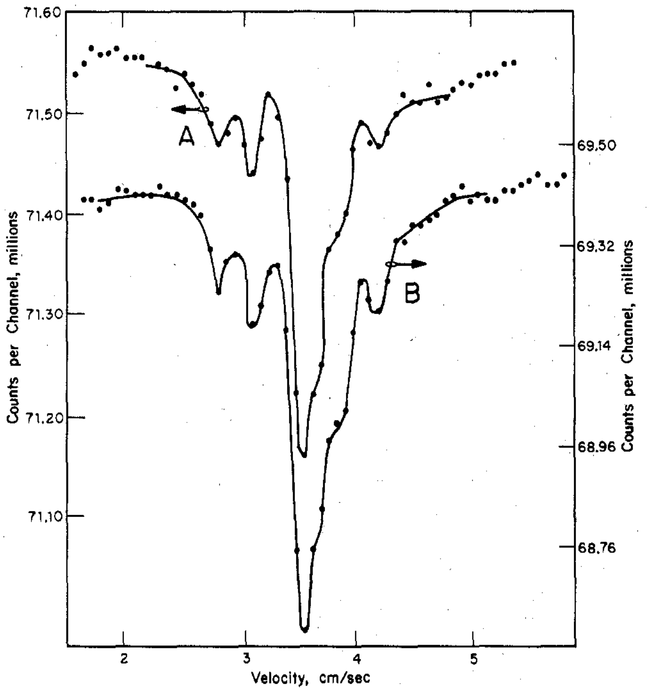

Figure 2. Mössbauer spectra of (A) "$KNpCl_4$" and (B) a mixture of K_2NpCl_5 and $NpCl_3 \cdot 4CH_3CN$.

either broader lines or splitting of lines. An example of these spectra is shown in Figure 2A, for "$KNpCl_4$". The spectrum of "$KNpCl_4$" could be reproduced by the spectrum of an equimolar mixture of K_2NpCl_5 and $NpCl_3 \cdot 4CH_3CN$ (Figure 2B). The obvious conclusion is that "$KNpCl_4$" is a mixture of K_2NpCl_5 and $NpCl_3 \cdot 4CH_3CN$. It is still possible that the compound $KNpCl_4$ exists with Np^{3+} ions in two different sites. Unfortunately, repeated attempts to obtain X-ray powder diffraction patterns on these compounds failed. However, from the Mössbauer evidence, the existence of $MNpCl_4$ must be regarded as dubious.

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Registry No. K_2NpCl_5, 73284-55-6; $(NH_4)_2NpCl_5$, 73272-81-8; Rb_2NpCl_5, 73272-82-9; $NpCl_3 \cdot 4CH_3CN$, 73272-83-0; $NpCl_4$, 15597-84-9.

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Single-Crystal Magnetic Susceptibility Study of the Linear-Chain Heisenberg Antiferromagnet Copper(II) Pyrazine Nitrate

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There is considerable interest in the magnetic properties of polynuclear and polymeric transition-metal complexes bridged by small diaza heterocyclic molecules[2,3] such as pyrazine. The complex dinitro(pyrazine)copper(II), $Cu(pz)(NO_3)_2$, consisting of linear chains of copper(II) ions bridged by 1,4-pyrazine molecules (Figure 1), is of interest in this context. The bulk magnetic susceptibility of this compound shows a broad maximum at about 7 K[4-6] with no evidence of any long-range interchain interactions down to 0.18 K. This then makes $Cu(pz)(NO_3)_2$ a very suitable system for the study of magnetic exchange interactions in an isolated linear chain of copper(II) ions.[7]

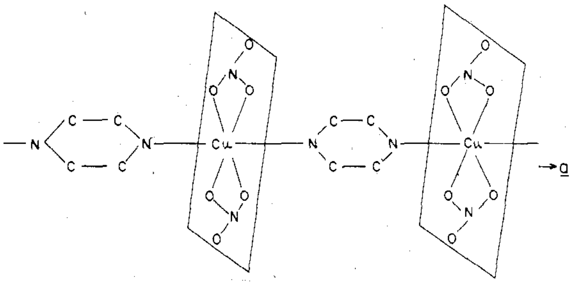

Figure 1. Pyrazine bridging in $Cu(pz)(NO_3)_2$.

