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Mössbauer Spectroscopy Studies of Complexes of Ruthenium in Y-Type Zeolites

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The incorporation and subsequent reactions of the $[Ru(NH_3)_5N_2]^{2+}$ ion in a Y zeolite have been investigated by Mössbauer spectroscopy. The ion could be incorporated into the zeolite by cation exchange, although upon exposure to the atmosphere, the ruthenium species was found to undergo oxidation. The exchanged dinitrogen complex could be reduced to the metallic state by low-temperature treatment with hydrogen. The resulting metal particles exhibited a high surface atom to bulk atom ratio as evidenced by a change in the Mössbauer spectrum upon exposure to air. Heating the exchanged dinitrogen complex under vacuum was found to oxidize the ruthenium to the 4+ state. The resulting tetravalent species reacted to give new complexes when exposed to NH_3 and NO atmospheres.

Introduction

We recently reported on the extension of Mössbauer spectroscopy studies of supported metal catalysts to include ruthenium systems.[2] Our studies confirmed that it is possible to obtain Mössbauer spectral data for unenriched ruthenium supported on an alumina or silica matrix. Data were obtained which demonstrated that Mössbauer spectroscopy could be used to determine the chemical state of the ruthenium on the support material. The Mössbauer spectral parameters were found to be very sensitive to certain types of catalyst treatment conditions, such as calcination and reduction. However, this study also demonstrated the inability of Mössbauer spectroscopy to observe chemisorption phenomena on alumina- and silica-supported ruthenium. Indications were that this inability could be due to a poor surface metal to bulk metal ratio in the catalyst samples studied.

For the purpose of studying surface phenomena, the surface to bulk metal atom ratio could possibly be improved by the use of ruthenium-atom-exchanged zeolite absorber samples. Such samples should have a high fraction of crystallographically well-defined surface ruthenium atoms. Because of the favorable structure of the zeolites and the great interest in the catalytic properties of supported ruthenium,[3] this system is a prime candidate for Mössbauer studies, thus, the rationale for this investigation.

For the purpose of this study, we have chosen to use the synthetic faujasite Y-type zeolite. Studies dealing with the properties of this zeolite have received a great deal of attention in recent years and a summary of the advances in this area can be found in a recent review by Sherry.[4] For the purpose of introducing ruthenium atoms into the zeolite framework, we chose to use the dinitrogen complex cation $[Ru(NH_3)_5N_2]^{2+}$. There were several reasons for choosing this species for our initial study. First, this compound offered the possibility for stripping the NH_3's and N_2 from the coordination sphere, leaving the base ruthenium ion in the zeolite, and, second, the N_2 group could possibly serve as a pathway for reversibly introducing such groups as CO, NO, etc. into the coordination sphere of ruthenium. In addition, the dinitrogen complex is one of the more stable complexes of Ru(II) and should therefore minimize decomposition problems during the exchange procedure.

Experimental Methods

Mössbauer Spectrometer. The Mössbauer spectra were obtained with the apparatus previously described.[2a,5] All spectra were obtained with the source and absorber maintained at 4.2 K. The source consisted of approximately 7 mCi of 16-day ^{99}Rh contained in a host lattice of rhodium metal prepared by New England Nuclear Corp., Boston, Mass. This source gave slightly broader line widths [0.45-mm/s peak half-width (Γ) for ruthenium metal] than previous sources prepared with a host lattice of ruthenium ($\Gamma = 0.32$ mm/s for ruthenium metal). However, spot checks with a second source in a ruthenium metal host lattice ($\Gamma = 0.31$ mm/s for ruthenium metal) reproduced the isomer shift and quadrupole splitting values reported here for the rhodium host source. Samples with absorber thicknesses in the range of 100–150 mg of natural Ru/cm^2 were used. The samples were treated and analyzed in quartz cells of the type described in ref 2a.

