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On the Spin Equilibrium in Bis(2, 2′, 2″Terpyridine) Cobalt (II) Salts

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The magnetic behavior of salts of the bis(2,2′,2″-terpyridine) Co(II) cation with seven different anions has been studied over the range 15-400°K. The temperature dependence of the moment is found to be dependent on both the anion and the degree of hydration. It is suggested that low symmetry field components are very important in determining the behavior. The electronic spectra have been studied at 77 and 300°K and data are reported.

Introduction

In recent years there has been a great deal of interest in the magnetic properties of six coordinate d^5, d^6 and d^7 complexes near the «cross-over» point.[1-4] The «cross-over» point is that value of Dq where the high-spin and low-spin states are of equal energy. At or near this value of Dq, one would expect both spin states to be populated. This would result in a magnetic moment intermediate between those normally found for the two spin states as well as a complicated temperature dependence.

It is generally found that the experimental moments cannot be adequately predicted from simple theoretical models. Thus Ewald, *et. al.*,[2] found that in order to get a reasonable fit of their experimental curves, they had to assume that a change in bond length resulted in going from the high-spin to the low-spin state and they introduced a correction to the distribution between states in the form of a ratio of vibrational partition functions. König and Madeja[3] found similar results in their study of some anomalous d^6 systems, although they did not explicitly correct for such changes in bond length since such a treatment did not improve agreement between theory and experiment. They did, however, support such a postulate with other data. In the instances quoted above, the effect of low symmetry components to the field were neglected.

The most elaborate and successful attempt to derive a theoretical model for spin equilibrium is that recently published by Williams, Smith and Stoufer[4] for the Co(II) system. Their model differs from those previously discussed in that states mix by spin-orbit coupling and they allow δ, the separation between the states, to vary with temperature. They then calculated theoretical $1/\chi$ vs. T curves for different dependences of δ on T and obtained good agreement with their experimental results for nine different Co(II) compounds which exhibit anomalous magnetic behavior.

The anomalous magnetic behavior of $Co(terpy)_2^{2+}$ (terpy = 2,2′,2″-terpyridine) was first reported by Hogg and Wilkins,[5] although they made no extensive magnetic studies. They also observed that the magnetic properties were somewhat dependent on the anion present and these results have since been confirmed by Stoufer, *et. al.*[6,7] who also report ESR data which support the idea that the ions are in a doublet spin state at low temperatures.

It is the purpose of this paper to present detailed magnetic data on salts of $Co(terpy)_2^{2+}$ with a variety of anions which suggest that any theoretical treatment of these systems which neglects low symmetry fields is likely to be inadequate.

Experimental Section

Preparation of Compounds. For the most part, the preparation of the various salts followed the same procedure. The appropriate Co(II) salt was dissolved in water and an excess of terpyridine added. The volume of solution was then reduced and the solution cooled. In some cases, an alkali metal salt of the anion was added to aid precipitation. For those compounds for which the appropriate cobalt salt was not available, $Co(terpy)_2Cl_2 . 3H_2O$ served as the starting material. The desired salt was then obtained by adding an excess of the potassium salt of the anion to an aqueous solution of the chloride complex. Lower hydrates were prepared by simply heating the higher hydrate at constant temperature. An anhydrous chloride was obtained by heating $Co(terpy)_2Cl_2 . 3.5H_2O$ in the magnetic balance. The weight loss corresponded to that expected for 3.5 molecules of water (weight loss calc., 9.4%; observed, 11.8%) and became constant after about 45 minutes. No analysis was obtained on the sample after the magnetic measurements because the sample was quite hygroscopic. Attempts to prepare a bis-terpyridine mined by comparison with a similar nickel compound, to be $[Co(terpy)_2][Co(CN)_4]$. Analytical data for the salts obtained are given in Table I.

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(1) R. C. Stoufer, D. H. Busch and W. B. Hadley, *J. Am. Chem. Soc.*, *83*, 3732 (1961).

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

(3) E. König and K. Madeja, *Inorg. Chem.*, 6, 48 (1967).

(4) David L. Williams, Darwin W. Smith and R. Carl Stoufer, *Inorg. Chem.*, 6, 590 (1967).

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

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

(7) I. G. Schmidt, W. S. Brey Jr. and R. C. Stoufer, *ibid.*, 6, 268 (1967).