In an earlier study the average susceptibility, $\bar{\chi}$, of $Cu(pz)(NO_3)_2$ was reported to 2 K, and the data were analyzed in terms of an antiferromagnetic Ising chain with $J = -6.0$ cm^{-1}.[4] Subsequently a "single-crystal" study was performed by Losee and co-workers[5] on a bundle of crystals all oriented along the *a* axis but with the *b* and *c* axes of the orthorhombic crystal randomly oriented.[8] The *a* axis of the crystal is also the direction of the linear chain, and so $\chi_{\|}$, the susceptibility parallel to the *a* axis, was χ_a and $\chi_{\perp}$, the susceptibility perpendicular to the *a* axis, was some average of χ_b and χ_c. The data were shown to be described by the isotropic Heisenberg model.[5] A further study of the bulk susceptibility also showed the behavior expected of an antiferromagnetic Heisenberg chain with $J/k = -5.5$ K.[6]

Single-crystal ESR data[9,10] on $Cu(pz)(NO_3)_2$ gives $g_a = 2.05$, $g_b = 2.27$, and $g_c = 2.06$, showing that the *g* anisotropy lies between the *b* axis and the *ac* plane. On this basis it would then be expected that χ_a and χ_c should be of similar magnitude and differ markedly from χ_b.

In the present work we report the determination of the principal crystal susceptibilities χ_a, χ_b, and χ_c of $Cu(pz)(NO_3)_2$ and analyze the data on the basis of the appropriate exchange model.

Experimental Section

Well-developed needle-shaped crystals of $Cu(pz)(NO_3)_2$ were grown by slow evaporation of an aqueous 1:1 solution of cupric nitrate and pyrazine.[8] Crystal axes were determined by Weissenberg and rotation X-ray photography. The principal crystal magnetic susceptibilities χ_a, χ_b, and χ_c were determined from measurement of the magnetic anisotropies $\chi_b - \chi_a$ and $\chi_b - \chi_c$ of the single crystal and the bulk susceptibility. The magnetic anisotropies of crystals weighing between 2-3 mg were measured by using the Krishan critical torque method, between 4.8 and 100 K, with equipment described earlier.[11] Measurements were made with the *a* and *c* axes vertical, giving $\chi_b - \chi_c$ and $\chi_b - \chi_a$, respectively. Measurements on three individual crystals did not show a scatter exceeding 2%. The magnetic fields used for the critical torque experiment ranged between 0.2 and 0.4 T. The

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(1) To whom correspondence should be addressed at the Tata Institute of Fundamental Research.
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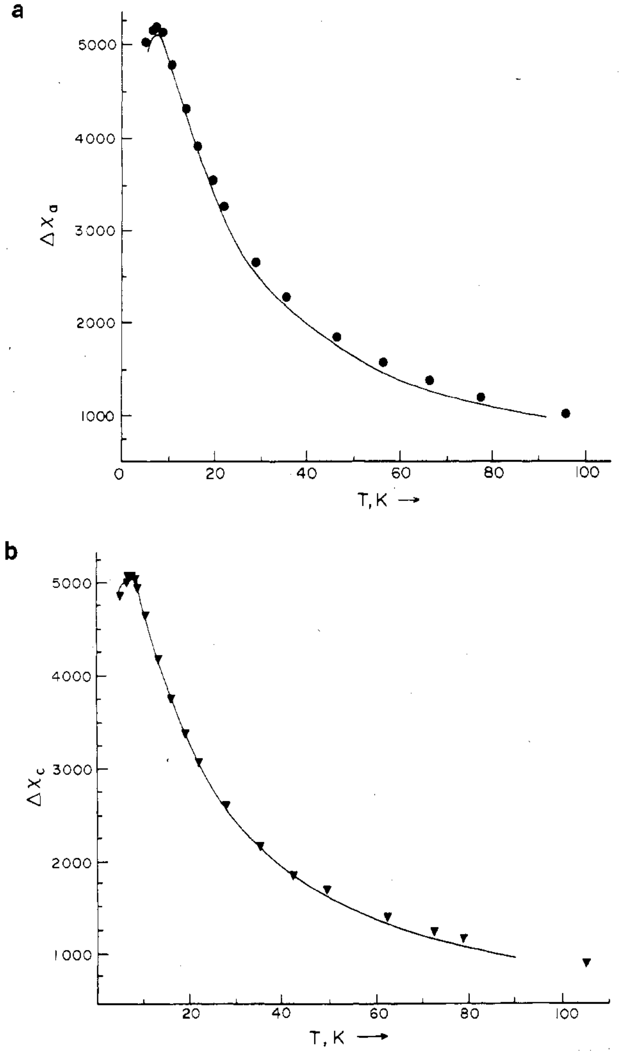