In general, the base line for each spectrum contained between 1 and 2 million counts/channel where the total spectrum was displayed in 254 channels of a Nuclear Data Model 2200 multichannel analyzer operating in the multiscaling mode. The relative percent absorption of the Mössbauer peaks were in the range of 0.1–0.5%. Data reduction was carried out on a PDP-10 computer system. The spectra were subjected to a least-squares fit to a Lorentzian line shape with both the experimental points and the calculated least-squares curve plotted out directly by a Calcomp Model 563 plotter. The Mössbauer hyperfine parameters were calculated from the least-squares fit assuming either a singlet (unresolved quadrupole interaction) or a doublet (resolved quadrupole interaction). This fitting assumes that the pair of triplets resulting from the quadrupole splitting of the $I = {}^3/_2$ to $I = {}^5/_2$ transition are not resolved [due to the fact that the nuclear quadrupole moment of the excited state ($Q_{I=3/2}$) is 3 times larger than the nuclear quadrupole moment of the ground state ($Q_{I=5/2}$)].[6-8] The quadrupole splittings reported are therefore the velocity difference between the peak minima of the apparent doublet. Error analysis for the isomer shift, quadrupole splitting, and peak full width at half-maximum values are given along with the data (see tables in Results and Discussion).

Materials. Na–Y zeolite (63.5% SiO_2, 23.5% Al_2O_3, and 13.0% Na_2O) was obtained from the Linde Co. $RuCl_3{\cdot}(1{-}3)H_2O$ was purchased from the A. D. Mackay Co. Ammonia and nitric oxide were obtained from the Matheson Gas Co. and were purified by repeated distillation. All other chemicals used were reagent grade.

The $[Ru(NH_3)_5N_2]Cl_2$ complex was prepared according to the method of Allen, et al.[9] Cation exchange of this complex was performed in the following manner. The complex (1.8–2.2 g) was added to deoxygenated water (100 mL) and an appropriate amount of Na–Y zeolite (6–7 g) was then added and the exchange allowed to proceed for 12–16 h with shaking under a nitrogen atmosphere. The zeolite was filtered, washed several times with water, and then dried over P_2O_5 under vacuum in a desiccator for 48 h. After drying, the powdered zeolite samples were placed in quartz cells and all further treatments were carried out on the sample in these cells. Based on the percent of sodium ions displaced, the exchange of $[Ru(NH_3)_5N_2]^{2+}$ was in the range of 60–70% for all samples prepared by the procedure outlined above. X-ray diffraction patterns of the samples indicated that very little loss in the zeolite's crystalline structure occurred during the exchange.

Results and Discussion

Listed in Table I are the Mössbauer parameters obtained for the $[Ru(NH_3)_5N_2]^{2+}$–Y zeolite sample and several related ruthenium compounds. The Mössbauer spectra for two of the zeolite samples are shown in Figure 1. The spectra are presented as relative count rate vs. velocity in mm/s. The relative count rate is determined from the ratio N/N_∞ where N is the count rate for a given velocity and N_∞ is the baseline count rate. The sample referred to as 1A in Table I corresponds to a portion of the $[Ru(NH_3)_5N_2]^{2+}$–Y zeolite after drying for 48 h under vacuum. The sample was held under

Table I. Mössbauer Parameters for Ruthenium-Exchanged Zeolites

Sample no.	Treatment	Absorber thickness, mg of Ru/cm^2	Isomer shift,[a] mm/s	Quadrupole splitting, mm/s	Peak width (Γ) half-height, mm/s
1A	$[Ru(NH_3)_5N_2]^{2+}$-Y dried and evacuated to 10^{-5} Torr at 25 °C	125	−0.80 ± 0.04	0.56 ± 0.04	0.61 ± 0.05
1B	Sample 1A exposed to air for 2 days at 25 °C	125	−0.37 ± 0.03	0	0.79 ± 0.05
1C	Sample 1B reduced in H_2 at 400 °C for 4 h	125	+0.02 ± 0.03	0	0.61 ± 0.04
1D	A portion of sample 1A reduced in H_2 at 400 °C for 4 h	110	+0.01 ± 0.02	0	0.52 ± 0.03
1E	Sample 1D exposed to air for 24 h at 25 °C	110	−0.10 ± 0.03	0	0.67 ± 0.04
Ru metal powder		225	+0.00 ± 0.02	0	0.45 ± 0.03
$[Ru(NH_3)_5N_2]Cl_2$		175	−0.76 ± 0.04	0.22 ± 0.03	0.51 ± 0.03
$[Ru(NH_3)_5OH]Cl_2$		190	−0.39 ± 0.03	0	0.49 ± 0.03

[a] Zero velocity is taken to be the center of the spectrum of a standard metal sample.