Table I.

Compound	Carbon Calc. (Found)	Hydrogen Calc. (Found)	Nitrogen Calc. (Found)
$Co(terpy)_2Cl_2 . 3.5H_2O$	54.64 (54.78)	4.43 (4.26)	12.74 (12.76)
$Co(terpy)_2Br_2 . 3H_2O$	48.74 (49.10)	3.82 (4.04)	11.37 (11.13)
$Co(trepy)_2I_2 . H_2O$	45.19 (45.40)	3.04 (3.25)	10.54 (10.15)
$Co(terpy)_2I_2$	46.24 (46.08)	2.85 (2.90)	10.78 (10.90)
$Co(terpy)_2F_2 . 4.5H_2O$	55.90 (56.01)	4.85 (5.03)	13.04 (13.08)
$Co(terpy)_2F_2 . 3.5H_2O$	57.51 (57.53)	4.67 (4.41)	13.41 (13.11)
$Co(terpy)_2(ClO_4)_2$	49.74 (49.79)	3.06 (3.28)	11.60 (11.75)
$Co(terpy)_2(SCN)_2 . H_2O$	58.26 (58.07)	3.67 (3.75)	16.99 (17.40)
$Co(terpy)_2(NO_3)_2$	55.48 (56.16)	3.42 (3.76)	17.32 (17.29)
$Co(terpy)_2Co(CN)_4$	59.32 (59.45)	3.22 (3.22)	20.35 (20.16)
$Ni(terpy)_2Ni(CN)_4$	59.35 (58.93)	3.22 (3.59)	20.36 (19.85)
$Ni(terpy)_2Br_2H_2O$	51.24 (51.24)	3.44 (4.09)	11.95 (11.57)

Physical Measurements. Infrared spectra were obtained in KBr pellets using a Perkin-Elmer 521 grating spectrophotometer.

Electronic spectra were obtained using a Cary Model 14. Reflectance spectra were obtained using the Cary Model 1411 Diffuse Reflectance Accessory with $MgCO_3$ as the reference material. An Air Products Cryo Tip refrigeration system was used for the low temperature spectra.

Magnetic measurements were performed on a Faraday type balance which used a Varian 4" electromagnet and associated power supply and current regulator. The pole caps were the constant force type which gave a force constant to 1% over a 4 mm. vertical distance. The balance used was a Cahn Model RG recording electrobalance. The sample size was of the order of 50 mg. which resulted in forces of 1-20 mg. The balance was calibrated using $Hg[Co(NCS)_4]$ as a standard. The magnetic moments were calculated from the measured susceptibility using the relationship $\mu = 2.83(\chi_m'T)^{1/2}$. Diamagnetic corrections were made using Pascal's constants. All measurements were made at three different field strengths and no field dependence was observed. The sample was cooled using a Gifford-McMann gas balancing, two stage refrigerator manufactured by Cryomech Corp., Syracuse, N. Y. The refrigerator is capable of operation over the range 15-300°K.

X-ray powder data were obtained using either nickel filtered CuK_α radiation or Zr filtered MoK_α radiation and a standard G. E. powder camera.

Results and Discussion

Magnetic Data. Magnetic data at selected temperatures are tabulated in Table II and plots of μ vs. T for four of the compounds which exhibit drastically different behavior are shown in Fig. 1. It can readily be seen that both the actual values of the moments obtained as well as the temperature dependence varies with the anion and the degree of hydration. Thus the fluorides with 3.5 water molecules is essentially low spin between 20 and 300° while that with 4.5 waters has a much higher moment. For the chloride, loss of water seems to result in a raising of the moment, since Stoufer[6] reports that the pentahydrate has a moment of 2.51. There is a similar variation for the anhydrous salts, the chloride being high-spin at all temperatures

