ture. The line shape is Lorentzian at all observed temperatures. The increased line width at temperatures below T = 15 K is an additional indication of magnetic ordering at low temperatures,[18] leading to a decrease in exchange frequency.

^{87}Rb NMR. On a polycrystalline sample of RbBp·2Ttg, a ^{87}Rb NMR experiment has been carried out. A single resonance line was observed with a derivative line width of 8 G. This line was not shifted with respect to the ^{87}Rb resonance line of a RbCl solution in water. These observations are in agreement with the crystallographic structure, where it was found that the Rb cation is almost spherically surrounded by two tetraglyme molecules. Such a structure will lead to a small electric field gradient and a zero spin density at the Rb nucleus, giving rise to a single, unshifted resonance line.

Conclusion

In conclusion the RbBp·2Ttg crystal can be described as a solvent-separated ion pair. In this regard, it substantiates the conclusions drawn by Canters and de Boer[19] for the RbBp ion-pair structures in solvents of high solvating power. From the shift and the line width of the Rb resonance line, it was concluded that solvent-separated ion pairs existed in the solution, as is now also borne out in the solid state.

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Supplementary Material Available: Structure factor tables (34 pages). Ordering information is given on any current masthead page.

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Magnetic Investigation of the Electronic Structure of Hexakis(pyridine *N*-oxide)cobalt(II) Perchlorate

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Abstract: Although the CoO_6 coordination sphere of $[Co(C_5H_5NO)_6](ClO_4)_2$ is perfectly octahedral, it is shown from a magnetic study at low temperatures that the cobalt ion suffers a large electronic or crystal field distortion. The g values are $g_{\|} = 2.26 \pm 0.01$ and $g_{\perp} = 4.77 \pm 0.01$ from EPR measurements of cobalt doped into $[Zn(C_5H_5NO)_6](ClO_4)_2$, while the parameters $g_{\|} = 2.49 \pm 0.05$, $g_{\perp} = 4.70 \pm 0.05$ were obtained from susceptibility studies on the pure cobalt compound. The compound obeys the Curie–Weiss law, 1.5–20 K, with $\theta_{\|} = -0.28 \pm 0.05$ K, $\theta_{\perp} = -0.52 \pm 0.05$ K. The g values and TIP terms also allow an estimate of the position of the low-lying components of the $^4T_1(F)$ state.

The recent discovery[1-3] that $[Zn(C_5H_5NO)_6](ClO_4)_2$, where C_5H_5NO is pyridine *N*-oxide, assumes a rhombohedral crystal structure with but one molecule in the unit cell, makes this lattice an attractive one for a variety of physical studies. This molecule, as well as its isomorphous manganese, cobalt, and nickel congeners, has been known for some time[4] and although an extensive transition metal chemistry of aromatic *N*-oxides has since developed,[5] there have been relatively few single-crystal studies. The EPR spectrum of manganese(II) doped into the zinc lattice was recently reported,[1] and, although the molecules are geometrically undistorted,[2,3] a rather large zero-field splitting was observed. It was reported[6] that no EPR spectrum was observed for powdered samples of $[Ni(C_5H_5NO)_6](ClO_4)_2$ at room temperature, and we have found that no such spectrum is observable at X-band in doped $[Ni,Zn(C_5H_5NO)_6](ClO_4)_2$ single crystals even at helium temperatures. These results are consistent with a large zero-field splitting also occurring for the nickel system.

We have chosen the cobalt(II) ion as a probe for continuing our studies of crystal field effects in this lattice. The theory of the electronic structure of the hexaaquocobalt(II) ion is particularly well developed[7-10] and one expects that the metal-oxygen bond in the pyridine *N*-oxide complexes will be sufficiently similar to allow this theory to be used here. EPR studies at helium temperatures of divalent cobalt doped into $[Zn(C_5H_5NO)_6](ClO_4)_2$ are reported along with the magnetic susceptibilities of pure $[Co(C_5H_5NO)_6](ClO_4)_2$ in the temperature region 1.5-20 K. The cobalt(II) ion is effectively spin ½ at these temperatures and so the normal zero-field splitting terms in the spin-Hamiltonian are necessarily zero. The observed g-value anisotropy will be shown, however, to be consistent with large crystal field distortions in the lattice. Similar, qualitative conclusions were arrived at earlier on the basis of vibrational and electronic spectra and high temperature magnetic data.[11]

