This system shows promise as a model for studying ruthenium surface reactions by Mössbauer spectroscopy. We have also found that the heat treatment of the exchanged dinitrogen ruthenium cation produces tetravalent species which are capable of reacting with gaseous molecules. It is possible that this system could also prove to be of value in studying the chemistry of ruthenium surfaces. In future studies, we hope to extend these preliminary studies to several different ruthenium–zeolite systems and to exploit the ^{99}Ru Mössbauer effect as a tool for studying these important materials.

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Registry No. $[Ru(NH_3)_5N_2]^{2+}$, 19504-40-6.

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(16) One reviewer has suggested that the Mössbauer parameters of sample 2A could be interpreted as the formation of small clusters of Ru^0 or clusters such as Ru_4^+ since the observed isomer shifts are similar to those of ruthenium metal. The suggested mechanism for this reduction is via the ruthenium-catalyzed dissociation of NH_3 to N_2 and H_2. If this is indeed the case, then the air exposure of sample 2A to produce 2B would involve the oxidation of ruthenium metal to Ru(IV), with the subsequent complete conversion to RuO_2 by heating the sample in air at 400 °C to produce sample 2C. This explanation of the observed results is certainly worthy of further examination. However, we have no previous indication that small clusters of low-valence ruthenium exist or what their possible Mössbauer parameters might be. Hopefully subsequent studies will make it possible to choose between the explanation in the text and the one outlined above by the reviewer or to propose yet another reaction mechanism.

Contribution from the Department of Chemistry,
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Spectroscopic Study of the One- and Three-Dimensional Magnetic Interactions of a Linear-Chain Antiferromagnet. Temperature Dependence of the Zero-Field Mössbauer Spectrum of Hydrazinium Ferrous Sulfate, $Fe(N_2H_5)_2(SO_4)_2$

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The temperature dependence of the zero-field iron-57 Mössbauer spectrum of hydrazinium ferrous sulfate, $Fe(N_2H_5)_2(SO_4)_2$, has been studied over the range 1.65–78 K. Between ca. 15 and 7 K the spectra display a gradual broadening process whose features are consistent with the one-dimensional antiferromagnetic interactions observed by others as well defined but broad maxima in the temperature dependence of the magnetic heat capacity (C_M) and molar susceptibility (χ_M'). As the temperature is further decreased, the spectrum exhibits fully resolved hyperfine splitting ($H_n \approx 260$ kG) of a three-dimensionally ordered state at $T = 6.29$ K. This agrees with the previous observation of a sharp λ anomaly in C_M at 6.05 K corresponding to antiferromagnetic ordering.

Introduction

There has been considerable recent interest in the magnetic and electronic properties of highly anisotropic one-dimensional chain and two-dimensional layer chemical structures.[1-5] Direct evidence for the low-dimensionality interactions of these systems comes from investigations of the heat capacity and neutron diffraction studies. Indirect evidence comes from the study of the temperature variation of bulk susceptibility for powder and single crystals. In this work, Mössbauer spectroscopy is applied to the problem of observing one-dimensional magnetic effects, e.g., antiferromagnetic spin correlation along a linear chain, in the temperature region just above that at which extended three-dimensional antiferromagnetic ordering occurs.

The system investigated, hydrazinium ferrous sulfate $Fe(N_2H_5)_2(SO_4)_2$, is shown schematically in Figure 1. The compound has a linear-chain structure (chemical chain along the direction of the SO_4^{2-} bridging) that is isomorphous[6] to the zinc analogue for which a complete single-crystal molecular structure determination has been made. In addition to being a chemical linear chain, hydrazinium ferrous sulfate, as well as the Mn, Co, Ni, and Cu analogues, is shown by recent[7,8] magnetic susceptibility and heat capacity studies to exhibit linear-chain antiferromagnetic properties. For the ferrous compound, fits to χ_M' and C_M for Heisenberg and Ising chain models indicate a weak intrachain exchange, $J \approx -2$ cm^{-1}. The interchain exchange (J') that is presumably responsible for the ultimate three-dimensional ordering is even weaker such that $J'/J \approx 3 \times 10^{-3}$. A reflection of the one-dimensional nature of the magnetic interactions in the iron compound is the well-defined, broad maximum in C_M at 12.3 K[8] and χ_M' at 15.3 K.[7] The onset of low-temperature 3-D ordering is clearly seen as a very sharp λ-like anomaly in C_M at 6.05 ± 0.02 K. In this work aspects of the preceding one- and three-dimensional interactions are investigated using Mössbauer spectroscopy over the range 15–1.7 K.

