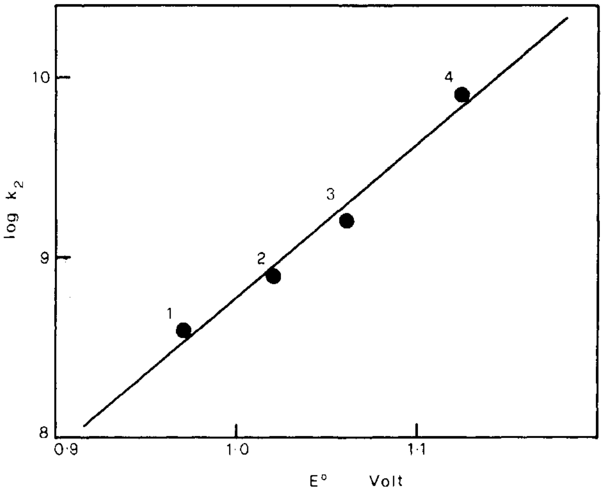

Figure 2. Relationship between the logarithms of the specific rate constants for the oxidation of ascorbic acid by different $Fe^{III}L_3$ (20.0 °C, $\mu = 1.0$ M) and the formal oxidation potentials of $Fe^{III}L_3/Fe^{II}L_3$ couples: (1) Fe^{III}dmphen$_3$; (2) Fe^{III}mphen$_3$; (3) Fe^{III}phen$_3$; (4) Fe^{III}cphen$_3$.

medium and temperature, and w_r and w_p are the coulombic work for bringing together reactants and products).

$$\Delta G^* = w_r + \lambda(1 + \Delta G^{\circ\prime}/\lambda)^2/4 \tag{8}$$

When both reactants are charged, the term w_r is given by

$$w_r = \frac{z_1 z_2 e^2}{D_s r^*} e^{-\kappa r^*} \tag{9}$$

where z_1 and z_2 are the charges of reactants, e the electron charge, D_s the static dielectric constant, and r^* the radius of the activated complex; the exponential coefficient is the Debye–Hückel term, where κ is the reciprocal Debye radius. It can be seen that at the present ionic strengths and with the investigated reagents the work terms are small.

The application of eq 8 to the present systems needs the knowledge of $\Delta G^*_{HA\cdot/HA^-}$ and $E^0_{HA\cdot/HA^-}$, coupled with $\Delta G^*_{Fe^{III}L_3/Fe^{II}L_3}$ and $E^0_{Fe^{III}L_3/Fe^{II}L_3}$. For $Fe^{III}L_3$, data concerning the oxidation potentials are available in the literature,[6] while for the intrinsic parameter both kinetic experiments and recent applications of Marcus theory suggest a value around 2.5–3.5 kcal mol^{-1}.[13] However, unfortunately no data are available for the parameters concerning ascorbic acid. The rate of electron exchange between HA^- and HA· should lie in the region 1×10^7–1×10^9 l. mol^{-1} s^{-1}, as observed for a series of reactions between radicals and parent molecules (see, for example, phenoxide ion with phenoxy radical[14] and the values previously derived for semiquinone/aromatic diol systems).[12]

Under these assumptions $\Delta G^*_{HA\cdot/HA^-}$ should be estimated to have a value ranging from 2.5 to 5.5 kcal mol^{-1} and tentatively ΔG^0 could be evaluated from the experimental ΔG^* of the reactions with $Fe^{III}L_3$ and $Fe(CN)_6{}^{3-}$ (another outer-sphere reaction whose intrinsic parameter is known).[15,16]

Thus the estimated $E^0_{HA\cdot/HA^-}$ should fall between 0.80 and 1.00 V. For example, the values of specific rate constants, calculated according to eq 8 with $\Delta G^*_{HA\cdot/HA^-} = 4$ kcal mol^{-1} and $E^0_{HA\cdot/HA^-} = 0.93$ V, are reported, together with the experimental ones in Table II.

Acknowledgment. We wish to thank Professor R. A. Marcus for a stimulating discussion in Leeds. We thank also CNR (Rome) for financial support.

