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Complexes of Cobalt(II). IV. On the Electron Paramagnetic Resonance Spectra of Some Magnetically Anomalous Complexes of Cobalt(II)

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The electron paramagnetic resonance spectra of ten microcrystalline six-coordinate cobalt(II) compounds have been obtained over an extended temperature range. The majority of the complexes exhibit intermediate room-temperature magnetic moments and either anomalous Curie-Weiss behavior or rather large Weiss constants. The epr spectra of these compounds (including the low-spin standard) arise from transitions between the Zeeman states of the 2E level of cobalt(II) and are characterized by g values lying between 2.07 and 2.14. These spectra are the first reported to arise from transitions between the states of the ${}^2E(G)$ level of cobalt(II). Hyperfine splitting is observed in the solution spectra.

Introduction

One class of cobalt(II) compounds, containing a rapidly growing number of examples and in which the metal ions are presumably of coordination number six, exhibits an unusually large temperature dependence of the magnetic susceptibility.^{1,2} The room-temperature moments of those compounds are distributed throughout the range from those moments expected for low-spin octahedral complexes to those moments expected for high-spin octahedral complexes. Some of these complexes exhibit normal Curie-Weiss constants, the magnitude of which has been unexplained, whereas others of the group exhibit anomalous Curie-Weiss behavior.³

Several investigators have proposed the existence of an equilibrium mixture of levels characterized by more than one spin multiplicity to account for the anomalous behavior of these cobalt complexes¹⁻³ as well as that of some complexes of nickel⁴⁻⁷ and iron.⁸⁻¹⁰ Support for this proposal was found by Gibson, *et al.*, in the epr studies on methaemoglobin hydroxide.¹¹ Certainly, the epr technique, if experimentally applicable is frequently capable of providing more direct information concerning the nature of the lowest lying level of a system than does the measurement of average magnetic susceptibilities.

In principle, the epr spectrum of a system in which there exists a Boltzmann distribution over levels characterized by different spin multiplicities would be a composite of the spectrum resulting from transitions within each level populated at the temperature of measurement. Unfortunately, few pertinent data exist, characterizing the limiting types (high-spin and low-

spin) of microcrystalline cobalt(II) complex. These data could be used to help achieve a better understanding of the magnetically anomalous cobalt(II) compounds.

Nearly all of the epr work reported to the present time concerning octahedral cobalt(II) ions has utilized magnetically dilute single crystals, *e.g.*, Co^{2+} ions in MgO host, and has been carried out at very low temperatures. In the absence of trace impurities contributing to a rapid relaxation, the absorption peaks are rather narrow in most instances. Understandably, there are no reports in the literature pertaining to epr studies of cobalt(II) compounds conducted at room temperature because, at temperatures well above that of liquid helium, the epr absorption becomes so broad as to escape detection by the epr equipment. Presumably the broadening arises from a decrease in the spin-lattice relaxation time, T_1 , which accompanies either an increase in temperature or an increase in orbital contribution to the magnetic susceptibility. There are no data in the literature pertinent to low-spin cobalt(II) compounds; however, less broadening is expected for the epr absorption attributable to the 2E level because of the small orbital contribution to the total angular momentum of the system. Thus, between liquid nitrogen temperature and room temperature it is anticipated that only the 2E absorption will be detected in those compounds which represent the type of equilibrium mixture of levels described.

The present paper reports results got from an epr investigation of ten microcrystalline six-coordinate cobalt(II) compounds, some of which exhibit anomalous Curie-Weiss behavior and for which an equilibrium mixture of high-spin and low-spin complexes has been suggested.

Results and Discussion

Epr Spectra of Microcrystalline Compounds.—Of the compounds investigated (Table I), $[Co(o\text{-phen})_2](ClO_4)_2$ was selected to serve as a representative high-spin complex; only this complex had a spectrum characteristic of octahedral high-spin cobalt(II). The spectrum of the microcrystalline solid yields a g value of 4.2 ± 0.1 , identical within experimental error with that

- (1) R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc.*, **78**, 6016 (1956).
- (2) R. C. Stoufer, W. B. Hadley, and D. H. Busch, *ibid.*, **83**, 3732 (1961).
- (3) R. C. Stoufer, D. W. Smith, E. A. Clevenger, and T. E. Norris, *Inorg. Chem.*, **5**, 1167 (1966); H. M. Fisher and R. C. Stoufer, *ibid.*, **5**, 1172 (1966).
- (4) L. Sacconi, R. Cini, J. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).
- (5) C. J. Ballhausen and A. D. Liehr, *ibid.*, **81**, 538 (1959).
- (6) R. H. Holm and T. M. McKinney, *ibid.*, **82**, 5506 (1960).
- (7) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 379 (1964).
- (8) L. Cambi and L. Szego, *Ber.*, **66B**, 656 (1933).
- (9) J. S. Griffith, *J. Inorg. Nucl. Chem.*, **2**, 229 (1956).
- (10) A. H. White, R. Roper, E. Kokot, H. Waterman, and R. L. Martin, *Australian J. Chem.*, **17**, 294 (1964).
- (11) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discussions Faraday Soc.*, **26**, 72 (1958).