Experimental Section

The samples of $Fe(N_2H_5)_2(SO_4)_2$ were studied as polycrystalline powders. They were prepared by the method given in the literature[6] and gave the appropriate analytical results. Mössbauer parameters

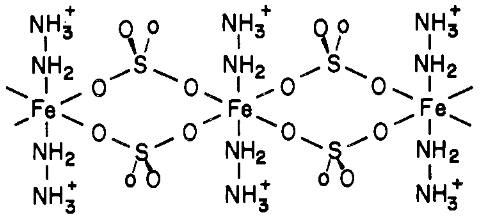

Figure 1. Schematic representation of the linear-chain antiferromagnet $Fe(N_2H_5)_2(SO_4)_2$.

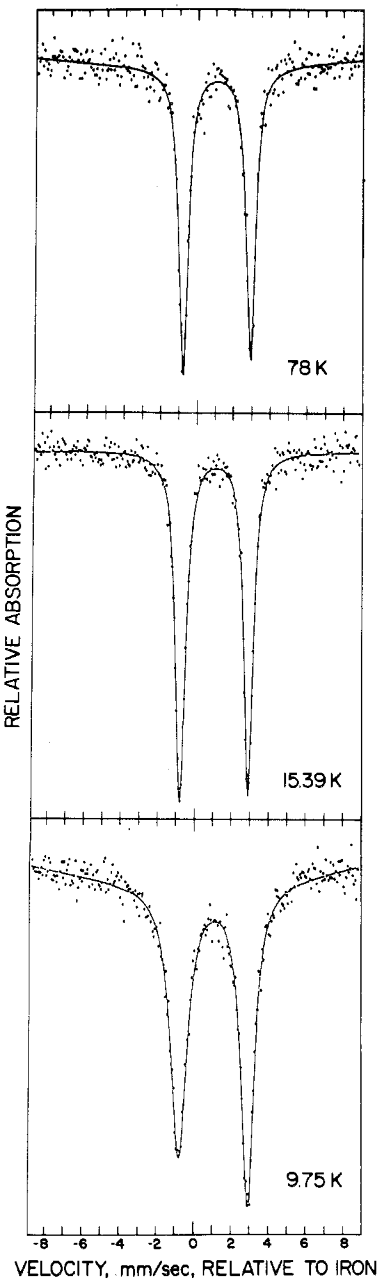

Figure 2. Mössbauer spectra of $Fe(N_2H_5)_2(SO_4)_2$: top, 78 K; middle, 15.39 K; bottom, 9.75 K.

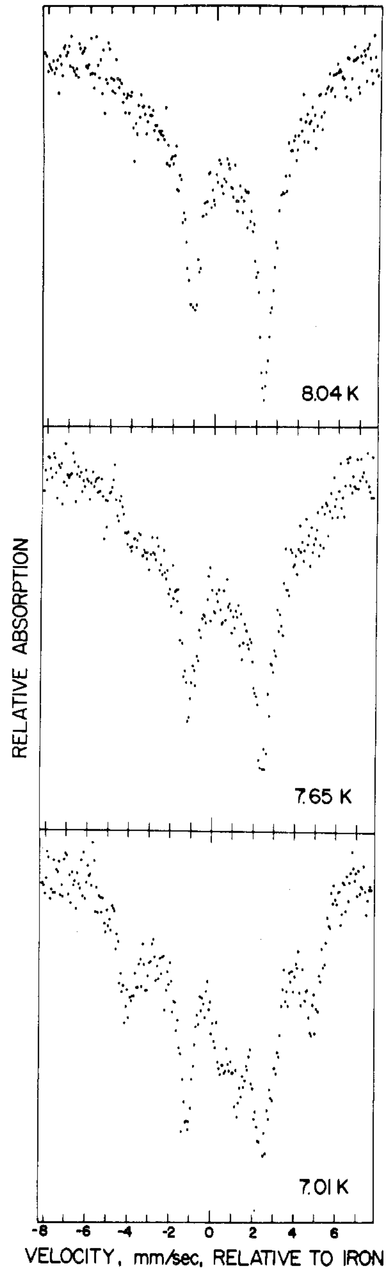

Figure 3. Mössbauer spectra of $Fe(N_2H_5)_2(SO_4)_2$: top, 8.04 K; middle, 7.65 K; bottom, 7.01 K.