Experimental Section

The EPR[1] and magnetic susceptibility[12] procedures are as before. The space group of the crystals is[3] $R\bar{3}$, $Z = 1$, in the rhombohedral setting. The lattice constants determined in the present work are $a = 9.607$ Å and $\alpha = 81° 20'$ for the zinc compound; $a = 9.617$ Å and $\alpha = 81.16°$ for the isomorphous cobalt compound.[3]

Hexakis(pyridine *N*-oxide)cobalt(II) perchlorate and the diamagnetic $[Zn(C_5H_5NO)_6](ClO_4)_2$ were prepared by mixing together stoichiometric methanolic solutions of the hydrated metal perchlorates and purified pyridine *N*-oxide.[4] The pyridine *N*-oxide was obtained from Aldrich and purified by vacuum sublimation. Single crystals of $[Co^{2+},Zn(C_5H_5NO)_6](ClO_4)_2$ doped at between a half and one percent were prepared by mixing the metal perchlorates and then causing them to react with pyridine *N*-oxide. Both the pure cobalt and zinc doped with cobalt single crystals were grown by slow evaporation of concentrated DMF solutions.

The spectra at X-band were taken at 4.2 K. Crystals were aligned for EPR studies using the precession camera and a transfer goniometer for mounting on a quartz rod. Alignment for susceptibility was done using the morphological properties of the crystals, and susceptibilities were measured parallel and perpendicular to the hexagonal c axis.

Theory and Results

Cobalt(II) is a d^7 ion, with $S = \frac{3}{2}$, the ground state being $^4T_1$ in octahedral fields. The spin-orbit coupling constant is large, λ −180 cm^{-1} in the free ion, and so the resolution of the degeneracy of the ground state into six widely spaced doublets by spin-orbit coupling is an important feature of the electronic structure of this ion. Two parameters have been introduced that are useful for the empirical representation of magnetic data. The first of these, a Landé factor, variously called γ[9] or α[7,10] ($\gamma \equiv -\alpha$) refers to the strong-field ($\alpha = 1$) and weak-field ($\alpha = \frac{3}{2}$) limits and its diminution in value from $\frac{3}{2}$ is a measure of the orbital mixing of $^4T_1(F)$ and $^4T_1(P)$. The lowest electronic level in an axial field with spin-orbit coupling is a Kramers doublet and so cannot be split except by magnetic fields. At temperatures where only this level is populated, which are usually $T < 20$ K, this system corresponds to an effective $S' = \frac{1}{2}$. The orbital contribution of the nearby components of the $^4T_1(F)$ state causes the ground doublet in the weak cubic field limit to have an isotropic $g = 4\frac{1}{3}$, a result in agreement with experiments on cobalt in MgO,[13] but large anisotropy in the g values is expected as the crystal field becomes more distorted. The three orthogonal g values are expected to sum in first order to the value of 13.[7,8]

The second parameter, δ, is an axial crystal field splitting parameter that measures the resolution of the degeneracy of the $^4T_1$ state, and thus is necessarily zero in a cubic crystal. The isotropic g value is then $(\frac{2}{3})(5 + \alpha)$, to first order.[13] In the limit of large distortions, δ may take on the values of $+\infty$ or $-\infty$, with the following limiting g values resulting:

$$\delta = +\infty:\ g_\parallel = 2(3 + \alpha),\ g_\perp = 0$$

$$\delta = -\infty:\ g_\parallel = 2,\ g_\perp = 4$$

For a given α, the two g values are therefore functions of the single parameter δ/λ and so they bear a functional relationship to each other.[7,9] Abragam and Pryce have presented the general result,[7] but there are more parameters in the theory than can be obtained from the available experimental results. With the approximation of isotropic spin-orbit coupling, they derive (to first order) the following equations which should provide a useful *estimate* of crystal distortions.