Registry No. Fe(III)nphen$_3$, 22327-24-8; Fe(III)cphen$_3$, 22327-23-7; Fe(III)phen$_3$, 13479-49-7; Fe(III)mphen$_3$, 15226-32-1; Fe(III)dmphen$_3$, 17378-72-2; ascorbic acid, 50-81-7.

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Magnetic Properties of $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$ and Its Deuterium Analogue

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Measurements are reported of the specific heat and single-crystal principal susceptibilities in the helium region of $[(CH_3)_3ND]CoCl_3 \cdot 2D_2O$ and compared with those of the protonic material. The effect of deuteration on the magnetic ordering temperature as well as on the exchange parameters is negligible. Because of the weak ferromagnetism of this material, sample size and shape affect the accuracy of magnetic measurements, causing a larger effect on the results than does the replacement of hydrogen by deuterium.

Introduction

A number of magnetic properties, as well as the synthesis and crystal structure, of orthorhombic $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$ have been reported.[1-4] The material consists of chains of edge-sharing *trans*-$[CoCl_4(OH_2)_2]$ octahedra running parallel to the *b* axis; two chlorine atoms bridge the cobalt atoms. An additional chlorine atom in the lattice links the chains together by hydrogen bonding into a planar lattice with highly anisotropic magnetic behavior, and the trimethylammonium groups separate the planes both spatially and magnetically. With an antiferromagnetic T_c of 4.135 K, the zero-field magnetic susceptibilities and specific heat were well described by the lower dimensional Ising model both above and below T_c. The chains are ferromagnetically oriented. Finally, canting due to the Dzyaloshinsky–Moriya interaction was indicated by these measurements and confirmed by independent NMR measurements.[2] The canting leads to a weak ferromagnetism in the ordered state.

Several attempts[5–7] to elucidate the superexchange mechanisms which occur in hydrated crystals have depended on replacing the hydrogen atoms by deuterium. The critical temperature is usually found to change upon deuteration, varying as much as +6% in $CoCl_2 \cdot 6H_2O$[5] and as little as +0.8% in $(NH_4)_2CuBr_4 \cdot 2H_2O$.[6] Both positive and negative signs for ΔT_c have been observed. In the case of $CoBr_2 \cdot 6H_2O$, deuteration has even been found[7] to alter the crystallographic and magnetic space groups. These results have been discussed in terms of the change in the potential functions of the proton in a hydrogen bond.

We have previously noted[8] that T_c of $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$ changes negligibly upon deuteration to form $[(CH_3)_3ND]CoCl_3 \cdot 2D_2O$. It was argued that this was reasonable because the intrachain exchange constant, J, would not be expected to be much affected by deuterium substitution. Though J', the second-dimensional exchange constant, ought to be affected by deuteration, it is small, and because of the Ising nature of the lattice, a change of J' of as much as 20% will affect T_c by only about 4% in the present situation.

We have now extended the measurements on $[(CH_3)_3ND]CoCl_3 \cdot 2D_2O$ and have determined the exchange parameters, which are more meaningful than the value of T_c alone. Small changes in the experimental arrangement since the earlier report[1] necessitated a remeasurement of some of the properties of the protonic material, because it was found that the effect of deuteration on the magnetic properties of this substance really is so small that it lies within the bounds of our experimental error. In an instructive example, the large susceptibilities encountered here, caused by the weak ferromagnetic moment, require an estimate of the effects of demagnetization corrections.

Experimental Section

Trimethylammonium chloride was dissolved in D_2O and then dried under vacuum. Equimolar amounts of this salt and dehydrated cobalt(II) chloride were dissolved in D_2O under dry nitrogen. The resulting solution was allowed to evaporate slowly in a desiccator over concentrated sulfuric acid, to yield small single crystals of the desired salt, $[(CH_3)_3ND]CoCl_3 \cdot 2D_2O$. Isotopic purity was determined by NMR methods, as described below.

Proton NMR spectra were recorded of solutions of the deuterated and hydrated compounds at approximately 0.5 M in Me_2SO-d_6 and D_2O solvents. Blank spectra of the pure solvents were run to determine the concentration of H_2O impurity in each of the solvents and these values were used to correct for the presence of H_2O in the other runs.