at ~100 K are in agreement with those previously reported,[9] i.e., $\delta_{\mathrm{Fe}=0}$ 1.31 mm/s and $\Delta E = 3.71$ mm/s. The Mössbauer spectra in the vicinity of 4.2 K were obtained on a conventional constant-acceleration spectrometer operated in the time mode using a γ-ray source of 100-mCi ^{57}Co in a rhodium metal matrix. Temperature control was achieved using an uncalibrated silicon diode coupled to a Lake Shore Cryotronics Model DT-500 C set point controller. Temperature measurements were made with a Leeds and Northrup K-4 potentiometer or a six-place Dana Model 5330 digital voltmeter using a calibrated silicon diode driven by a 10-μA constant-current source. The temperature stability was continuously monitored by following the error signal of a silicon diode (~50 mV/K) after precise compensation via the K-4 potentiometer and was typically of the order ±0.005 K. Sub helium temperatures were obtained through controlled pumping (L J Engineering Model 329 vacuum regulator valve) on the Janis cryostat diffuser assembly while the temperature was determined from the vapor pressure of helium measured via a Wallace-Tiernan Model FA-160 absolute-pressure gauge. Least-squares–Lorentzian fits to Mössbauer spectra were accomplished using the program of Stone.[10]

Results

The temperature dependence of the Mössbauer spectrum is shown in Figures 2 and 3. The spectrum at 15 K is essentially the same as that at 78 K. There is some slight temperature-independent asymmetry over this range and we attribute this to sample texture. As the temperature is decreased between ca. 15 and 10 K, the lower energy transition broadens somewhat and there is a reversal of the spectral asymmetry with the spectrum appearing symmetric but

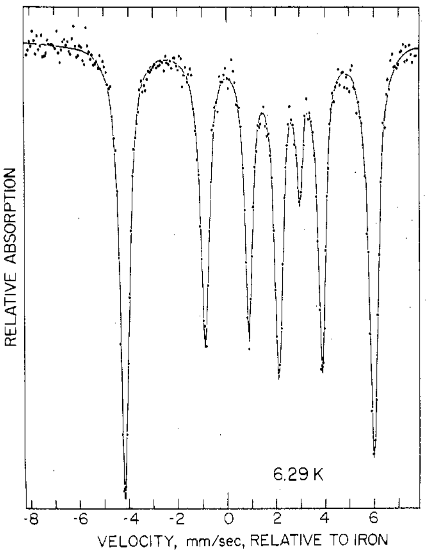

Figure 4. Mössbauer spectrum of $Fe(N_2H_5)_2(SO_4)_2$ at 6.29 K.

broadened at 13 K. On increasing the temperature the process is reversed over the range 15–20 K with the spectrum nearly symmetric at ~17 K. This suggests some hysteresis to the process.

We have determined the sign of the principal component of the electric field gradient tensor (V_{ZZ}) to be *positive* with a small asymmetry parameter $\eta < 0.3$, i.e., near axial. This was acertained from the magnetically perturbed Mössbauer spectrum in a longitudinal field of 50 kG at 78 K, a temperature at which $Fe(N_2H_5)_2(SO_4)_2$ is a rapidly relaxing paramagnet. Nieuwpoort and Reedijk[9] have analyzed the temperature dependence (300–78 K) of the quadrupole splitting of $Fe(N_2H_5)_2(SO_4)_2$ and obtained results that are consistent with a ground d_{xy} orbital ($^5B_2$ term) for which V_{ZZ} and the quadrupole interaction are positive. Positive quadrupole splitting and a ground d_{xy} are expected in view of the local coordination, i.e., stronger axial hydrazinium nitrogen bonding than in-plane sulfate oxygen ligation resulting in a tetragonal compression as a low-symmetry ligand field component. Hence there is little doubt that the broadened, lower energy transition of the paramagnetic phase Mössbauer spectra is the σ ($|^1/_2, \pm^1/_2\rangle \rightarrow |^3/_2, \pm^1/_2\rangle$) while the higher velocity transition is the π ($|^1/_2, \pm^1/_2\rangle \rightarrow |^3/_2, \pm^3/_2\rangle$). We will refer to this result in the subsequent discussion.

As the temperature is further decreased, the compound exhibits magnetic hyperfine splitting corresponding to its three-dimensional antiferromagnetic ordering. Somewhere between 6.90 and 6.29 K the quadrupole doublet of the paramagnetic phase disappears and we take the Néel temperature to be in this interval. The sharp λ anomaly was observed[8] in the temperature dependence of C_M at 6.02 ± 0.05 and thus there is reasonable agreement between the two methods. The slightly higher T_N from Mössbauer spectroscopy is perhaps not surprising since one is observing the ordering from a microscopic local environment point of view, i.e., the growth of a hyperfine field at each ferrous site. On the other hand, in measurements of the heat capacity one is seeing thermal effects in a bulk sample of a particular size.