Figure 2. Measured anisotropic susceptibility (a) $\Delta\chi_a$ (●) and (b) $\Delta\chi_c$ (▲) in the temperature range 4.8–100 K for $Cu(pz)(NO_3)_2$. Full lines are calculated for least-squares best-fit parameters in Figure 3. The anisotropies are in 10^6 cm^3/mol.

average susceptibility was measured by using a modified Oxford Instruments Faraday balance described earlier.[11]

Results and Discussion

Figure 2 shows the measured anisotropies $\Delta\chi_a$ and $\Delta\chi_c$ in the temperature range 4.8–100 K. The measured average susceptibility data $\bar{\chi}$ agreed well with the reported values.[4,6] The calculated values of χ_a, χ_b, and χ_c between 5 and 100 K are shown in Figure 3. The principal susceptibilities pass through a broad maximum at 7.1 K as found previously[3–6] with χ_a approximately equal to χ_c ($\chi_a \simeq \chi_c$) and $\chi_b > \chi_a$ or χ_c throughout the temperature range. Thus the anisotropy in susceptibility is found to be between the *b* axis and the *ac* plane. In the work of Losee et al.[5] the anisotropy in the *bc* plane was averaged out by the use of several crystals bundled together along the *a* axis. χ_a found in this work corresponds to their $\chi_{\parallel}$ while $\chi_{\perp}$ is the average of χ_b and χ_c. The true anisotropy of the system is larger than previously measured, for example, at 7 K the maximum anisotropy is 5.0×10^{-3} as against 1.3×10^{-3} reported by Losee et al.[5]

The temperature dependence of χ_a, χ_b, and χ_c and the magnitude of the anisotropy suggests that $Cu(pz)(NO_3)_2$ behaves as an antiferromagnetic Heisenberg chain.[7] The limiting behavior of antiferromagnetic Heisenberg chains in the case of infinite chains has been investigated by Bonner and Fisher.[12] From their calculations values of *J*, the Heisenberg isotropic exchange parameter, and *g*, the Zeeman splitting factor, may be estimated by using $kT_{max}/|J| = 1.282$ and $\chi_{max}|J|/N\beta^2g^2 = 0.07346$, where T_{max} is the temperature corresponding to the maximum in susceptibility χ_{max}.

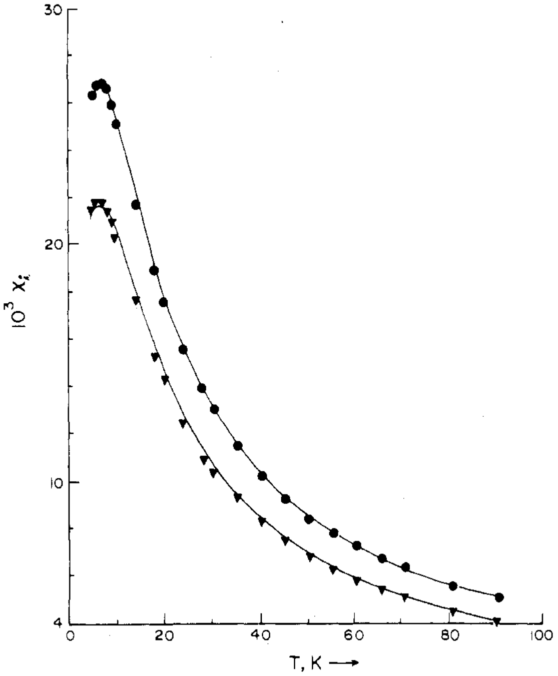

Figure 3. Principal susceptibilities χ_a ($\simeq\chi_c$) (▼) and χ_b (●) of $Cu(pz)(NO_3)_2$ in the temperature range 4.8–100 K. Full lines show curves calculated from least-squares best-fit parameters (χ_b: g_b = 2.27, $N\alpha_{(b)} = 85 \times 10^{-6}$ cm^3/mol, $J/k = -5.3$ K. χ_a: g_a = 2.05, $N\alpha_{(a)} = 19 \times 10^{-6}$ cm^3/mol, $J/k = -5.4$ K). Experimental values are interpolated values of the bulk susceptibilities and anisotropies at the same temperature. The susceptibilities are in 10^6 cm^3/mol.