Table I. Experimental Parameters

(a) From EPR

$g_\parallel = 2.26 \pm 0.01$
$g_\perp = 4.77 \pm 0.01$
$A = (1.86 \pm 0.01) \times 10^{-3}$ cm^{-1}
$B = (3.84 \pm 0.01) \times 10^{-3}$ cm^{-1}

(b) From Susceptibility

$g_\parallel = 2.49 \pm 0.05$
$g_\perp = 4.70 \pm 0.05$
$\theta_\parallel = -0.28 \pm 0.05$ K
$\theta_\perp = -0.52 \pm 0.05$ K
$\mathrm{TIP}_\parallel = (1.1 \pm 0.7) \times 10^{-3}$ emu mol^{-1}
$\mathrm{TIP}_\perp = (2.4 \pm 0.7) \times 10^{-3}$ emu mol^{-1}

$$g_\parallel = 2 + 4(\alpha + 2)\left[\left(\frac{3}{x^2} - \frac{4}{(x+2)^2}\right) \Big/ \left(1 + \frac{6}{x^2} + \frac{8}{(x+2)^2}\right)\right] \quad (1)$$

$$g_\perp = 4\left[\left(1 + \frac{2\alpha}{x+2} + \frac{12}{x(x+2)}\right) \Big/ \left(1 + \frac{6}{x^2} + \frac{8}{(x+2)^2}\right)\right] \quad (2)$$

where x is a dummy parameter which for the lowest energy level is positive with limiting values of 2 (cubic field, $\delta = 0$), 0 ($\delta = +\infty$), and ∞ ($\delta = -\infty$). The splitting parameter δ is found as

$$\delta = \alpha\lambda\left[\frac{x+3}{2} - \frac{3}{x} - \frac{4}{x+2}\right] \quad (3)$$

The observed g values for octahedral environments with either trigonal or tetragonal fields should therefore all lie on a universal curve. Such curves are illustrated by Abragam and Pryce,[7] Griffith,[9] and Orton,[10] and a satisfactory relationship of theory and experiment has been observed. The observation of $g_\parallel$ and $g_\perp$ allows the solution of eq 1 and 2 for α and x, and these parameters in turn may be applied to eq 3.

The spin-Hamiltonian used here is

$$\mathcal{H} = \mu_B H[g_\parallel \cos\theta S_z + g_\perp \sin\theta(S_x + S_y)] + AI_zS_z + B[I_xS_x + I_yS_y] \quad (4)$$

where $S = \frac{1}{2}$ and $I = \frac{7}{2}$, and θ is the angle between the external field and the rhombohedral axis. The second-order terms have been neglected in solving this Hamiltonian, and so the center of resonance has an effective g value given by

$$g(\theta) = [g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta]^{1/2} \quad (5)$$

The parameters obtained from the EPR analysis of $[Co,Zn(C_5H_5NO)_6](ClO_4)_2$ appear in Table I. The g values were obtained by fitting the angular dependence of the resonance field to eq 5. A plot of $g^2(\theta)$, the effective g value, against $\cos^2\theta$ yields a straight line, as illustrated in Figure 1. The anticipated hyperfine splitting was also observed, and the resulting parameters are also listed in Table I.

Additional, weak spectra were observed on the flanks of the principal spectrum. These lines had their maximum intensity as the angle θ moved away from both of the principal axes. The maximum g values of the two sites are 5.2 and

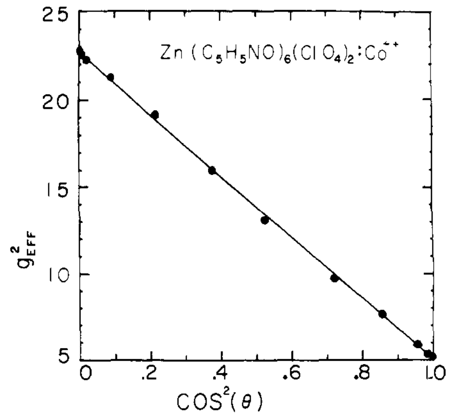

Figure 1. Plot of effective g values of the electron resonance spectrum as a function of angle between the magnetic field and principal axis.

