAH)_3](BF_4)_2$. The large Weiss constant of $[Co(BdH)_3]I_2$, $\theta = 142°$, suggests an antiferromagnetic interaction; however, considerable doubt is cast upon an explanation involving antiferromagnetic interactions because of the similarity of this complex to the anomalous members of the series for which we can exclude the antiferromagnetic interaction.

We are unable at the present time to assess the (subtle) factors leading to relatively large differences in the magnetic properties of the several compounds investigated, produced, apparently, by relatively small changes in the nature of the ligand molecules. Clearly, the data provide evidence for a solid-state effect within the terpyridine systems. Indeed, it is possible that the observations reported herein are principally attributable to solid-state effects. Nonetheless, the properties of the six complexes exhibiting intermediate room-temperature magnetic moments and anomalous Curie-Weiss behavior are consistent with only one of the several possible explanations discussed, *viz.*, the existence of a Boltzmann distribution over several thermally accessible levels arising from unperturbed levels of different spin multiplicities, spin-orbit coupling having been taken into account as a perturbation. This model arises as a natural consequence of the application of the ligand field theory to cobalt(II) systems in moderately strong ligand fields. Multiple bonding involving the unsaturated ligand nitrogen donor atoms and the metal ion is probably an important factor in reducing the electron-electron repulsions on the metal and, hence, in lowering the energy required to pair electron spins. Should an axial distortion be important in bringing these systems near the crossover point, the model proposed would, in principle, be correct; however, it would become very much more complicated in detail.

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