TABLE I
 MAGNETIC DATA FOR COBALT COMPOUNDS

Compound ^a	T, °K	Normal-ized signal intensity	Sweep, kgauss	Half-width, gauss	μ_{epr} , BM	μ_{eff} , BM	θ , °K	% ² E
K ₂ Ba[Co(NO ₂) ₆]·H ₂ O	113	1548 ^b	1.0	72	1.84	1.7 ^c	125	100 ^b
	413	1692	1.0	400	1.84	1.9 ^c
[Co(PBI) ₂] ₂ I ₂	113	1364	2.5	177	1.80	2.40	...	91
	303	202	10.0	2446	1.80	3.77	...	11
[Co(PvdH) ₃] ₂ Br ₂	113	1128	10.0	220	1.84	2.92	...	71
	223	153	10.0	280	1.84	3.95	...	5
[Co(PMI) ₃](BF ₄) ₂	113	1412	2.5	310	1.81	2.19	...	91
	243	156	10.0	1460	1.81	3.86	...	11
[Co(terpy) ₂] ₂ Cl ₂ ·5H ₂ O	113	1310	2.5	112	1.80	2.10	...	99
	293	966	10.0	1262	1.80	2.50	...	60
[Co(terpy) ₂] ₂ Br ₂ ·H ₂ O	113	1578	2.5	300	1.80	1.83	...	99
	313	223	10.0	2200	1.80	2.76	...	13
[Co(terpy) ₂](ClO ₄) ₂ ·H ₂ O	113	670	2.5	380	1.79	3.27	65	42
	303	81	10.0	584	1.79	3.75	...	5
[Co(PAH) ₃] ₂ I ₂	113	374	10.0	460	1.84	4.22	19	24
	203	103	10.0	700	1.84	4.52	...	7
[Co(BdH) ₃] ₂ I ₂	113	1040	10.0	360	1.85	3.45	142	76
	183	299	10.0	2800	1.85	4.14	...	20
[Co(o-phen) ₃](ClO ₄) ₂	113	5.5 ¹⁶

^a The following abbreviations are used throughout this paper: PBI, 2,6-pyridindialbis(benzilimine); PvdH, pyruvaldihydrazone; PMI, 2-pyridinalmethylimine; terpy, 2,2',2''-terpyridine; PAH, 2-pyridinalhydrazone; BdH, biacetyldihydrazone; o-phen, 1,10-phenanthroline. ^b Taken as basis for calculation. ^c B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

of cobalt(II) ions located in octahedral sites in a MgO lattice.¹²⁻¹⁵ An isotropic value of 4 is expected in the strong-field limit and of 4.333 in the weak-field limit for the $S' = 1/2$ level of the octahedral high-spin d^7 ion. The absorption is very broad between 113 and 143°K requiring high signal amplification and becoming hardly distinguishable from the base line at higher temperatures.

Of the nine remaining complexes, several exhibit anomalous Curie-Weiss behavior. Two exhibit normal Curie-Weiss behavior but have larger than normal Weiss constants. One compound, [Co(PAH)₃]₂I₂, exhibits both a normal Curie-Weiss behavior and a reasonably small Weiss constant (19°). In contrast to the o-phen complex, however, these microcrystalline compounds have g values in the range 2.07-2.14, rather close to the spin-only value of 2.00229 and the isotropic value of 2 predicted for the ²E level.

The complex K₂Ba[Co(NO₂)₆]·H₂O, selected as a representative low-spin complex, exhibits an average magnetic susceptibility consistent with that expected for such a complex.¹⁶ This observation is entirely consistent with the consistency of the g value and of the normalized relative signal intensity (as defined below) we have observed over a 310° temperature range. Because of the close correspondence of the spectra of the remaining compounds to that of the low-spin standard, no doubt there exists population of the ²E level in each of these complexes. The effective magnetic moment got from average susceptibility data, the low-spin moment calculated from the epr data,

and the normalized relative signal intensity data for the complexes investigated are reported in Table I.