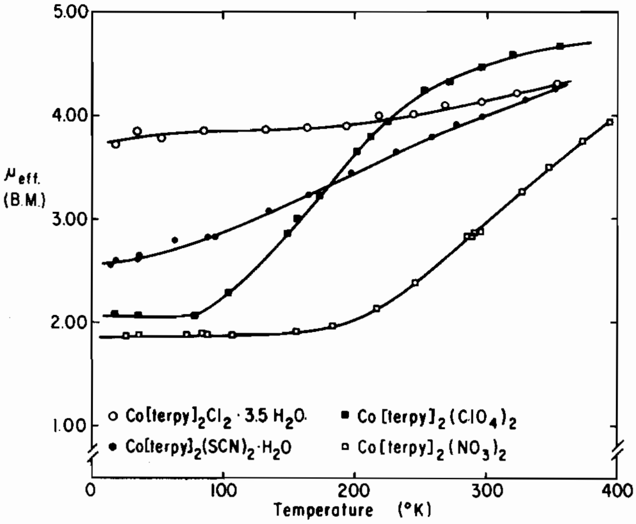

Figure 1. Plot of μ vs. T for $Co(terpy)_2(ClO_4)_2$; $Co(terpy)(NO_3)_2$; $Co(terpy)(SCN)_2 . H_2O$; $Co(terpy)_2Cl_2 . 3.5H_2O$.

Table II.

Compound T (°K) =	15	20	30	60	100	150	200	250	300	350	400
			Effective	Magnetic	Moments						
$Co(terpy)_2^{2+}$ (soln)									3.3		
$Co(terpy)_2Cl_2 . 3.5H_2O$	3.75	3.78	3.81	3.83	3.84	3.87	3.94	4.04	4.17	4.31	
$Co(terpy)_2Cl_2$	4.17	4.20	4.30	4.37	4.46	4.57	4.61	4.62	4.65	4.70	4.73
$Co(terpy)_2Br_2 . 3H_2O$						2.26	2.41	2.66	2.94	3.24	
$Co(terpy)_2I_2 . H_2O$	1.89	1.91	1.94	1.96	2.03	2.23	2.63	3.05	3.40		
$Co(terpy)_2I_2$	2.14	2.14	2.15	2.16	2.31	2.84	3.38	3.74	3.97	4.11	
$Co(terpy)_2F_2 . 3.5H_2O$		1.94	1.94						2.15		
$Co(terpy)_2F_2 . 4.5H_2O$						3.56	3.71	3.86	4.00		
$Co(terpy)_2(ClO_4)_2$	2.07	2.07	2.07	2.08	2.25	2.89	3.62	4.17	4.49	4.66	
$Co(terpy)_2(SCN)_2 . H_2O$	2.57	2.58	2.61	2.72	2.82	3.13	3.43	3.75	4.01	4.25	
$Co(terpy)_2(NO_3)_2$	1.87	1.87	1.87	1.87	1.88	1.89	2.04	2.42	2.96	3.52	4.00
$[Co(terpy)_2][Co(CN)_4]$[a]		2.12	2.27	2.43	2.58	2.73	2.90	3.06	3.21	3.53	3.58
$[Ni(terpy)_2][Ni(CN)_4]$[a]						3.01	3.06	3.08	3.11	3.12	
$Ni(terpy)_2Br_2 . H_2O$						3.00	3.05	3.09	3.13	3.17	

[a] Moments reported are for the cation only, assuming that the moment of the cobalt anion is 2.20 BM with a TIP susceptibility of 200×10^{-6} cgsu and for the nickel anion is zero.

while the perchlorate is high-spin at 350° but nearly totally low-spin at 15°. The others exhibit different behavior in moment and temperature variation.

The reason for the temperature dependence of the moments on anion and degree of hydration is not clear and is surely not simple. There are a number of possible reasons which can be suggested. Williams, Smith, and Stoufer[4] have proposed that δ, the separation between high-spin and low-spin states, is a function of temperature, and have proposed that a relationship of the type

$$\delta = \delta_0 + aT + bT^2 + cT^3$$

can adequately fit the observed results. That the observed results for the series of compounds reported here is due to such a variation in δ seems to us to be doubtful, although certainly the data can be fit with an appropriate choice of constants. For one thing, δ for different salts would require in some cases drastically different functions of temperature. For example, $[Co(terpy)_2][Co(CN)_4]$ gives values which can be explained by approximately the same value of δ from 20 to 350°K, while δ for the perchlorate salt must change by over 1000 cm.$^{-1}$ over the same temperature range. Similarly, the large differences in δ which would be required to explain the changes in moment observed on altering the degree of hydration are difficult to accept.