The observation of seven lines in the low-temperature spectrum (Figure 4) indicates some mixing of the M_I states and weak allowedness of the $\Delta M_I = \pm 2$ transitions. Ideally then, there are four pairs of transitions in the ordered state for which the excited-state terminus is the same within each pair; their pair separation thus gives the $I = {}^1/_2$ ground-state Zeeman splitting and the effective internal hyperfine field.[11] Furthermore, the intensity of any such pair should be one-fourth of the total spectral intensity in a thin absorber approximation. Using this type of analysis in conjunction with least-squares fits to the magnetically split spectra, we obtain an internal field of $H_n = 254$ kG. The preceding is a reasonable value[12] for a high-spin iron(II) compound in which there is a large quadrupole interaction. The quadrupole splitting reflects substantial quenching of H_L, the orbital contribution to H_n that is of opposite sign to the Fermi contribution. Hence a relatively large internal field is expected. The internal field shows little temperature dependence over the range 1.76–6.29 K and then as seen from the figure collapses rather rapidly between 6.2 and 7.60 K.

Discussion

Three-dimensional magnetic ordering of the system is obvious in the low-temperature magnetically split spectrum. The possible observation of one-dimensional effects is now considered. To our knowledge the only other Mössbauer study[13] with this aim in mind is that of $KFeCl_3$ which is also a linear-chain antiferromagnetic compound. The latter system exhibits considerably stronger magnetic interactions and a higher Néel temperature ($T_N \approx 18.5$ K). Thus, for this compound one-dimensional effects can be studied from two points of view: (a) observation of unusual (non-Brillouin) behavior in the temperature dependence of magnetization (internal field) just above and below T_N; (b) similar observation of unusual broadening and line shapes. Both (a) and (b) were observed[13] for $KFeCl_3$ and tentatively attributed to residual one-dimensional correlation above T_N. Owing to the small temperature range (~1.3 K) over which resolved hyperfine splitting is observed for $Fe(N_2H_5)_2(SO_4)_2$, we have made no attempt at the (a) type of analysis. On the other hand there are certain features of the broadening process above the Néel temperature of $Fe(N_2H_5)_2(SO_4)_2$ that are noteworthy. In particular the temperature range in which broadening occurs coincides closely with the broad maxima observed in C_M[8] and χ_M'.[9] In addition the broadening–hyperfine splitting process appears to be gradual rather than abrupt. More important is a consideration of which line apparently broadens first, i.e., the low-energy, σ transition. A theory[14,15] for the relaxation broadening of the quadrupole transitions of a fixed electric field gradient in a fluctuating magnetic field has been developed for the case of slow, single-ion paramagnetic relaxation. In the case of an axially symmetric electric field gradient tensor, it is the π transition that broadens initially for internal magnetic field fluctuation collinear to the principal axis of the electric field gradient while the σ transition broadens first for a field fluctuating perpendicular to V_{ZZ}. In the absence of a single-crystal Mössbauer study we make the *assumption* that the principal axis of V_{ZZ} in $Fe(N_2H_5)_2(SO_4)_2$ is along the trans hydrazinium direction. The initial broadening of the σ transition of the Mössbauer spectrum thus implies the existence of a fluctuating magnetic field perpendicular to V_{ZZ} and in the present compound probably along the direction of the chemical linear chain. This is the direction in which a fluctuating exchange field resulting from the onset of one-dimensional magnetic interaction is expected.

It must be admitted that the foregoing analysis is circumstantial and somewhat tentative. The broadening above T_N could be due to some type of single-ion, slow relaxation process such as might arise from a large negative zero-field splitting; i.e., $D < 0$ to give a slowly relaxing ($m_s = \pm 2$) ground Kramers doublet. However, previous analysis[8,9] of the temperature dependence of χ_M' and C_M required $D > 0$, although matters are complicated by the fact that D is apparently of the same order or slightly larger in magnitude than J, $|D|/|J| \approx 2$. Finally, we mention that slow single-ion paramagnetic relaxation is rare for high-spin iron(II) owing to the possibility of relaxation by both spin–spin and spin–

lattice mechanisms. In conclusion, we note that the broadening process observed in the present study is strongly coincidental with effects associated with the one-dimensional behavior of $Fe(N_2H_5)_2(SO_4)_2$ in studies of χ_M' and C_M and may indeed be a spectroscopic reflection of such interactions. We also mention that the one-dimensional magnetic interaction in $Fe(N_2H_5)_2(SO_4)_2$ has been studied[16] using high-field Mössbauer spectroscopy and magnetization methods. For powder samples in applied fields of ~75 kG, the decoupling of antiferromagnetically coupled spins along the chain begins to occur and is complete at ca. 125 kG.

