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Magnetic Properties and Crystal Structure of (2,3-Pyrazinedicarboxylato)copper(II) Hydrochloride: A Pyrazine-Bridged Ferromagnetic Linear Chain[1]

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The crystal structure and variable-temperature magnetic susceptibility measurements are reported for the title complex Cu(pzdc)·HCl where pzdc is 2,3-pyrazinedicarboxylate. The complex crystallizes in space group $Pna2_1$, as infinite linear chains which are propagated along the [011] axis at $x = {}^1/_4$ and along the $[0\bar{1}1]$ axis at $x = {}^3/_4$. The magnetic data is consistent with ferromagnetic intrachain exchange. The $S = {}^1/_2$ Heisenberg ferromagnetic linear chain analysis results in magnetic parameters of $g = 2.26$ and $J/k = 1.9$ K. An interesting structural feature which may explain the ferromagnetic exchange is the nearly right angle orientation (91°) of the next neighboring intrachain pyrazine-bridging planes. Crystal data: space group $Pna2_1$, $Z = 4$, $a = 9.552$ (2) Å, $b = 10.888$ (2) Å, $c = 7.719$ (11) Å^3, $R = 0.06_7$ for 806 reflections.

Introduction

There are relatively few examples in the literature of ferromagnetic coupling in one-dimensional linear chains. Calculations which describe the temperature-dependent magnetic behavior of these systems have been known for quite some time, but, until recently, there have been no experimental models to test these theories. Recently, several linear-chain complexes have been prepared which exhibit ferromagnetic coupling.[4-7] However, to date, all known examples of one-dimensional ferromagnetic materials are bridged by single-atom bridges. We report here on the first example of a linear-chain complex bridged by a substituted pyrazine ligand, which exhibits ferromagnetic intrachain coupling.

Pyrazine is well-known to act as a bridging ligand, especially in low-dimensional materials.[8-12] These types of systems are particularly informative since the use of a relatively simple bridging ligand (pyrazine) permits a study of the mechanism of magnetic coupling over extended distances. Magnetic studies of pyrazine-bridged complexes have usually been with unsubstituted pyrazine ligands. By adding a coordinating substituent group to the pyrazine ring, one may investigate whether there is a steric restriction on the effectiveness of the bridge as a magnetic-exchange pathway. A recent report[13] has shown that pyrazinecarboxylic acid (**1**) and 2,3-pyrazinedicarboxylic acid (**2**), when complexed with cobalt(II) chloride, result in weak magnetic coupling between monomeric molecular units. We are continuing this study of the effects of substituted-pyrazine ligands using copper(II) as the central metal with **2** as the coordinating ligand. We report on the X-ray crystal structure and powder magnetic susceptibility measurements from 6 to 300 K for Cu(pzdc)·HCl, where pzdc = 2,3-pyrazinedicarboxylate.

Experimental Section

Synthesis. Hydrated copper(II) chloride reagent and 2,3-pyrazinedicarboxylic acid were dissolved in 6 N HCl solutions. The two solutions were then mixed and allowed to stand in a beaker covered with a watch glass. After several days, well-developed single crystals were deposited. A single crystal was chosen for X-ray studies, and the remainder of the polycrystalline sample was used for susceptibility studies.

Magnetic Susceptibility. Static magnetic susceptibility measurements were recorded on an alternating force magnetometer (AFM).[14-16] The magnetic force is detected with a Cahn 2000 electrobalance, and the sample is suspended from the balance by nylon and quartz fibers. The sample is placed in a high-purity quartz bucket. The temperature is varied from 6 to 300 K with a helium-transfer Dewar[17] and a digital temperature controller.[18] The static magnetic field, H, is provided by a large electromagnet which is capable of generating fields of up to 10 kOe. The field gradient, dH/dz, is generated by Lewis field gradient coils[15,16] and a bipolar power supply[16] which is capable of reversing current polarity and changing the direction of the magnetic force on the sample. The maximum current of 20 A through the Lewis coils produces a field gradient of about 180 Oe/cm. Operating in its most sensitive mode, the AFM generates a value of $H(dH/dz) > 10^6$ Oe^2/cm. A high degree of precision and accuracy may be obtained with the instrument. The instrument was calibrated with cobalt mercury thiocyanate and a single crystal of manganese Tutton salt. Both calibrations agreed to within 1%. A 130-mg polycrystalline sample was used for susceptibility measurements of Cu(pzdc)·HCl. The magnetic susceptibility data are listed in Table 2 (supplementary material).