The spectra of $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$ solutions showed a pronounced broadening and also a shift in position due to the presence of the paramagnetic cobalt ions. The positions of the peaks were determined relative to an external TMS standard. The approximate position of the water resonance in the presence of cobalt ions was determined by taking the spectra of $CoCl_2 \cdot 6H_2O$ in the solvent D_2O. A broad resonance appeared at δ 1.4 ppm relative to the external TMS standard. The spectrum of $[(CH_3)_3ND]CoCl_3 \cdot 2D_2O$ was taken separately in Me_2SO-d_6 and D_2O and showed the peaks due to methyl protons and water protons. These peaks were compared with the spectra of the undeuterated compound. The integrated intensities were standardized to the methyl groups and, correcting for H_2O solvent impurities, the relative concentrations of hydrogen and deuterium were determined. Using this method, the isotopic purity of the deuterated $[(CH_3)_3ND]CoCl_3 \cdot 2D_2O$ was determined to be approximately 94–98%.

The isothermal magnetic susceptibilities were measured from 1.5 to 25 K by the mutual inductance procedure, as before.[9] However, the cryostat has been modified to permit a precise centering of the sample. The sample holder is designed so that the sample can be moved relative to the coil and adjusted to a position of maximum susceptibility. The region of uniformity of the field of the measuring coil was also measured with a small sample of manganese Tutton salt at 1.5 K, and the sizes of the present samples were chosen so as to be smaller than this uniform region. The susceptibility of the sample holder alone was also measured over the entire temperature range and was fitted to a fifth degree polynomial in temperature. This correction was applied to each of the measured susceptibilities. A newly calibrated germanium thermometer was also used for temperature measurements.

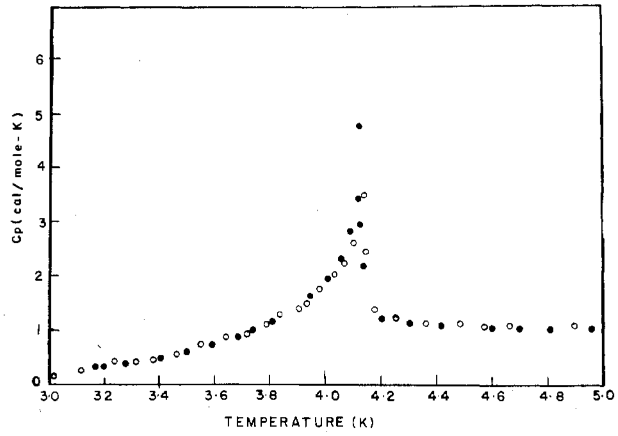

Figure 1. Heat capacity of the hydrated salt (open circles) and deuterated salt (solid circles).

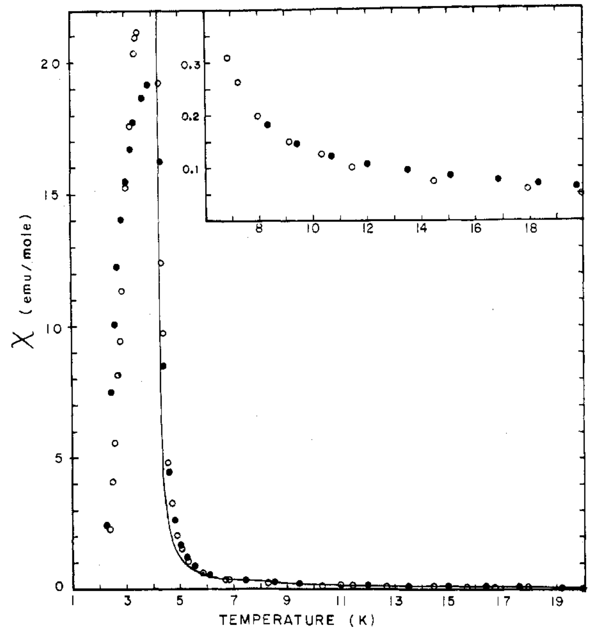

Figure 2. The a-axis susceptibilities of the two salts: solid line, fit to $\chi_a(D)$; solid circles, data for deuterated salt; open circles, data for hydrated salt; inset, high-temperature data on an expanded scale.