As has been pointed out,[4] covalency effects cannot be very important in determining the magnetic changes, and can certainly not explain the anion dependence. We have performed calculations of the moments expected using widely different amounts of orbital angular momentum and it is clear that such an effect cannot explain the observed results, although if the covalency effect is allowed to change widely with temperature one can get results similar to those obtained by allowing δ to vary. That such an effect could be responsible for the observed results, however, does not seem reasonable.

We would like to suggest that the influence of low symmetry components to the field is important in determining the magnetic properties. There is certain evidence to support this contention. The structure of $Zn(terpy)Cl_2$ has been determined by x-ray methods by Corbridge and Cox[8] and later refined by Einstein and Penfold.[9] There are two important results relative to our work. First, the angle formed by the metal and the two outer nitrogens of the terpyridyl is 145°. In the six coordinate compounds under discussion, these nitrogens would have to span *trans* positions. Second, the metal-nitrogen bond distance for the center nitrogen is 0.1 - 0.15 Å shorter than for the outer nitrogens and Einstein and Penfold suggest that this condition is required by the geometry of the ligand. In light of these facts, it is clear that there is appreciable distortion from octahedral symmetry in the cobalt complexes. Effects of these distortions are apparent in both the electronic[10] and Mössbauer spectra[11] of $Fe(terpy)_2^{2+}$. It is worth mentioning that we have prepared a series of Fe(II) complexes which are isomorphous to those of cobalt reported here and their Mössbauer spectra do show a slight dependence on the anions. These compounds are being studied more carefully and will be reported at a later date.

The quantitative inclusion of low symmetry fields in the treatment of the magnetic data is a difficult problem, and we have not yet done this. The actual symmetry can be no more than C_{2v} and consideration of this along with spin-orbit coupling of comparable magnitude in the treatment of spin equilibrium requires the introduction of many parameters. It is possible that the approximation of a somewhat higher symmetry such as D_4h might be reasonable, and we are currently working on this problem.

In spite of the lack of a quantitative treatment, however, it seems reasonable to suggest the dependence of the magnetic properties on the anion is due, at least in part, to changes in the symmetry around the cobalt due to packing effects in the solids. This might also explain the dependence on the degree of hydration. Nonetheless, it should be pointed out that there is no way at present of estimating the magnitude of the effect of packing or even knowing for sure what effect the inclusion of low symmetry components to the field would have on the moment.

Magnetic data for two nickel complexes are also reported in Table II. These are given merely to confirm the structure proposed for $[Co(terpy)_2][Co(CN)_4]$. The moment for $Ni(terpy)_2Br_2$ is seen to be normal for nickel(II). If the material having an empirical formula $Ni(terpy)(CN)_2$ is formulated as the cation-anion compound as indicated, then the moment for the cation, assuming the anion to have a zero moment, is as expected. There is further evidence to support this formulation in the infrared and visible spectra. There is a single sharp CN^- band near 2135 cm.$^{-1}$ in the infrared[12] and the visible spectrum is typical for $Ni(terpy)_2^{2+}$. Since the analogous cobalt compound has an identical x-ray powder pattern, it is assigned the same structure.

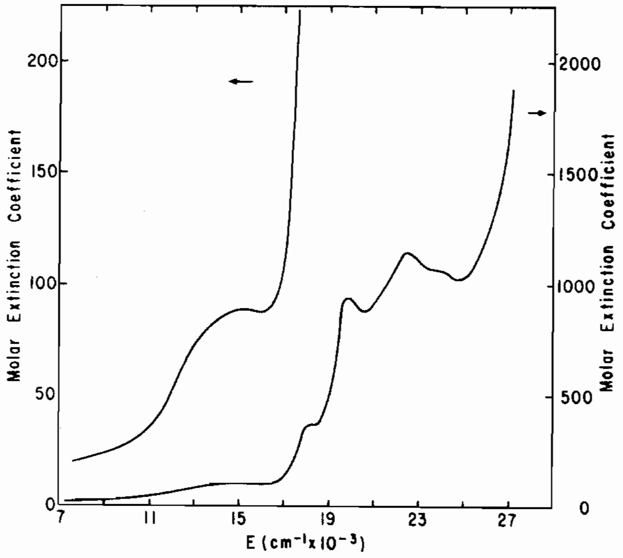

Figure 2. Solution spectrum of $Co(terpy)_2^{2+}$.