4.7, while the minimum g values are, respectively, 2.9 and 2.6. While the g values are similar to those for the major site, the orientations ($\|,\perp$) are not the same. A similar occurrence was reported[8] earlier by Bleaney and Ingram for cobalt in another trigonal crystal, $ZnSiF_6{\cdot}6H_2O$, and was assigned by them to cobalt residing in defect lattice sites. Another possibility, suggested by Abragam and Pryce[7] is that some of the cobalt ions may have another cobalt ion among their nearest neighbors instead of only zinc ions, and this will cause a distortion of the crystalline field. We adopt the same explanations here, and point out for future reference below the implication of this on the crystal field distortions suffered by the transition metal ions.

Following earlier studies[14,15] of the magnetic susceptibility of hexaquocobalt(II) ion at helium temperatures, the behavior of the zero-field anisotropic susceptibilities has been described by a Curie-Weiss law, eq 6,

$$\chi_i = \frac{Ng_i^2\mu_B^2S(S+1)}{3k(T-\theta_i)} + \mathrm{TIP}_i \qquad (6)$$

$$i = \|,\perp;\ S = \tfrac{1}{2}$$

where an additional temperature-independent term, TIP, due to coupling of the ground state with low-lying excited states, is included. Good fits to the data between 1.5 and 20 K, uncorrected for diamagnetism, were obtained with the parameters reported in Table I. The Curie-Weiss plots are illustrated in Figure 2. Aside from the relatively large values of the Weiss constants, which are antiferromagnetic in sign, the data have offered no evidence that magnetic exchange influences the measured susceptibilities.

Discussion

As has been implied above, the discussion will center on the relatively large distortions in the crystal field which occur in these compounds. Thus, the EPR g values, when applied to eq 1-3, yield the set of parameters $x = 5.56$, $\alpha = 1.15$, and $\delta = (-670 \pm 30)\ \mathrm{cm}^{-1}$, when the free-ion spin-orbit coupling constant is used; a decrease in λ from the free ion value to $-140\ \mathrm{cm}^{-1}$ will cause a proportionate decrease in δ to $-520\ \mathrm{cm}^{-1}$. As described above, the value of δ derived is necessarily approximate; δ changes quite appreciably for small changes in α as well as when α is allowed to become anisotropic, and therefore too much weight should not be attached to the calculated values. If the g values from the susceptibility measurements are used, then $x = 4.33$, $\alpha = 1.10$, and $\delta = (-460 \pm 30)\ \mathrm{cm}^{-1}$. The negative sign of δ implies that the orbital singlet component of $^4T_1(F)$ is lowest. There are no independent measurements of δ available for comparison but it should be pointed out that the observed g-value anisotropy approaches the upper theoretical limit for the case of $g_\perp > g_\|$. Three surveys[10,16,17] of the EPR spectra of cobalt show that the usual situation observed is in fact for $g_\|$ to be greater than $g_\perp$, and it is significant that one of the few known cases of a lattice doped with cobalt(II) ions that has g values similar to those reported here is aluminum oxide, Al_2O_3.[18] Two sites were observed, with g values respectively of (1) $g_\| = 2.292$, $g_\perp = 4.947$, and (2) $g_\| = 2.808$, $g_\perp = 4.855$. A large value of δ is implied, which is consistent with the mismatch of ionic charge that occurs on placing Co^{2+} into A_2O_3.

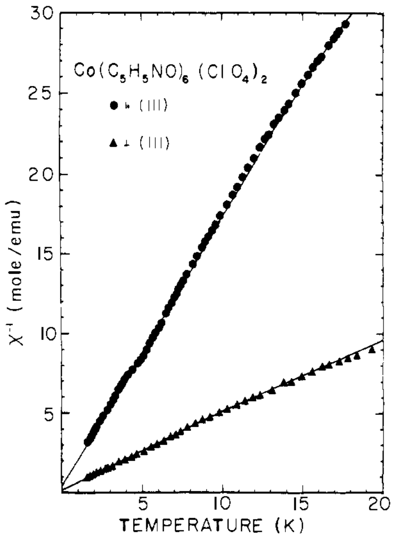

Figure 2. Curie-Weiss plots of inverse magnetic susceptibility of $[Co(C_5H_5NO)_6](ClO_4)_2$.