Crystal Structure Determination. A green octahedral crystal of the copper complex, approximately 0.25 mm across, was used in determining symmetry, cell dimensions, and data taking. Systematic extinctions [($0kl$), $k + l = 2n + 1$; ($hk0$), $h = 2n + 1$] limited the space group choices to $Pna2_1$ and $Pnma$. The successful solution of the structure in space group $Pna2_1$ verified this as the correct space group. Lattice constants were determined by a least-squares fit of 24 carefully measured 2θ values (1° takeoff angle and 0.05° slit) of the copper Kα doublet for reflections with $2\theta > 65°$. The resultant lattice constants and their estimated standard deviations are

$$a = 9.552\ (2)\ \text{Å} \qquad b = 10.888\ (2)\ \text{Å} \qquad c = 7.719\ (1)\ \text{Å}$$

The experimental density, 2.10 g/cm^{-3} as measured by flotation techniques, agrees with a calculated density of 2.16 g/cm^{-3} for four molecules per unit cell.

Three-dimensional intensity data were collected on a General Electric XRD-490 fully automated diffractometer using balanced nickel and cobalt filters with Cu Kα radiation. A total of 925 reflections were measured to a 2θ maximum of 140°. Of these, 806 (86%) were considered statistically significant by the criterion

$$[I_{\text{Ni}} - 2\sigma(I_{\text{Ni}})] - [I_{\text{Co}} - 2\sigma(I_{\text{Co}})] > T$$

where $T = 125$ and the σ's were based entirely on counting statistics.