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[8] D. F. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956).

[9] Frederick W. B. Einstein and Bruce R. Penfold, *Acta Cryst.*, *20*, 924 (1966).

[10] P. Krumholz, *Inorg. Chem.*, *4*, 612 (1965).

[11] L. M. Epstein, *J. Chem. Phys.*, *40*, 435 (1964).

[12] Kazuo Nakamoto, «Infrared Spectra of Inorganic and Coordination Compounds», John Wiley, New York, 1963, p. 166.

Electronic Spectra. The electronic spectra over the range 5000 to 30,000 cm.$^{-1}$ have been obtained by various techniques. The solution spectrum of Co(terpy)$_2^{2+}$ is shown in Figure 2. The reflectance spectrum and that observed in pressed pellets of KBr at 77° and 300° for Co(terpy)$_2$Cl$_2$. 3.5H$_2$O and Co(terpy)$_2$(ClO$_4$)$_2$ are shown in Figures 3 and 4 respectively. The most notable feature of the various spectra is their great similarity. In all cases there is a broad band centered near 14,000, two sharp bands at about 18,200 and 19,800 and a band near 23,000 cm.$^{-1}$ which is very distinct and somewhat structured in solution but is less clear in the solid. It can also be seen that there is an increase in intensity of the bands upon cooling to 77°K, particularly for the 18,200 and 19,800 cm.$^{-1}$ bands.

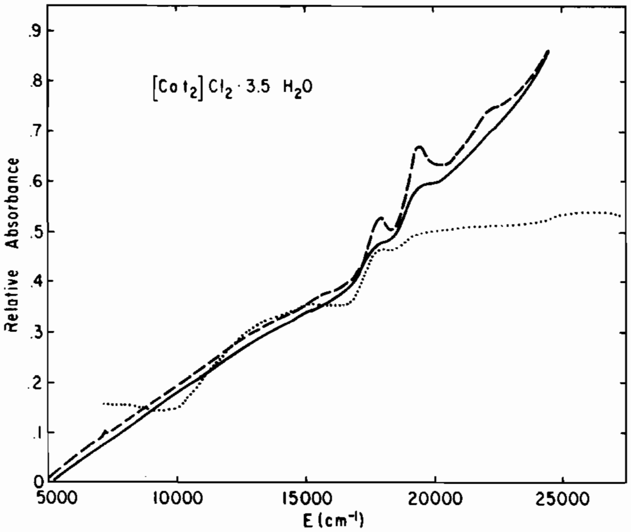

Figure 3. Solid state spectrum of Co(terpy)$_2$Cl$_2$. 3.5H$_2$O in reflectance (· · · · ·) and KBr pellets at room temperature (———) and 77°K (— — —).

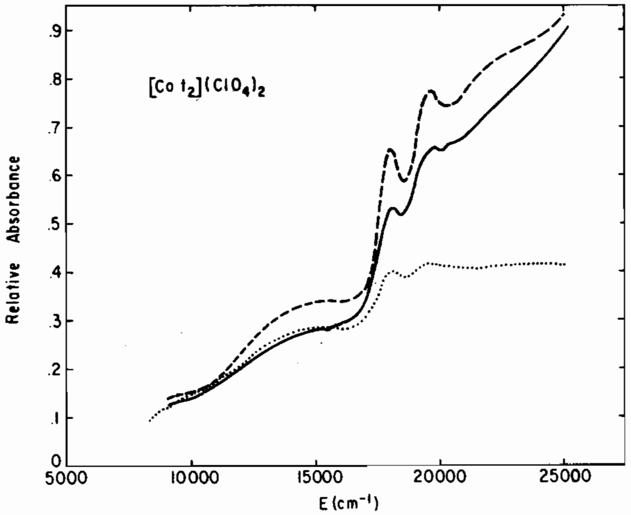

Figure 4. Solid state spectrum of Co(terpy)$_2$(ClO$_4$)$_2$ in reflectance (· · · · ·) and KBr pellets at room temperature (———) and 77°K (— — —).

The spectra are not amenable to an obvious interpretation, but on the basis of extinction coefficients measured in solution, we feel that the bands are essentially *d-d* in character. The measured extinction coefficients of the bands are between 100 and 1000. Although the higher energy bands appear to be rather intense for *d-d* spectra, it should be pointed out that they are on the side of steeply rising charge-transfer band and therefore the actual intensities are much less than appears from the spectrum.