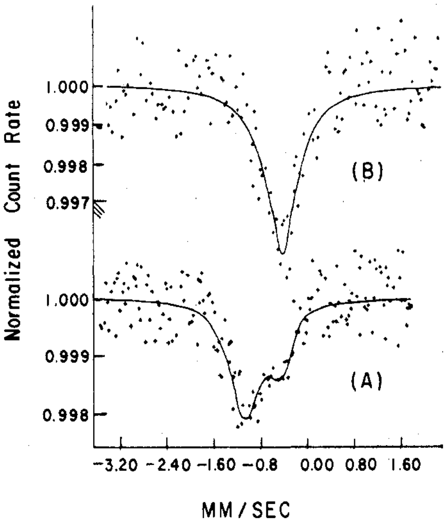

Figure 1. Mössbauer spectra of (A) sample 1A ($[Ru(NH_3)_5N_2]^{2+}$-Y zeolite after drying) and (B) sample 1B (this is sample 1A after exposure to air).

a pressure of 10^{-5} Torr while the spectrum shown in Figure 1(A) was obtained. The isomer shift and relative line intensities observed for this sample agree with those obtained for a crystalline sample of $[Ru(NH_3)_5N_2]Cl_2$. However, the quadrupole splitting for the zeolite sample (0.56 mm/s) was greater than that observed for the $[Ru(NH_3)_5N_2]Cl_2$ sample (0.22 mm/s). This suggests that the $[Ru(NH_3)_5N_2]^{2+}$ group is exchanged without undergoing oxidation. However, the increase in quadrupole splitting indicates that some distortion or chemical change in the coordination sphere has occurred upon exchange. The increased electronic distortion may be produced by the loss of molecular N_2 upon evacuation as has been suggested by Laing et al.[10] or possibly by the rigid aluminosilicate structure of the zeolite. For example, cations exchanged in a zeolite have been found to be capable of occupying several different sites within the zeolite framework.[11-13] Since these sites are located on the sides and at the entrances of different-size and -shaped cavities, each site would be expected to impose its own characteristic structural and electronic requirements on the cation. Unfortunately, because of the limited number of Mössbauer studies dealing with this topic, it is not possible to identify the position of the $[Ru(NH_3)_5N_2]^{2+}$ cation in the Y zeolite from a single Mössbauer spectrum.

Upon exposure of sample 1A to the atmosphere at 25 °C, it slowly turned a wine color. After 2 days, the color appeared to stabilize and the spectrum shown in Figure 1(B) was obtained. This sample is referred to as sample 1B in Table I. As can be seen, the Mössbauer parameters have changed significantly. The change in isomer shift from −0.80 to −0.37 mm/s indicates that the ruthenium has undergone oxidation from the 2+ state to the 3+ state.[5] The only 3+ wine-colored ruthenium compound that could be found in the literature corresponds to $[Ru(NH_3)_5OH]Cl_2$. The Mössbauer spectral parameters for this compound as shown in Table I agree with those observed for the wine-colored compound in the zeolite. The broader line widths for the zeolite sample may result from the presence of smaller concentrations of other ruthenium species or possibly $[Ru(NH_3)_5OH]^{2+}$ groups at different sites in the zeolite.

Laing et al.[10] have also observed that a $[Ru(NH_3)_5N_2]^{2+}$-Y zeolite sample decomposes in air to give a wine-colored species. On the basis of infrared data, these workers have also suggested that the dinitrogen complex decomposes to the $[Ru(NH_3)_5OH]^{2+}$ species. They proposed that the decomposition may occur by the reaction

$$[Ru^{II}(NH_3)_5N_2]^{2+}\text{-Y} + H_2O \rightarrow [Ru^{III}(NH_3)_5OH]^{2+}\text{-Y} + NH_4^+ + \text{other products}$$

This type of reaction has also been proposed by Sigwart and Spence,[14] who studied the photochemical oxidation of $[Ru(NH_3)_5N_2]^{2+}$ and found that, following exposure to UV light from a mercury lamp, $[Ru(NH_3)_5OH]^{2+}$ was formed in neutral solution.