The low-spin magnetic moment for each compound characterized by the low-spin absorption was obtained by using the expression $\mu_{\text{epr}} = g[S'(S' + 1)]^{1/2}$ where $S' = 1/2$ for the ²E level. The average of the g values obtained for each complex over the smallest sweep range was taken to represent the best g value.

The magnetic moment of K₂Ba[Co(NO₂)₆]·H₂O calculated from the epr data, 1.84 BM, is the same as that obtained at room temperature in this laboratory from magnetic susceptibility data and, of course, is constant over the temperature range studied, 113-423°K. From susceptibility measurements, Figgis and Nyholm¹⁶ report a uniform variation of the effective magnetic moment from 1.73 BM at 90°K to 1.88 BM at 300°K. The small discrepancy between the epr moment and the moment got from susceptibility measurements may result from interaction between neighboring magnetic dipoles. These effects are observed as exchange narrowing and exchange broadening of the epr spectrum without a change in g value, and thus μ_{epr} would remain invariant, whereas these same effects would influence the average magnetic susceptibility.

The μ_{epr} values calculated for the remaining complexes vary from 1.85 to 1.79 BM. The accuracy of these moments is dependent upon the accuracy with which g values may be determined. The epr absorption for the low-spin standard is narrower than those of the other compounds and broadens but little as the temperature is increased. For this complex and for the MnSO₄·H₂O the absorption remains relatively narrow over the entire temperature range and the g value of each is invariant, *i.e.*, $g = 2.00 \pm 0.01$. The g values of the remaining complexes are more uncertain, how-

(12) W. Low, "Paramagnetic Resonance in Solids," Academic Press Inc., New York, N. Y., 1960.

(13) W. Low, *Phys. Rev.*, **108**, 256 (1958).

(14) W. Low and D. Shaltiel, *J. Phys. Chem. Solids*, **6**, 315 (1958).

(15) M. H. L. Pryce and H. H. Wills, *Proc. Roy. Soc. (London)*, **288**, 433 (1965).

(16) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

ever, because of the fact that the width of the characteristic absorption increases considerably as the temperature is increased. This broadening required an increase in signal amplification which, in turn, resulted in an observable drift of the base line. Thus, the location of the intercept of the first-derivative curve (corresponding to the maximum of the absorption curve) with the base line becomes correspondingly less precise. Nonetheless, within experimental error no variation of g value with changing temperature is observed for these complexes.

The approximate concentration of 2E level can, in principle, be calculated from the average normalized signal intensity of the standard compound and the corresponding data for the other compounds in which the 2E level is either of lowest energy or thermally accessible; the per cent low-spin level for each complex was calculated for each temperature at which a measurement was made. The values corresponding to the temperature extremes are recorded in Table I. The values range from a high of 99% 2E level for $[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ and $[\text{Co}(\text{terpy})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$ at 113°K to a low of 4.7% 2E level for $[\text{Co}(\text{PAH})_3]\text{Br}_2$ at 223°K. The maximum change in per cent 2E level, over which the temperature range data could be obtained, is found in the case of $[\text{Co}(\text{terpy})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$ which is approximately 99% 2E level at 113°K, but only 13% at 313°.

Consideration of the change in the relative normalized signal intensity of the absorption associated with the 2E level for all of the complexes which exhibit anomalous Curie-Weiss behavior reveals that there is a considerable decrease in population of the 2E level as the temperature increases. In fact, the rate at which the effective magnetic moment (got from average susceptibility data) increases with increasing temperature is very similar to that at which the corresponding signal intensity decreases. One example of these variations for such a system is provided in Figure 1 which represents the variation of effective magnetic moment and relative normalized signal intensity with temperature for the complex $[\text{Co}(\text{PMI})_3](\text{BF}_4)_2$.

It is possible to calculate the contribution to the average effective magnetic moment of the high-spin levels, at a particular temperature, from a knowledge of the average moment and the low-spin moment and by assuming that these contributions are additive. These calculations were carried out, and the average energy difference between these levels was estimated. Acceptance of the resulting data as correct leads to the inescapable conclusion that, for all of the complexes exhibiting anomalous Curie-Weiss behavior, the 2E level is of lowest energy at the lower temperatures whereas it lies above the $^4T_1(1/2)$ level at higher temperatures. Indeed, this inference may find correspondence to reality. Relatively little is known about the variation of Δ as a function of temperature^{17,18} and nothing has been published concerning the varia-