Though the g values of cobalt in this lattice have been measured by two independent methods, as reported in Table I, and are almost the same, there seems to be a slight difference between the two sets of parameters. This is as expected, for compressional and distortion effects will change as the cobalt ion is transferred from one lattice to the other, and the g values are quite sensitive to these changes. The apparent presence of defect lattice sites has already been pointed out. The situation is not unlike that reported earlier[19] for a variety of trivalent metal ions doped into $[C(NH_2)_3]Al(SO_4)_2{\cdot}6H_2O$. The change in g value upon changing the lattice is smaller in the present case than that reported for the $Co,ZnSiF_6{\cdot}6H_2O$ system. The EPR g values for the doped system are[8] $g_\| = 5.82$, $g_\perp = 3.44$, while the susceptibility results on the pure system[20] are $g_\| = 6.8 \pm 0.05$, $g_\perp = 2.5 \pm 0.05$. The zinc compound contains regular octahedra, but the cobalt octahedron is elongated.[21] Unfortunately, this system undergoes a crystallographic phase transition as it is cooled below room temperature. We have no information on whether or not the pyridine *N*-oxide compounds retain their room temperature crystal structure, but the crystals are neither shattered nor cracked upon regaining room temperature.

The TIP parameters are smaller than those reported[14] for $La_2Co_3(NO_3)_{12}{\cdot}24H_2O$. They arise from a term of the form

$$\mathrm{TIP} \sim \sum_i |\langle i|\ \mu_B H \cdot (L + 2S)|0\rangle|^2/E_i$$

which is a magnetic field mixing of the excited states $|i\rangle$, into the ground state, $|0\rangle$. In the present situation, the most important excited states are the spin-orbit components of the $^4T_1(F)$ state. The parameters obtained above allow an estimate of the energy, E_i, that these states lie above the ground state. Through use of eq 3.5 of Abragam and Pryce[7] as corrected by Leask and Wolf,[14] we find that there are doubly degenerate levels at about 125, 379, 629, 703, and

787 cm^{-1}, above the ground state. The intervals are not large, but even the lowest one of these states will have a negligible population at the temperatures of concern here. Thus, they contribute to the magnetic properties only incidentally and indirectly, through the TIP term. High-temperature measurements, such as Cossee carried out[22] on Co^{2+}:MgO, would allow verification of these splittings.

The particular values of the g values displayed by this compound have further implications for the magnetic properties at lower temperatures. The susceptibility measurements indicate the presence of a small antiferromagnetic interaction between the cobalt ions in $[Co(C_5H_5NO)_6](ClO_4)_2$. Assuming six nearest magnetic neighbors, an exchange constant of the order of $J/k = -0.2$ K may be derived from $\theta_{\perp} = -0.52$ K. The ordering temperature will be below 1 K. These results are corroborated by specific heat studies on this compound, performed at the Kamerlingh Onnes Laboratory of the University of Leiden.[23] The heat capacity is found to display a sharp λ-type anomaly at $T_c = 0.42$ K. Preliminary analyses of these data in terms of the simple cubic XY model of magnetic phase transitions[24] yield a good fit of theory to experiment, with an exchange constant $J/K = -0.21$ K. As has recently been discussed,[25] the applicability of the XY model in describing the low-temperature magnetic properties of the present cobalt compound is warranted by the form of the g tensor, which we have shown to be of unaxial symmetry with $g_{\perp} \gg g_{\parallel}$.

Conclusion

It has been demonstrated that the cobalt(II) ion suffers a large electronic distortion in the $[Co(C_5H_5NO)_6](ClO_4)_2$ lattice. Contrary to the case with such spin ½ ions as copper(II) and vanadyl, the effective spin ½ cobalt(II) ion is a useful probe for such effects because of the peculiarities of its electronic structure, which are due to spin-orbit coupling effects.

The question remains as to *why* this electronic distortion occurs in this series of compounds. After all, the CoO_6 coordination sphere is perfectly octahedral within experimental error.[3] The answer must lie with the remainder of the ligand molecule. The Co-O-N bond angle of 119.5° shows that the oxygen atom is sp^2 hybridized, and a molecular orbital model would therefore have to take account not only of the orientation of the -N-O grouping but also of the symmetry-allowed π-bonding.

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