Sample 1C in Table I corresponds to sample 1B after treatment in a stream of hydrogen for 4 h at 400 °C. The Mössbauer parameters for this sample indicate that all of the ruthenium has been reduced to the metallic state. However, x-ray analysis of this sample indicated that a significant amount of crystallinity in the zeolite framework was lost upon reduction. Therefore, a new portion of sample 1A was reduced in a hydrogen stream and this sample is referred to as 1D. Again, the Mössbauer data show that all of the ruthenium has been reduced to the metallic state. X-ray analysis[2a] of this sample also indicated that very little loss in crystallinity of the zeolite structure occurred during reduction. The x-ray analysis also indicated that all of the ruthenium was in the form of particles smaller than 80 Å in diameter, for no ruthenium could be detected in the x-ray pattern. When this sample was exposed to the atmosphere, the Mössbauer data designated for sample 1E in Table I were obtained. The observed change in isomer shift and line width upon exposure to the atmosphere indicates that some form of interaction has occurred between the small ruthenium metal particles and the gaseous components of air. The change in isomer shift by −0.10 mm/s is greater than the experimental error in the measurement and indicates that a majority of the ruthenium atoms in the sample have experienced a reduction in s-electron density.[5] This could be accomplished by increased shielding brought about by chemisorbed groups occupying p and d ruthenium orbitals or by direct s-electron withdrawal by the adsorbed species. In any case, the fact that some form of interaction could be observed indicates that a more favorable surface atom to bulk atom ratio exists in this sample than in those supported on

Table II. Mössbauer Data for Heat Treated Ruthenium-Exchanged Zeolite Samples

Sample no.	Treatment	Absorber thickness, mg of Ru/cm^2	Isomer shift,[a] mm/s	Quadrupole splitting, mm/s	Peak width (Γ) half-height, mm/s
2A	A portion of sample 1A heated to 400 °C at 10^{-5} Torr	130	−0.06 ± 0.03	0.43 ± 0.04	0.55 ± 0.04
2B	Sample 2A exposed to air at 25 °C for 8 h	130	−0.10 ± 0.03	0.74 ± 0.05	0.49 ± 0.03
			−0.13 ± 0.03	0	0.54 ± 0.04
2C	Sample 2B exposed to air at 400 °C for 4 h	130	−0.28 ± 0.03	0.45 ± 0.04	0.51 ± 0.04
2D	A portion of sample 2A exposed to NH_3	110	−0.25 ± 0.06	0	0.98 ± 0.07
2E	A portion of sample 2A exposed to NO	120	−0.01 ± 0.06	0	1.10 ± 0.10
RuO_2		340	−0.23 ± 0.03	0.51 ± 0.05	0.54 ± 0.04

[a] Zero velocity is taken to be the center of the spectrum of a standard ruthenium metal sample.

alumina and silica where no interaction with air could be observed by Mössbauer spectroscopy.[2a] Therefore, it appears that the zeolite-supported ruthenium can be used as a model system for studying surface phenomena by the Mössbauer technique. A recent study by Gallezot et al.[15] on the location and dispersion of platinum in Pt–Y zeolites by small-angle x-ray scattering techniques has shown the significance of sample treatment (particularly temperature) on the states of dispersion of platinum in the zeolite matrix. Thus, any subsequent studies on these ruthenium systems will need to consider different oxidation–reduction cycles and temperature variations as a function of metal cluster size and zeolite crystallinity.

Another phase of our study dealt with an attempt to generate and study a 2+ ruthenium ion trapped in the Y zeolite framework. We tried to generate this species by evacuating the $[Ru(NH_3)_5N_2]^{2+}$–Y sample to 10^{-6} Torr and then heating the sample to 400 °C for the purpose of driving off the NH_3 and N_2 groups. The Mössbauer data obtained for these samples are shown in Table II and representative spectra are shown in Figure 2.