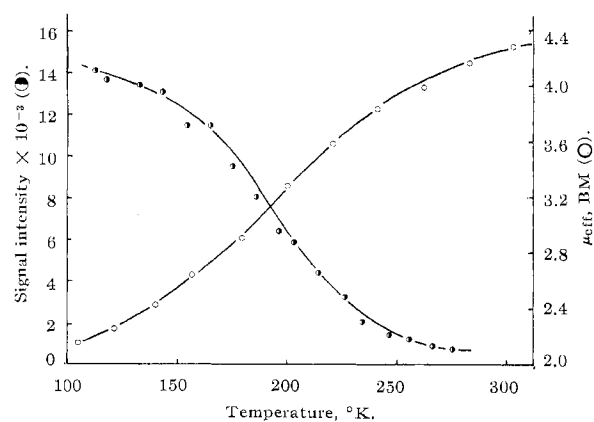


Figure 1.—Temperature dependence of the magnetic moment and normalized epr signal intensity of $[\text{Co}(\text{PMI})_3](\text{BF}_4)_2$.

tion of Δ in the vicinity of the crossover point; however, we believe that these values of the per cent 2E level contain a large and systematic error which increases with increasing temperature because of the broadening of the absorption; *i.e.*, the relative normalized signal intensities progressively decrease more rapidly than the population of 2E level although g remains constant.

It is not a simple matter to assess the reasons for the broadening of the absorption of the complexes of interest because the half-width of the low-spin standard remains reasonably constant over the entire temperature range. Thus, it appears that the broadening does not arise from the interaction of like spins. It may be, however, that as the 2E level loses population density to the 4T_1 level, the effect of the larger moments is to broaden the resonance of the 2E complexes which remain. With peak broadening, it becomes increasingly difficult to measure accurately the area in the "tails" of the absorption.

An alternative explanation can be found by consideration of rates of interconversion of the two spin states. If $^2E \xrightleftharpoons[k_{-1}]{k_1} ^4T_1$, k_1/k_{-1} , and also k_1 increase at higher temperatures, the average lifetime of a Co(II) in the E state decreases; if k_1 becomes comparable to the width of the epr spectrum, broadening will result.

Epr Spectra of Solutions.—It was suggested in a previous paper³ that one could not exclude the possibility that the anomalous Curie-Weiss behavior characterizing a number of these cobalt(II) compounds might be attributed principally to solid-state effects. In fact, data were presented to demonstrate the fact that solid-state effects are responsible for rather large apparent changes in the magnetic properties of certain of these complexes. Some illustrative data are found in Table I; *viz.*, both the magnitude of the magnetic susceptibility (moment) and the nature of its variation with temperature for the several salts containing the bis(terpyridine)cobalt cation vary significantly from salt to salt.^{19,20} For this reason we have applied the epr technique to solutions of several

(17) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **27**, 707 (1957).

(18) W. M. Walsh, Jr., J. Juner, and N. Bloembergen, *Phys. Rev.*, **139**, 1338 (1965).

(19) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962).

(20) H. M. Fisher and R. C. Stouffer, submitted.

magnetically anomalous complexes, employing both methanol and dimethyl sulfoxide as solvent. Absorptions were observed near and below the temperatures at which the solutions became viscous and are independent of the solvent; *i.e.*, both methanol dimethyl sulfoxide solutions of a given compound have spectra corresponding to the same g value ($g = 2.1 \pm 0.1$) and to the same half-width at a given temperature. More important, however, is the fact that the several different salts of the terpyridine complex, exhibiting rather large differences in absorption half-width and signal intensity when in microcrystalline form, have solution epr spectra which are essentially identical. Therefore, we conclude that in these systems the cobalt(II) ion has been brought near the crossover point by the nitrogen-containing ligand molecules so that the 2E level is either thermally accessible or of lowest energy. The pairing of electrons is made possible by a reduction of the pairing energy in the complex to about 75% of the free-ion value. This reduction is most probably associated with the metal-ligand π bonding tendency to shift metal electrons toward the available ligand orbitals thereby decreasing electron-electron repulsions.

Near liquid nitrogen temperature, the solution spectra exhibit hyperfine splitting into eight components. This hyperfine splitting arises from the interaction of electron spin with the nuclear spin of $7/2$ of ^{59}Co . The splitting of the principal absorption disappeared gradually as the temperature was increased although the principal absorption persisted to temperatures above those at which the glassy solutions became fluid and absorption of the microwave energy by the solvent became a distinct problem. No attempt was made to obtain the areas under the solution absorptions.