A detailed theoretical analysis of the one-dimensional behavior or the present system would attempt to correlate the observed broadening in terms of relaxation times with the magnitude of a (growing) intrachain exchange field, J, or possibly J/D for $T > T_N$. For $Fe(N_2H_5)_2(SO_4)_2$ this will be a formidable problem from a number of points of view. Previous attempts at analysis of the susceptibility[7] and heat capacity[8] data gave poor agreement and suggest that its chain behavior is intermediate to the Heisenberg and Ising extremes. This is perhaps expected for high-spin iron(II) for which considerable single-ion anisotropy is possible. In the former extreme D is neglected while in the latter the existing theory is relatively complete for $S = {}^1/_2$ (Bonner–Fisher type calculations[17]) but not for $S = 2$. As the heat capacity of $Fe(N_2H_5)_2(SO_4)$ shows a change in entropy of the spin system at T_N corresponding to $S = 2$, simple effective spin ${}^1/_2$ models are clearly inappropriate. Finally, the observation[8] $D \approx J$ adds to the mathematical intractability and makes the problem well beyond the scope and purpose of the present work.

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Registry No. $Fe(N_2H_5)_2(SO_4)_2$, 53091-69-3.

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Contribution from the Lash Miller Chemistry Laboratory and Erindale College,
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Titanium Hexacarbonyl, $Ti(CO)_6$, and Titanium Hexadinitrogen, $Ti(N_2)_6$. 1. Synthesis Using Titanium Atoms and Characterization by Matrix Infrared and Ultraviolet–Visible Spectroscopy

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The matrix cocondensation reactions of Ti atoms with CO and N_2 either pure or diluted with the inert gases at 10–15 K are investigated for the first time by infrared and ultraviolet–visible spectroscopy. Ti and CO concentration experiments, matrix variations, warm-up studies, and comparisons with $V(CO)_6$ and $Cr(CO)_6$ formed in similar V/CO, Cr/CO matrix reactions provide convincing evidence that the green, highest stoichiometry product of the Ti/CO reaction is titanium hexacarbonyl, $Ti(CO)_6$, the first example of a binary titanium carbonyl complex. The corresponding data for the reddish-yellow, highest stoichiometry product of the Ti/N_2 reaction resemble closely those obtained for $Ti(CO)_6$ as well as those available for the novel compounds $V(N_2)_6$ and $Cr(N_2)_6$, arguing in favor of a titanium hexadinitrogen complex, $Ti(N_2)_6$. Trends in ν_{CO}, ν_{NN}, and $10Dq$ for the series $M(CO)_6$ and $M(N_2)_6$ (M = Ti, V, or Cr) support the $Ti(CO)_6/Ti(N_2)_6$ assignment and are discussed in some detail. The infrared data for $Ti(CO)_6$ and $Ti(N_2)_6$ indicate that both complexes are closely related structurally and subject to a Jahn–Teller distortion. The 40-cm^{-1} splitting observed for the T_{1u} ν_{CO} stretching mode in solid CO is retained in Ar, Kr, and Xe matrices. Both components of this split degeneracy yield linear Buckingham plots, which supports the designation of an inherent molecular distortion for $Ti(CO)_6$ rather than a matrix effect. However, the magnitude of the distortion is probably quite small, as the electronic spectra of $Ti(CO)_6$ and $Ti(N_2)_6$ display the gross features expected for low-spin d^4 octahedral complexes.

Introduction

At 10–70 K the reaction of titanium atoms and benzene yields the electron-rich, 16-electron, red complex bis(benzene)titanium(0), a long-sought-after molecule from a synthetic and catalytic point of view.[1] Apart from this work, little else is known about the reactivity of the early transition elemental vapors toward other reactive partners. Recently we turned our attention to the more fundamental question as to the fate of these metals when cocondensed at low temperatures in the presence of a nonreactive partner and have succeeded in synthesizing and characterizing for the first time relatively large amounts of Sc_2,[2] Ti_2,[2] V_2,[3] and Cr_2.[4]

In view of the direct syntheses of the 17- and 18-electron systems $V(CO)_6$[5]/$(C_6H_6)_2V$[6] and $Cr(CO)_6$[7]/$(C_6H_6)_2Cr$[8] by metal vapor cocondensation techniques, it occurred to us by analogy with the 16-electron $(C_6H_6)_2Ti$ complex that the 16-electron $Ti(CO)_6$ complex would be a worthwhile synthetic goal. Furthermore, the recently established 17- and 18-electron