When a portion of sample 1A was heated to 400 °C for 4 h at 10^{-5} Torr, ammonia was observed to be given off. The temperature was gradually raised to 400 °C over a 6-h period. The resulting material, sample 2A, as indicated by the Mössbauer parameters shown in Table II has undergone a change in oxidation state. An isomer shift of −0.06 mm/s with a quadrupole splitting of 0.43 mm/s in sample 2A suggests that the ruthenium has been oxidized from the 2+ state to the 4+ state. When sample 2A was exposed to the atmosphere for 8 h at 25 °C, sample 2B was generated. The Mössbauer spectrum for this sample as shown in Figure 2(C) contains three peaks and is quite different from that of sample 2A. A three-line fit to the data gave the best statistical analysis. For example, a single-line fit gave a χ^2 value of 403. A two-line fit gave 1109 and a three-line fit gave a χ^2 value of 215. The Mössbauer parameters for the three-line fit as given in Table II indicate that two different ruthenium species are present. The isomer shifts indicate that both are in the 4+ oxidation state. However, they differ in either the composition and/or structure of the coordination sphere, for they have significantly different quadrupole splittings. This could indicate that the ruthenium species produced by the heat treatment procedure occupy two different sites in the zeolite framework and that the absorption of gaseous molecules from the air destroys the degeneracy of their Mössbauer parameters.[16]

When sample 2B was heated to 400 °C for 4 h, its spectrum was observed to change to that represented in Figure 2(B). The Mössbauer parameters for this sample, sample 2C, agree very closely with those found for RuO_2. This suggests that all of the ruthenium in this sample has been converted to small particles of RuO_2. It should also be pointed out that x-ray diffraction data indicated that there was a significant loss in zeolite crystallinity by this treatment.

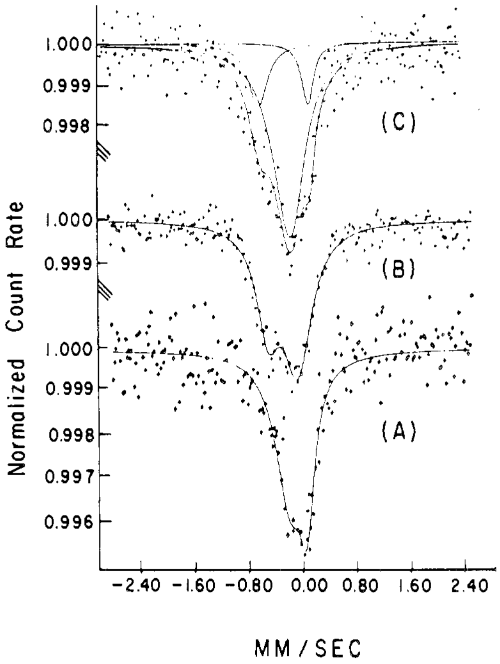

Figure 2. Mössbauer spectra of (A) sample 2A (heat-treated $[Ru(NH_3)_5N_2]^{2+}$–Y zeolite sample), (B) sample 2C (sample 2B exposed to air at 400 °C), and (C) sample 2B (sample 2A exposed to air at 25 °C).

Since exposure to air was observed to change the spectrum of the species produced in sample 2A, we were interested to learn about the changes that would occur by exposing this sample to other gases. Therefore, a portion of sample 2A was exposed to an atmosphere of NH_3 at 200 Torr for 4 h and another portion was exposed to an atmosphere of NO at 50 Torr for 4 h. The Mössbauer spectrum for each sample consisted of a single very broad line. The broad lines must result from either an unresolved quadrupole splitting or the presence of ruthenium atoms at two or more dissimilar sites. However, if the center of the broad peak can be taken to represent the center of the spectrum for the complex, or complexes, present in each sample, then an isomer shift can be extracted from the data. It is interesting to note that the isomer shifts fall in the region where they should, based upon the electron-withdrawing and -donating abilities of NH_3 and NO. On the basis of previous studies,[5] NH_3 would be expected to decrease the isomer shift of sample 2A when it is absorbed by a ruthenium site and NO would be expected to increase the isomer shift. The measured isomer shifts are found to agree with this prediction.

Conclusions

This study has shown that a favorable metallic ruthenium surface atom to bulk atom ratio can be produced by the reduction of an exchanged ruthenium cation in a Y-type zeolite.

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.

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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