The heat capacity was measured in the 1–5-K range in the same cryostat described earlier.[9] The thermometer was recalibrated against the ^4He vapor pressure and the appropriate correction was applied.

Results

The measured heat capacity of the deuterated salt is shown in Figure 1 (solid circles), together with the results for the hydrated salt (open circles) from the previous measurements.[1] The two sets of data are seen to coincide very well. The maxima of the two curves are found to be separated by approximately 20 mK. This difference, which amounts to less than $^1/_2$% of T_c, lies on the border of our estimated experimental error.

The molar susceptibilities measured along the crystallographic a, b, and c axes are shown in Figures 2–4. The open

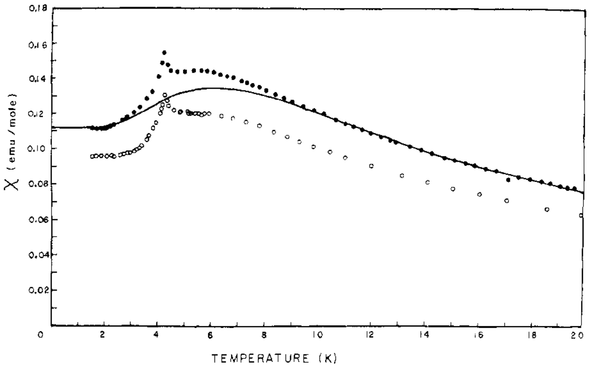

Figure 3. The *b*-axis susceptibilities of the two salts and the fitted curve for the deuterated salt data: solid circles, deuterated salt; open circles; hydrated salt.

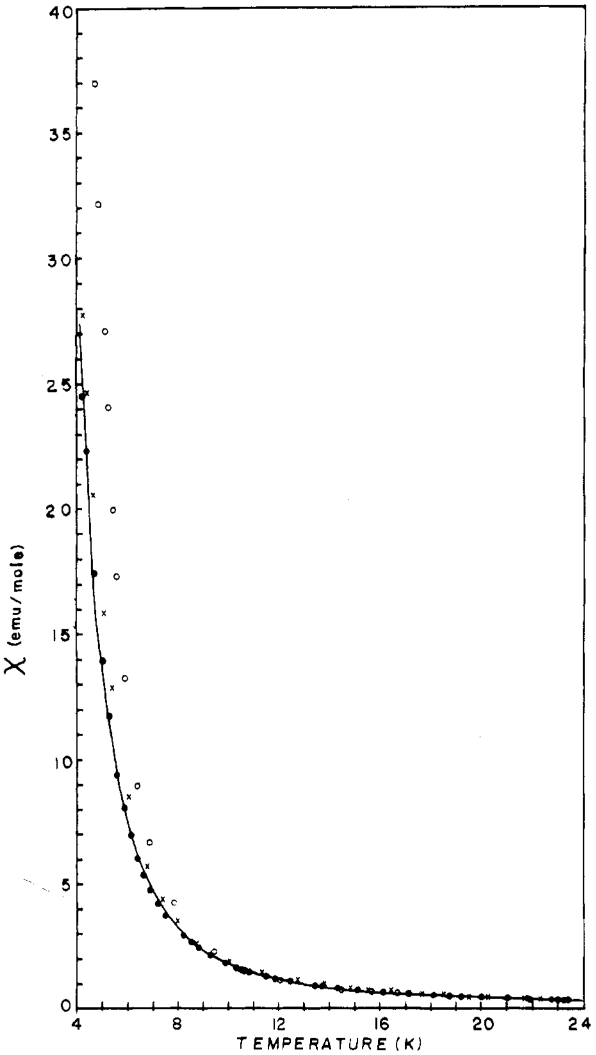

Figure 4. The *c*-axis susceptibilities for the two salts, showing significant differences. Crosses (X) show the new measurement of χ_c(H).

circles again represent the earlier, corresponding measurements of the hydrated salt. Qualitatively, the data may be seen to agree very well but there are some quantitative differences. On the high-temperature side, the susceptibilities of the deuterated salt are seen to be slightly larger than those of the hydrated crystal for all three directions of measurement. This is most likely attributed to the fact that the hydrated crystals were not properly centered in the measuring coil. The effect is seen to be largest for the smallest susceptibility, χ_b. On the low-temperature side, where the susceptibility grows to very large values, demagnetizing effects in the sample are seen to dominate the measurements.