From Figure 3 a maximum in the principal susceptibility occurs at $T_{max} = 6.9 \pm 0.2$ K, giving an estimate of J/k as -5.3 K from the first formula of Bonner and Fisher. With use of this value of *J* and the principal susceptibilities χ_a, χ_b, and χ_c at 6.9 K the calculated values are $g_a = g_c = 2.05 \pm 0.02$ and $g_b = 2.27 \pm 0.02$.

Recently the numerical results of Bonner and Fisher[12] have been fitted to a rational function of powers of $X = |J|/kT$ by Hall and Hatfield[13] (eq 1), where $N\alpha_i$ is the temperature-independent paramagnetism.

$$\bar{\chi} = \frac{Ng^2\beta^2(0.25 + 0.1995X + 0.30094X^2)}{kT(1.04 + 1.9862X + 0.68854X^2 + 6.0626X^3)} + N\alpha_i$$

A least-squares fitting procedure was used to fit the above equation to the measured susceptibilities χ_b and $\chi_{a,c}$. In the first instance the *g* values used were those determined above which are similar to the ESR values determined experimentally[9] (g_b = 2.27, $g_a = g_c$ = 2.05). Contributions to the susceptibility of temperature-independent paramagnetism were estimated by using orbital energies previously determined from optical spectra[9a] and assuming the splitting of the *xz*, *yz* orbitals to be small such that the environment about any copper ion was electronically axial. The data were then fitted by using only *J* as a variable parameter to give $J/k = -5.3$ K for χ_b (g_b = 2.27, $N\alpha_{(b)} = 85 \times 10^{-6}$ cm^3/mol) and $J/k = -5.4$ K for $\chi_{a,c}$ ($g_{a,c}$ = 2.05, $N\alpha_{(a)} = 19 \times 10^{-6}$ cm^3/mol). The values of *J* agreed to within experimental error. Figure 3 shows the curves calculated for each

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of these sets of parameters. To within the experimental error the value of the isotropic exchange parameter agrees with that reported by previous works of 5.5[6] and 5.3 K.[4,5]

Conclusion

The present study shows that the three principal crystal susceptibilities of even very small weakly anisotropic single crystals can be conveniently determined by combining magnetic anisotropy and average susceptibility data. The present data of principal susceptibilities of $Cu(pz)(NO_3)_2$ over the entire temperature range was found to conform well by using experimental *g* values, as expected, with an isotropic Heisenberg chain.

Registry No. $Cu(pz)(NO_3)_2$, 28209-64-5.

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Single-Electron Reactions of Vitamin B_{12s}: Reduction of Chromium(III) Complexes

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Vitamin B_{12s} is a cobalt(I) corrin complex, also known as cob(I)alamin, having a formula we abbreviate as $[Co^I]^-$. Other derivatives referred to in this work are vitamins B_{12r} and B_{12a} (aquocobalamin), $[Co^{II}]$ and $[Co^{III}]^+$, respectively, and organometallic derivatives such as the alkylcobalamins, R[Co]. B_{12s} is a powerful nucleophile toward organic halides[1] (RX) (eq 1) and toward acetylenic compounds[2] (eq 2).

$$[Co^I]^- + RX \rightarrow R[Co] + X^- \qquad (1)$$

$$[Co^I]^- + HC{\equiv}CH + H_2O \rightarrow H_2C{=}CH[Co] + OH^- \qquad (2)$$

On the other hand, only a very limited amount of work has been done relating to another aspect of the chemistry of B_{12s}, its reactivity as a powerful one-electron reducing agent. Our earlier work[3] on this aspect of B_{12} chemistry included a study of its reaction with aquo- and hydroxocobalamin. Instability of the cobalt(I) compound toward hydrogen evolution in neutral or acidic solution[4,5] has hindered the study of a wider range of metal complexes. We have now found that B_{12s} can be generated electrochemically at pH 2.5–3.2 in aqueous glycine buffers to yield solutions that are reasonably stable over several hours. We report here on the kinetics of reduction of a family of chromium(III) complexes, $(H_2O)_5CrX^{2+}$ with X = F^-, Cl^-, Br^-, N_3^-, NCS^-, OAc^-, SH^-, and OH^-. The reaction produces B_{12r} and $Cr^{2+}(aq)$ as shown in eq 3.

$$[Co^I]^- + (H_2O)_5CrX^{2+} \rightarrow [Co^{II}] + Cr^{2+}(aq) + X^- \qquad (3)$$

Experimental Section

Solutions of vitamin B_{12a} (Sigma Chemicals Co.) were made up in 0.05 M sodium perchlorate and 0.05 M glycine to which sufficient perchloric acid had been added to adjust the pH to its desired value in the range 2.5–3.2. The B_{12} solutions, under argon, were reduced to B_{12s} at an applied potential of −1.5 V supplied by a Princeton Applied Research potentiostat. The electrochemical cell consisted of a mercury pool cathode, a platinum wire anode, and a saturated calomel reference electrode separated from the cell by a bridge containing 0.05 M sodium perchlorate.