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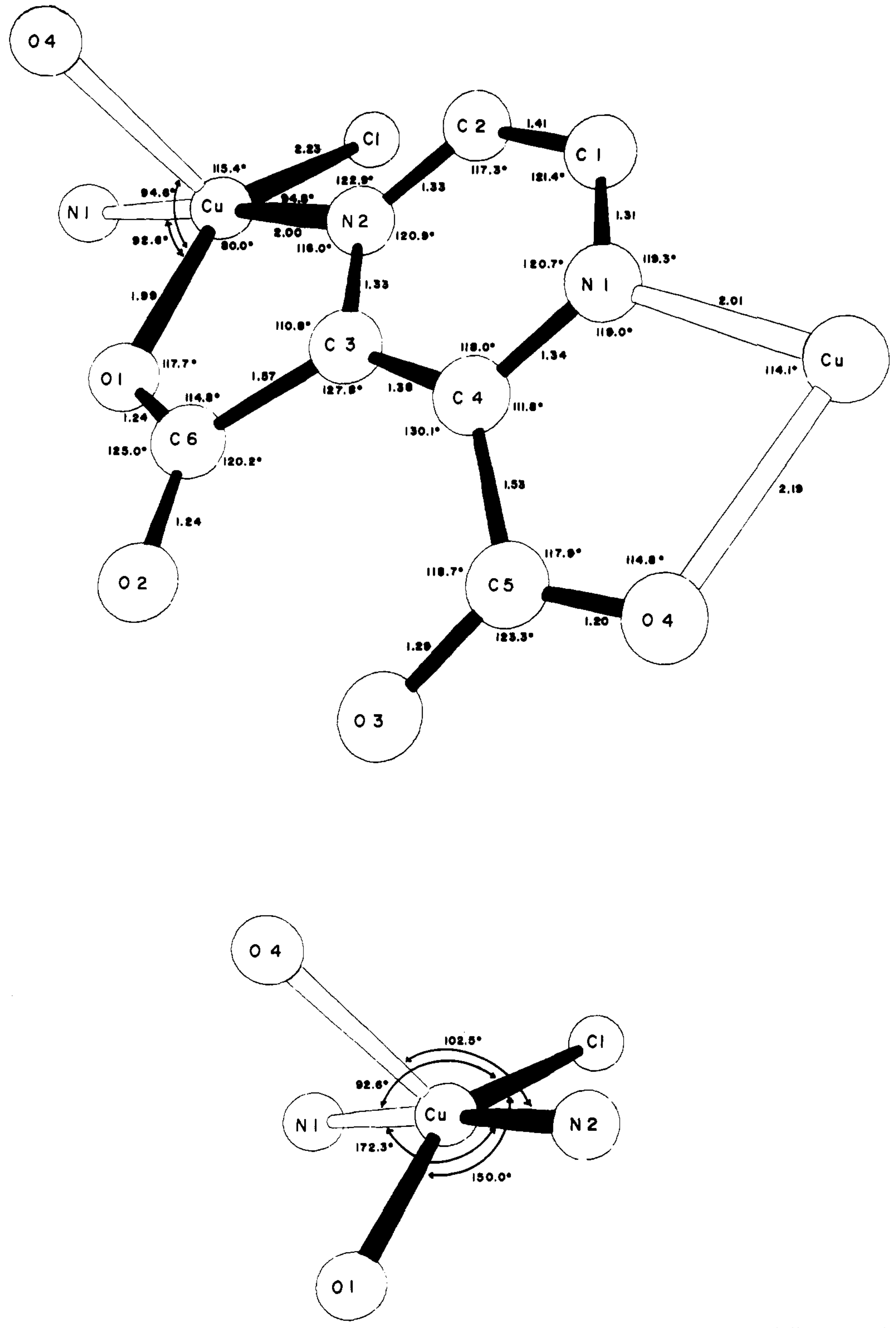

Figure 1. Schematic drawing of one asymmetric unit of the chain including bonding distances and angles and distanes and angles about the copper.

The intensities were corrected and reduced to structure amplitudes in the usual manner.

Heavy-atom techniques including solving of the Patterson function, followed by alternant Fourier and least-squares procedures, ultimately led to a reliability index of $R = 0.069$[19] with unit weights. Using hydrogens with fixed coordinates and isotropic temperature factors (4.0 $Å^2$) and using $1/\sigma^2$ weights, least-squares refinements for the 17-atom structure were continued until the magnitudes of the shifts were less than 0.1 of the estimated standard deviations, leading to a final value of $R = 0.06_7$. A difference map showed no peaks whose magnitudes were as large as one-fourth that expected of hydrogens.

Results and Discussion

The final least-squares coordinates and temperature factors with estimated standard deviations for each parameter are summarized for the copper complex in Table I. The estimated standard deviations (esd's) are less than 0.012 Å for Cu–N and Cu–O distances, 0.004 Å for the Cu-Cl distance, and 0.4° for angles around the Cu atom. Figure 1 shows the coordi-

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(19) The conventional reliability index $R = \sum w|K|F_o| - |F_c||/\sum w|F_o|$ is cited throughout the paper. Scattering factors for carbon, nitrogen, oxygen, and copper are taken from the paper by: Cromer, D. T.; Waber, J. T. *Acta. Crystallogr.* **1965**, *18*, 104. That for hydrogen is from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. III.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for Cu(pzdc)·HCl

atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.2375 (2)	0.2231 (2)	0.2500 (0)	47 (2)	10 (1)	56 (3)	−1 (2)	−7 (3)	−17 (2)
Cl	0.1975 (4)	0.3305 (4)	0.0095 (6)	88 (5)	39 (3)	61 (6)	19 (3)	−6 (5)	1 (4)
O1	0.3665 (11)	0.1708 (8)	0.4380 (13)	77 (13)	14 (7)	75 (19)	9 (9)	−25 (14)	−39 (11)
O2	0.4791 (11)	0.2299 (8)	0.6716 (12)	74 (13)	10 (8)	85 (19)	21 (9)	−31 (14)	−13 (11)
O3	0.5247 (11)	0.4209 (8)	0.8219 (15)	75 (13)	18 (8)	112 (21)	23 (9)	−71 (16)	−30 (11)
O4	0.4358 (11)	0.6059 (8)	0.8362 (15)	57 (12)	18 (8)	121 (22)	21 (8)	−54 (15)	−43 (12)
N1	0.2344 (11)	0.5661 (10)	0.6177 (14)	31 (12)	12 (9)	41 (20)	−7 (9)	4 (14)	−10 (11)
N2	0.2218 (11)	0.3679 (10)	0.4085 (15)	23 (12)	21 (9)	43 (20)	−5 (9)	−1 (13)	5 (12)
C1	0.1452 (16)	0.5635 (11)	0.4898 (21)	56 (17)	6 (10)	89 (29)	10 (11)	−11 (21)	−3 (15)
C2	0.1366 (16)	0.4622 (11)	0.3775 (19)	37 (16)	10 (10)	73 (25)	16 (10)	−15 (17)	−32 (14)
C3	0.3095 (14)	0.3698 (11)	0.5414 (16)	34 (14)	6 (9)	6 (21)	9 (10)	2 (14)	8 (12)
C4	0.3238 (14)	0.4725 (11)	0.6435 (18)	34 (15)	6 (10)	46 (23)	8 (10)	12 (17)	6 (13)
C5	0.4338 (14)	0.5036 (12)	0.7802 (18)	50 (16)	26 (11)	46 (30)	6 (11)	−26 (19)	−6 (15)
C6	0.3942 (15)	0.2465 (12)	0.5526 (17)	54 (17)	5 (9)	37 (23)	1 (11)	13 (17)	4 (14)

atom[a]	x/a	y/b	z/c	atom[a]	x/a	y/b	z/c
H1	0.0789 (0)	0.6332 (0)	0.4659 (0)	H3	0.4850 (0)	0.3200 (0)	0.7200 (0)
H2	0.0697 (0)	0.4615 (0)	0.2745 (0)				

[a] B_{iso} for the H atoms is 4.0 (0) Å^2.

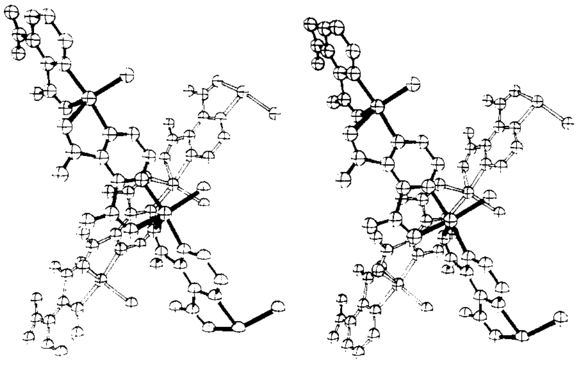

Figure 2. Orientation of structural chains in the crystal lattice. One chain is propagated along [011] while the other chain is propagated along [0$\bar{1}$1].