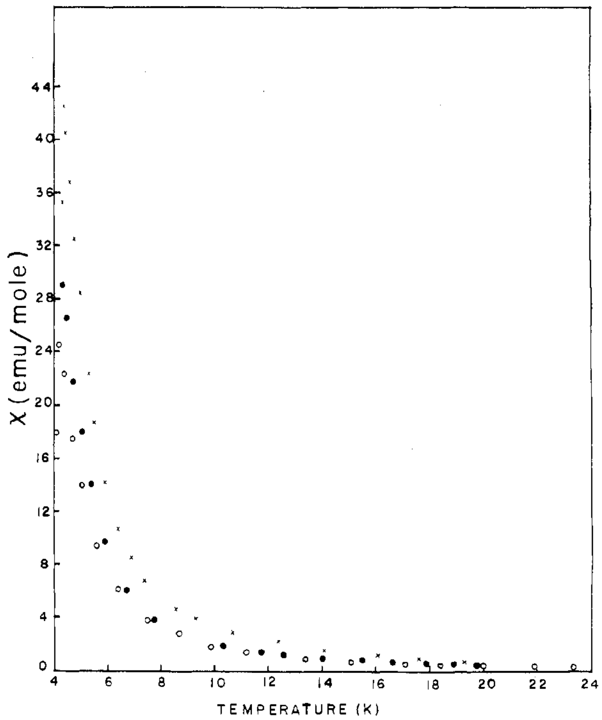

Figure 5. χ_c(D) for three samples of different sizes showing the presence of demagnetizing fields: X, sample I; ●, sample II; ○, sample III.

The measured susceptibility was also found to depend upon the size of the sample used. In Figure 5 are shown the experimental results of χ_c(D) measured for three different samples of weights, 0.58 mg (henceforth called sample I), 4.01 mg (sample II), and 8.68 mg (sample III). The samples were used in their natural shapes. The measured molar susceptibility is different for each sample, being largest at all temperatures for the smallest sample. Any differences in orientation are expected to play an insignificant part here, because as pointed out earlier,[1] it is very easy to orient the *c* axis of these crystals with a polarizing microscope due to the pronounced optical dichroism.

The crystals grow as prisms elongated along the *b* axis and bounded by (100), (201), and (011) planes.[1] These needles were always seen to grow thin and long and it was found difficult to grow them thicker. Samples of different weights were therefore cut to different lengths from these needles and will consequently have different thickness-to-length ratios. For the smallest sample used this ratio is expected to be close to 1 and for the largest sample (III) about 0.2. If the prisms are treated as ellipsoids of revolution as a very rough approximation and this ratio is taken as the ratio of minor and major axes, the demagnetization factor N can be estimated for these samples as $N_{\mathrm{I}} \approx \pi$ and $N_{\mathrm{III}} \approx 0.2\pi$. It can be easily derived that the measured susceptibility χ_m is related to the true susceptibility, χ_0, in the presence of demagnetization effects, by

$$\chi_m = \frac{\chi_0}{1 + (4\pi/3 - N)\chi_0} \qquad (1)$$

For $N < 4\pi/3$, this shows χ_m will be larger for the larger N, precisely the effect seen above.