Although the mixture of cobalt ions in 2E and 4T_1 levels is expected, in principal, to result in a composite spectrum (*vide anterior*), the spectra obtained demonstrate that the contribution to the spectrum from ions in the $^4T_1(1/2)$ level is spread over such a very broad range of magnetic field strengths that the contribution at any given field strength is negligible.

Experimental Section

Magnetic Measurements.—A Varian Associates epr spectrometer system, V-4502-14, was used for this investigation consisting of a V-4501 console, a V-4500-41A microwave bridge, a V-4500 100-kc field modulation and control unit, a V-3610 12-in. magnet, and a V-Fr2503 magnetic power supply. A V-4531 multipurpose cavity was used in combination with a variable-temperature accessory.

All spectra obtained were over a time lapse of 5 min and at a constant field modulation amplitude of 800. Room-temperature dry nitrogen gas was passed through the cavity to prevent condensation of water within the cavity walls.

The temperature-dependent epr spectrum for $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, obtained over a 300° temperature range, was taken as a standard

for obtaining the g value of all the compounds investigated. Experimental g values are based on a g value of 2.00 for the $\text{MnSO}_4 \cdot \text{H}_2\text{O}$.

Experimental signal intensities were obtained by numerical integration of the first-derivative curves of the absorptions. The actual areas calculated were subsequently corrected for sweep and signal amplitude before being multiplied by the absolute temperature to obtain the *signal intensity*. These experimental intensities were subsequently normalized to a total paramagnetic ion concentration of 10^{-4} mole/in. of sample. The average of the relative normalized *signal intensities* for $\text{K}_2\text{Ba}[\text{Co}(\text{NO}_2)_6]$ was taken as the reference signal intensity for 10^{-4} mole/in. of cobalt(II) complex in the 2E level.

Each sample was packed as uniformly as possible in a sample tube either within a stream of dry nitrogen gas or within a controlled-atmosphere box to avoid oxidation of the sample. Measurement of the height and mass of the sample in the tube enables one to calculate sample concentration in mole per inch. Each sample tube was closed with a plastic plug and sealed with wax.

Magnetic susceptibilities were obtained by the Gouy method using equipment described previously.³

Sample Preparation. Dipotassium Barium Hexanitrocobaltate(II) Monohydrate, $\text{K}_2\text{Ba}[\text{Co}(\text{NO}_2)_6] \cdot \text{H}_2\text{O}$.—This complex was prepared according to the method of Cuttica.²¹ Special precautions were taken to prevent air oxidation. The desired dark green complex exhibits a room-temperature magnetic moment of 1.84 BM. The effective moment reported by Figgis and Nyholm at 296° K is 1.87 BM.¹⁶

Tris(biacetyldihydrazone)cobalt(II) Iodide, $[\text{Co}(\text{PAH})_3]\text{I}_2$.—This complex was prepared according to the manner of Stouffer and Busch,¹ who reported an effective moment at 300°K of 4.63. The room-temperature magnetic moment previously obtained in this laboratory³ was 4.71 BM. The experimental moment obtained for the sample used in this investigation was 4.69.

Bis[2,6-pyridindialbis(benzylimine)]cobalt(II) Iodide, $[\text{Co}(\text{PBI})_2]\text{I}_2$.—The complex was prepared by the method of Lions and Martin.²² The effective moment reported by Lions and Martin was 3.8 BM. The moment obtained in this laboratory is 3.72 BM.

Bis(2,2',2''-terpyridine)cobalt(II) Perchlorate Monohydrate, $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.—A sample of this compound was kindly lent to us by Professor D. H. Busch, The Ohio State University.

Tris(pyruvaldihydrazone)cobalt(II) Bromide, $[\text{Co}(\text{PvdH})_3]\text{Br}_2$.—This compound was kindly supplied by Harold M. Fisher, University of Florida.²⁰

Bis(2,2',2''-terpyridine)cobalt(II) Salts, $[\text{Co}(\text{terpy})_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ and $[\text{Co}(\text{terpy})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$.—These were kindly supplied by Harold M. Fisher, University of Florida. These complexes were prepared in the manner of Hogg and Wilkins.¹⁹

Tris(2-pyridinalmethylimine)cobalt(II) Fluoroborate, $[\text{Co}(\text{PMI})_3](\text{BF}_4)_2$.—The preparation procedure was that of Figgis and Busch,²³ who reported an effective moment of 4.37 BM at 300°K. That obtained in this laboratory was 4.33 BM.

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(21) V. Cuttica, *Gazz. Chim. Ital.*, **53**, 185 (1923).

(22) F. Lions and K. Martin, *J. Am. Chem. Soc.*, **79**, 2763 (1957).

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