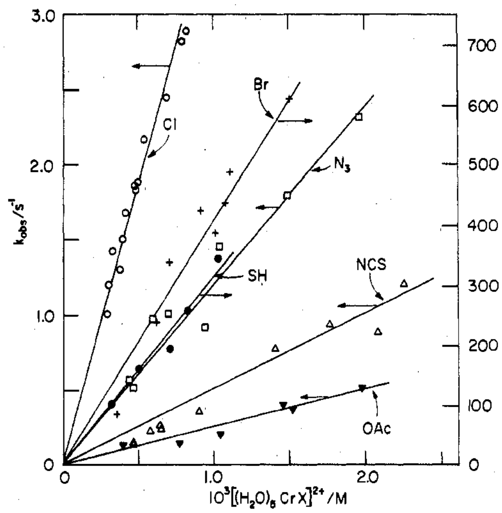

Figure 1. Plots showing the variation of the pseudo-first-order rate constants with the average concentration of the CrX^{2+} complex.

The chromium(III) complexes were prepared by standard methods:[6–10] (1) reaction of $(NH_3)_5CoX^{2+}$ with Cr^{2+} followed by ion-exchange chromatography for X = F (Bio-Rad Cellex P cation-exchange resin, elution with 0.1 M perchloric acid) and OAc (Sephadex C-25, elution with 0.18 M $LiClO_4$ and 0.02 M $HClO_4$); (2) reaction of X^- with $Cr(H_2O)_6^{3+}$ for X = Cl^- and NCS^- (Dowex 50W-X8, elution with 1 M $(Na,H)ClO_4$); (3) reaction of Cr^{2+} with Br_3^- (Dowex 50W-X8, elution with 0.8 M $NaClO_4$ and 0.05 M $HClO_4$); (4) reaction of Cr^{2+} with polysulfide,[9] volatilization of H_2S, oxygenation to remove excess Cr^{2+}, and separation on Dowex 50W-X8. Additional Cr^{2+} was added to the crude $CrSH^{2+}$, and the separation was repeated, yielding a pure product which was stable for 24 h at pH 2 and 0 °C. The products had UV–visible spectra which matched the published values.[6–10]

The reactions in eq 3 were monitored spectrophotometrically, following the decrease in $[B_{12s}]$ at 385 nm ($\epsilon \sim 3.08 \times 10^4$ M^{-1} cm^{-1}) or the increase in $[B_{12r}]$ at 470 nm ($\epsilon \sim 1.10 \times 10^4$ M^{-1} cm^{-1}) with use of a Cary 219 or a Durrum D-110 stopped-flow spectrophotometer. The conditions in the kinetic determinations were chosen with a large excess of the chromium(III) complex, yielding data which conformed to pseudo-first-order kinetics. Throughout the course of the reactions the solutions were maintained under rigorously oxygen-free conditions.

Results and Discussion

The 1:1 stoichiometry shown in eq 3 was confirmed by spectrophotometric titration, and the quantitative formation of B_{12r} confirmed by the product spectra. The Cr^{2+} formed in the reaction of B_{12s} and $CrNCS^{2+}$ was detected by addition of $Co(NH_3)_5Cl^{2+}$ to convert Cr^{2+} to $CrCl^{2+}$. The resulting solution was first passed through a column of the macroreticular XAD-4 resin to remove all B_{12} species, and subsequently $CrCl^{2+}$ was separated from Co^{2+} by chromatography on a Dowex 50W-X8. The identity of $CrCl^{2+}$ was confirmed by its absorption spectrum, and the yield in two experiments was 68 and 86% of the value expected from eq 3 and the amount of B_{12s} taken. These findings confirm the production of Cr^{2+} and, considering the practical difficulties and separations, especially the problem of quantitative assay of the highly reactive and oxygen-sensitive B_{12s}, also constitute reasonable

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