In order to bypass these effects, we remeasured χ_c of the hydrated salt, choosing a crystal of weight (8.42 mg, IV) very close to that of sample III of the deuterated salt. These measurements are shown as crosses (×) in Figure 4. On the high-temperature side the two data sets agree within the experimental error (±0.04 emu/mol), but the data differ a little on the low-temperature side. For comparison, the previous measurements of Losee and co-workers on a specimen of 0.23-mg weight are also shown. This latter susceptibility is found to be higher than the new measurements at all temperatures below ~10 K, attaining a maximum value almost twice as high as we now find. The temperatures at which these maximum susceptibilities are attained are also different. Both of our measurements of χ_c(D) and χ_c(H) show this temperature to be 4.18 ± 0.01 K whereas Losee's apparently erroneous result showed it to be slightly higher than 4.30 K. Our value of $T_c(\chi_{\max})$ is closer to the T_c (4.131 K) obtained from the heat capacity measurements.

Discussion

Reference is made to the earlier paper[1] for the rationale behind the data analysis which follows. For the susceptibility along the quantization direction in an Ising chain

$$\chi_z = \frac{Ng_z^2\mu_B^2}{4kT}\exp(2J/kT) \tag{2}$$

and for the direction perpendicular to it

$$\chi_x = \frac{Ng_x^2\mu_B^2}{8J}\left[\tanh\frac{J}{kT} + \frac{J}{kT}\operatorname{sech}^2\frac{J}{kT}\right] \tag{3}$$

Because of the symmetry of the crystal, the crystal principal axes have been approximated as the same as the molecular principal axes.

The effect of the cross-linking of the chains was included in a molecular field approximation by assuming the interaction to be equivalent to a field H'

$$H' = \frac{2zJ'}{Ng_c^2\mu_B^2}\chi_c H \tag{4}$$

where χ_c is the new, exchange-corrected, principal crystal axis susceptibility. Equation 2 is then modified to

$$\chi_c = \frac{\chi_z}{1 - E\chi_z} \qquad E = \frac{2zJ'}{Ng_z^2\mu_B^2} \tag{5}$$

The crystallographic *c* axis was found to be the axis of quantization of the spins. The χ_c(H) data within the temperature range 4.3–20 K were fitted to eq 5 by choosing g_c and J'. The value of J/k (7.7 K) required[1] was the same as that derived from the heat capacity measurements. The effect of the J' term was observed to be significant only on the low-temperature side, and g_c = 6.54 ± 0.01 and J'/k = 0.085 ± 0.02 K were obtained from this procedure.

The same model was adopted for the deuterated salt, even though the same fitting procedure could not be used here. Because of the restricted range of temperature over which the heat capacity data were taken, these data could not be analyzed for J/k. Consequently in the following fits, J/k could not be fixed. Equation 5 was used to fit the data of Figure 4 for sample III. All three parameters J/k, J'/k, and g_c were chosen to fit these data over the entire range of temperature. The following values were taken as representing the best fits to the data: J/k = 7.45 ± 0.05 K, J'/k = –0.045 K, g_c = 6.6 ± 0.2, g_b = 4.20 ± 0.05.

These values of J/k, g_c, and g_b are quite comparable to those reported by Losee et al.[1] but that of J'/k not only is of different magnitude but also indicates an antiferromagnetic interaction between the chains as against the ferromagnetic interaction reported earlier. When our new data of χ_c(H) for sample IV were fitted to eq 5, a similar value of J'/k = –0.04 K was obtained.

The reversal of the sign of J'/k is considered as being due to an earlier neglect of the demagnetizing effects in interpreting the data. As mentioned above, these effects are extremely important in the region of temperature where the susceptibility grows to large values, and that is precisely the same region where the term of J'/k in eq 5 also has its maximum effect. This latter correction can be applied to eq 5 in the same molecular field approximation by adding an effective demagnetizing field

$$H_D = \left(\frac{4\pi}{3} - N\right)M = DM \qquad D = \frac{4\pi}{3} - N$$

to eq 4, where *N* is the demagnetizing factor as defined before and *M* is the magnetization. Equation 5 will then be modified to

$$\chi_c = \frac{\chi_z}{1 - (E - D)\chi_z} \tag{6}$$

where χ_z is still given by eq 2.