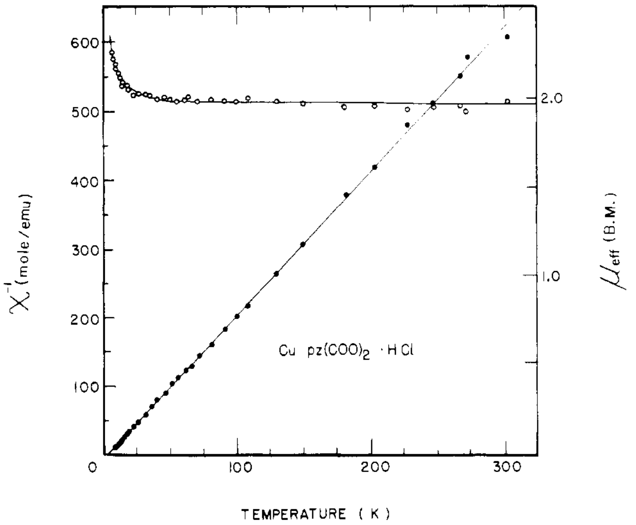

Figure 3. Inverse magnetic susceptibility and effective magnetic moment ($\mu_{eff} = (7.99\chi T)^{1/2}$) plotted as a function of temperature from 5 to 300 K. The line through the inverse susceptibility data points is the best fit to the Curie–Weiss law. The curve through moment data is the best fit of the data to the $S = {}^1/_2$ Heisenberg linear-chain model.

nation distances and angles around the copper and a schematic drawing of one unit of the chain with distances and angles indicated.

Each 2,3-pyrazinedicarboxylic acid ligand has six possible coordination sites of which four involve coordination to the copper atoms. The N1 and O4 atoms of a single ligand are coordinated to a copper atom while the N2 and O1 atoms of the same ligand are coordinated to an equivalent copper atom thus forming an infinite chain with the metal–ligand unit. There are two infinite chains in the unit cell. One chain propagates along the [011] axis, and due to the symmetry, the second chain is propagated along the [0$\bar{1}$1] axis as shown in Figure 2. There are no contact distances less than 2.90 Å between the two chains, and so there is no significant interaction between the chains. Although the Cu–Cu distance between the chains, 4.812 Å, is less than the Cu–Cu distance within a single chain, 6.678 Å, there is no apparent interchain exchange pathway, and the observed magnetic exchange is expected to be solely intrachain exchange except at very low temperatures ($T < 1$ K).

The copper atom is pentacoordinate where the sphere about any copper atom includes the N1, N2, and O1, O4, and Cl atoms. The coordination distances for the N1, N2, O1, and Cl are similar to those previously reported for copper(II) complexes whereas the Cu–O4 coordination distance of 2.19 Å is longer than the usual carboxyl oxygen to copper distance of 1.94 Å.[20] The average conjugated C–C bond distance (1.40 ± 0.02 Å) and C–N bond distance (1.33 ± 0.02 Å) compare favorably to the accepted literature values[21] (1.396 and 1.33 Å), while the average of the NCC angles 119.5 ± 1.0° is slightly less than the literature value of 122.4 ± 1°. The C5–O4 carbonyl bond distance (1.20 ± 0.02 Å) compares favorably with the 1.215 Å literature value while the CO distances are shorter than comparable literature references with the C6–O2 distance of 1.24 ± 0.02 Å slightly shorter than the usual distance of 1.322 Å.[4] The acid hydrogen bound to the O2 atom participates in a hydrogen bond to the O3 atom. The O2–H3 distance is 1.05 Å while the H3–O3 distance is 1.60 Å. The propagation of the chain is near linear as shown by the dihedral angle (172.6 ± 0.5°) between the copper atom and the pyrazine rings on either side. The plane of each pyrazine ring lies at nearly right angles (91 ± 1°) to that of the next neighboring bridging ring along the axis of chain propagation.

The magnetic data of a polycrystalline sample of Cu(pzdc)·HCl are plotted in Figure 3 as inverse magnetic susceptibility and effective magnetic moment as a function of temperature. Since the inverse susceptibility plot is linear as a function of temperature, the Curie–Weiss law (eq 1) was

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(20) "Molecular Structures and Dimensions", 1960–1965; Vol. A1.

(21) *Spec. Publ.—Chem. Soc.* **1958**, *No. 11*; *Suppl.* **1964**.

used in the preliminary fits of the data.

$$\chi = Ng^2\mu_B^2S(S+1)/3K(T-\Theta) \qquad (1)$$

The line through the inverse susceptibility data points in Figure 3 is the Curie–Weiss fit of the data with $S = {}^1/_2$ for copper(II), a g value of 2.28, and a Weiss constant Θ of +1.40 K. This is indicative of ferromagnetic coupling along the structural linear chain. The increase of the effective magnetic moment at low temperature is also consistent with ferromagnetic intrachain coupling.