From the magnetic moment in solution (3.3 B.M.), it appears that the percentage of molecules in each spin-state is approximately the same. The KBr pellet spectrum of the perchlorate at room temperature is essentially identical to the solution spectrum, although the magnetic data indicate that the perchlorate is essentially all high-spin at 300°. Cooling to 77° increase the intensities but produces no new bands and none decrease in intensity. This is somewhat unexpected since Holmes and McClure have observed that the bands in Co(H$_2$O)$_6^{2+}$ decrease upon cooling,[13] although of course the temperature dependence of the intensities depends upon the mechanism by which the transitions become allowed, and is not necessarily the same for the terpyridine complexes as for the hydrate.

Taking all of the above facts into account, we feel that the spectra can be reasonably interpreted using the energy level diagram of Liehr[14] and assuming that spin-orbit coupling partially breaks down the usual spin selection rule. The broad band at 14,000 cm.$^{-1}$ is then assigned to the transition to the various spin-orbit levels arising mainly from the $^4T_{2g}(4F)$ and $^2T_{1g}$, $^2T_{2g}(^2G)$ which approach each other closely at the cross-over point.[14] The increase of intensity observed upon cooling occurs because the ground state becomes increasingly spin-doublet at lower temperatures and the doublet transitions should be more intense than the quartet due to greater «covalency», *etc.* This explanation is compatible with the smaller intensity change observed for the cloride as compared to the perchlorate, since the moment of the chloride drops much less on cooling.

Assuming that Liehr's diagram[14] is applicable, the two bands at 18,200 and 19,800 cm.$^{-1}$ can only be assigned as transition to two levels which are essentially spin-doublets (Γ_8 and Γ_6 respectively). This accounts as before for the temperature dependence of the intensities. The observed separation of the bands is somewhat greater than that taken from Liehr's treatment, but it must be remembered that his complete calculation is valid only for his chosen values of B(835 cm.$^{-1}$), C(3340 cm.$^{-1}$) and the spin-orbit coupling constant (—450 cm.$^{-1}$) and can therefore be applied only qualitatively to other systems. The band at 23,000 cm.$^{-1}$ can then be assigned to a series of primarily quartet states, again consistent with the relatively small change in intensity on cooling. This band is not clear in the reflectance spectrum.

The interpretation given above is obviously conjectural and there are some weak points which should be mentioned. First, although the band positions are fairly easy to assign, the intensity changes are observed

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(13) Owen G. Holmes and Donald S. McClure, *J. Chem. Phys.*, *26*, 1686 (1957).

(14) Andrew D. Liehr, *J. Phys. Chem.*, *67*, 1314 (1963).

in KBr pellets and are therefore not quantitatively significant. Also, while the similarity of the pellet, reflectance and solution spectra preclude any replacement of ligands by bromide ion, the pellets must be pressed under high pressure and the effects of this pressure on the spectra are uncertain. As pointed out earlier, we have used the energy levels from the complete treatment of Liehr which is only useful in a qualitative way. Our observed values are all 1000-2000 cm.$^{-1}$ lower than predicted from his results which might simply reflect a lower value of B. Finally, it should be mentioned that similar intensity effects have been observed by Ewald, *et. al.*[2] in the spectra of their Fe(III) complexes which are apparently examples of systems near the cross-over point.

Conclusion

On the basis of the magnetic data, it is clear that the nature of the anion and the degree of hydration affect the distribution between spin states. These and other data suggest that an adequate explanation of the observed data must include a consideration of low symmetry fields.

From a consideration of spectral data, tentative band assignments can be made, although evaluation of Dq and the Racah parameters, B and C is not possible (although Dq must be of the order of 1400-1600 cm.$^{-1}$). It does appear that the spectra of complexes near the cross-over point cannot be interpreted in simple terms and does not readily yield information similar to that obtainable from purely low-spin or high-spin systems. This is due to the fact that the ground state cannot realistically be represented as either a spin-doublet or spin-quartet and the normal spin selection rules break down. The expected change in the spectrum from that observed for a normal high-spin Co(II) complex to that of a normal low-spin complex as the temperature is changed is therefore not observed.

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