In the actual fitting procedure, the coefficient of χ_z is changed as one parameter and the value of J'/k is derived by multiplying it with $Ng_c^2\mu_B^2/2zk$. The interchain exchange field is very small. Taking Losee's value of J'/k = 0.085 K, we find E = 0.02. On the other hand, the effective demagnetizing field can be very different depending on the size of the sample as mentioned above. For the small sample (sample I), where the demagnetizing field is very large, *D* is very close to zero, and the fitted parameter can have a positive value, as obtained by Losee. For larger samples (sample III), on the other hand, *D* is large and consequently the value of the fitted parameter $(E - D)$ and hence of J'/k will be negative. Thus it may be that the interchain interactions in these salts are ferromagnetic in nature, but due to the overwhelming effect of the demagnetizing field, one cannot ascertain that definitely from these measurements.

It is shown in ref 10 that for $c/a > 4$, the demagnetizing factor *N* varies very slowly with c/a. Therefore for larger samples the demagnetizing effects are not expected to vary drastically with the size of the sample. For that reason our measurement of the susceptibility along the crystallographic *a* axis for the deuterated salt, χ_a(D), agrees very well with Losee's measurement of χ_a(H) on the low-temperature side even though a somewhat larger sample (19.49 mg) was used for χ_a(D) as against ≃6.9 mg for χ_a(H). The maximum susceptibility attained in χ_a(D) is only slightly smaller than the corresponding maximum in χ_a(H). The temperature of this maximum could not be compared precisely for lack of χ_a(H) data in this temperature region. However, from measurements on two different crystals Losee has observed a temperature region of nearly constant susceptibility between 2.4 and 4.3 K, with the size of this region being dependent on the demagnetizing effects, decreasing for larger crystals. This constant behavior was interpreted as being due to the canting of the spins along the *a* axis. With a weakly ferromagnetic interaction between the spins, canting thus gives a permanent magnetic moment along this direction. The observed behavior was seen to be consistent with Moriya's[11] calculations of the susceptibility of a linear-chain system of spin $-^1/_2$, along the direction of weak ferromagnetic moment

$$\chi = Ng^2\mu_B^2(T - T_0)/4k(T^2 - T_c^2) \tag{7}$$

where

$$T_0 = -T_c/[1 + (D/J)^2]^{1/2}$$

J is the usual intrachain coupling parameter and *D* is the antisymmetric Dzyalozhinsky–Moriya interaction constant which is responsible for the canting of the spins.[11]

A similar canting behavior was observed for the deuterated salt also. Between 3.7 and 4.3 K, $\chi_a(\mathrm{D})$ was found to be constant. Below this temperature, it dropped off sharply to a constant value of 0.055 ± 0.002 emu/mol at the lowest temperatures. Both the drop off rate and the size of the region of constant χ are smaller here and appear to be consistent with Losee's conclusion of being due to larger demagnetizing effects. The value of the constant susceptibilities also agrees favorably with Losee's value of 0.056 emu/mol for $\chi_a(\mathrm{H})$.

Between 4.3 and 22 K, the data were fitted to eq 7 by varying simultaneously g_a and the constant D/J. Good fits within 10% of the measured susceptibilities were obtained for $g_a = 3.23 \pm 0.05$ and $|D/J| = 0.65 \pm 0.2$. Whereas this value of $|D/J|$ is the same as obtained by Losee for $\chi_a(\mathrm{H})$, g_a is somewhat larger than the earlier value of 2.95 ± 0.05.

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Registry No. $[(CH_3)_3NH]CoCl_3{\cdot}2H_2O$, 60294-92-0; $[(CH_3)_3ND]CoCl_3{\cdot}2D_2O$, 60294-94-2.

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Preparation and Photochemistry of Azidopentacyanorhodate(III) and -iridate(III)

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The potassium salts of the complex ions $[Rh(CN)_5N_3]^{3-}$ and $[Ir(CN)_5N_3]^{3-}$ have been prepared and characterized. Their electronic spectra show weak ($\epsilon \sim 230$) bands near 3.2 μm^{-1}, which are assigned to N_3^--localized electronic transitions. The photochemistry associated with these bands appears to be nearly exclusively simple aquation, with high quantum yields ($\Phi = 0.42$ for the rhodium complex and 0.60 for the iridium complex). The marked contrast between these results and those obtained by other workers for the analogous amine complexes is discussed.