There is no exact solution to the Van Vleck equation for a one-dimensional magnetic chain; however, the series expansion for the $S = {}^1/_2$ Heisenberg ferromagnetic linear chain has been calculated by Baker et al.[22] The magnetic data were fit to Baker's series expansion, and the result of this fit is shown as the smooth curve through the effective magnetic moment data in Figure 3. The intrachain coupling constant for the linear-chain model has a value of $J/k = +1.9$ K and a g value of 2.26. The exchange constant for the Heisenberg ferromagnetic linear-chain model may be compared with the value obtained from the molecular field treatment of the Curie law. The molecular field exchange constant may be calculated from the value of Θ extrapolated from the high-temperature regions of the data in the Curie–Weiss fit.[23] The value of J is

$$zJ/k = 3\Theta/2S(S+1) \qquad (2)$$

where, for a linear chain, the number of nearest neighbors (z) is 2. The molecular field value of J/k for an $S = {}^1/_2$ linear chain is equal to the Weiss constant obtained from the fit of the data to the Curie–Weiss law (eq 1).

The molecular field approach to fitting the magnetic data is valid only over temperatures where T is several times the value of J/k (or Θ). Since this criterion has been met in the present complex, it is not unreasonable to obtain equally good fits of the data with either the Curie–Weiss law or the linear-chain series-expansion model. It will be interesting to study this system at lower temperatures where the short-range order will dominate the susceptibility data. The series-expansion linear-chain analysis will be much more sensitive, and the susceptibility data over this temperature region should resolve the effects of any interchain coupling which might be present.

The most striking structural feature of the X-ray results is the orientation of one pyrazine unit relative to the nearest-neighboring pyrazine unit in the chain. All the atoms in the chain lie very nearly in the n glide of the $Pna2_1$ lattice. The direction of chain propagation is along the [011] axis at $x = {}^1/_4$ and along the $[0\bar{1}1]$ axis at $x = {}^3/_4$. Ideally all of the copper ions and the pyrazine nitrogens would be in the n-glide plane for a true structural linear chain. None of these atoms is more than 0.3 Å out of the $x = {}^1/_4$ plane. In addition, the asymmetric unit is oriented such that the n-glide operation results in the plane of the one pyrazine bridging ligand being oriented at nearly right angles (91°) to the next-neighboring pyrazine bridge in the chain. Figure 2 illustrates the propagation of the linear chain along the [011] and $[0\bar{1}1]$ directions in the unit cell.

All previous investigations of magnetic coupling in pyrazine-bridged complexes report antiferromagnetic coupling. It is interesting to speculate that the cause of the intrachain ferromagnetic exchange is the 90° interplanar angle of the collinear bridging pyrazine rings. This structural orthogonality is consistent with the Anderson overlap model because overlap orthogonality is a criterion for ferromagnetic exchange.[24] Since a σ-type exchange pathway is cylindrically symetrical about the bond axis, the overlap integral would not be affected by a collinear rotation of bridging orbitals. However, the overlap integral of the π-type exchange pathway would exhibit orthogonality from a 90° rotation about the bonding axis of one of the π-orbital sets. This implies that ferromagnetic exchange is propagated via a delocalized π-electron pathway. Hatfield et al. have previously shown that the π-electron pathway may contribute to the overall antiferromagnetic coupling, depending on the overlap orientation of the pyrazine π and metal d electrons. However, the complex discussed here is the first example of a bridging geometry in which the symmetry apparently requires π overlap to propagate magnetic exchange. Molecular orbital overlap calculations will be needed to further substantiate this hypothesis.

Registry No. Cu(pzdc)·HCl, 79329-64-9.

Supplementary Material Available: Listings of experimental magnetic susceptibility data for Cu(pzdc)·HCl and observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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