Introduction

A series of recent papers by Basolo and co-workers[1] has established a novel photochemical reaction of the complexes $M(NH_3)_5N_3^{2+}$, M = Rh and Ir, yielding intermediates, presumed to be coordinated nitrenes, $M(NH_3)_5N^{2+}$, which undergo reactions with nucleophiles to give characteristic products. An unresolved problem arising from this work is the nature of the reactive excited state. Basolo and co-workers[1] have argued that the reaction could not be associated with metal-centered ligand field excited states and suggested that it arose from states, postulated to be the lowest excited states available to the complexes, in which excitation is localized in the azide ligand. Unfortunately, the observed low-energy absorption bands of the complexes could be plausibly assigned to ligand field transitions,[1] and the ligand-localized transition could only be assumed to be weak and obscured by the other, stronger, absorption bands.

Our continuing interest in high-energy photochemical products led us to attempt the investigation of analogous azidopentacyano complexes. Previous work with other pentacyano derivatives[2,3] had shown that both ligand field and charge-transfer type electronic transitions are shifted to higher energy relative to pentaammine analogues. Consequently we anticipate that weak, ligand-localized transitions might be *directly* observable.

Experimental Section

Preparation of $K_3[Rh(CN)_5N_3]{\cdot}H_2O$ and $K_3[Ir(CN)_5N_3]{\cdot}H_2O$. Solutions of $K_2[Rh(CN)_5OH_2]$ or $K_2[Ir(CN)_5OH_2]$ were prepared by 254-nm photolysis of aqueous (adjusted to pH 1 with concentrated $HClO_4$) solutions of $K_3[Rh(CN)_6]$ or $K_3[Ir(CN)_6]$, as described by Geoffroy et al.[2] Our preparations employed ~200 ml of $\sim 10^{-3}$ M solution.

The volume of a solution prepared as described above was reduced to 10 ml under reduced pressure at 40 °C. The pH was then brought to 6 with concentrated aqueous KOH and ~1 g of KN_3 was added. After standing for 1–2 days, the solution was filtered and 250 ml of acetone was added to give an off-white precipitate. Operations from this point on were conducted with minimal exposure to light. The precipitate was extracted with 50 ml of warm methanol, and the resulting solution was filtered. Acetone (100 ml) and ether (35 ml) were added, precipitating about half of the dissolved material. The precipitate was filtered off and the mother liquor, containing mainly potassium azide, was discarded.

The above recrystallization procedure was repeated (usually two or three times) until the infrared spectrum (KBr pellet) of the white product showed no trace of the sharp bands of KN_3 at 650 cm^{-1} and 644 cm^{-1}. The infrared spectra indicated the presence of crystal water (moderately sharp bands at 3640, 3560, and 1605 cm^{-1} for both compounds), and a monohydrate formulation fits the analytical data reasonably well. Anal. Calcd for $K_3[Rh(CN)_5N_3]{\cdot}H_2O$: Rh, 25.08; C, 14.63; H, 0.49; N, 27,31; C:N, 0.536. Found: Rh, 25.23; C, 14.41; H, 1.03; N, 27.00; C:N, 0.532. Calcd for $K_3[Ir(CN)_5N_3]{\cdot}H_2O$: Ir, 38.47; C, 12.02; H, 0.40; N, 22.63; C:N, 0.536. Found: Ir, 39.65; C, 12.18; H, 0.58; N, 22.60; C:N, 0.539.

Strong infrared bands, in addition to those previously mentioned, were observed for the rhodium complex at 2135, 2072, and 1297 cm^{-1} and for the iridium complex at 2130, 2080, and 1295 cm^{-1}. These are assigned, for both complexes, to $\nu(CN)$, $\nu_{as}(N_3)$, and $\nu_s(N_3)$, in order.

Irradiation Procedures. Three-milliliter samples were irradiated using a merry-go-round,[4] employing filters to isolate the group of lines near 313 nm in the spectrum of a medium-pressure mercury lamp.