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Magnetism of an Unusual Polymeric Complex of Bivalent Silver

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The magnetic susceptibility of bis(nicotinato)silver(II) has been measured in the temperature range 4.2–275°K. The data reflect an antiferromagnetic interaction between silver ions and may be described by the Ising linear chain model yielding $J = -30.8 \pm 1.0$ cm^{-1} and $\langle g \rangle = 2.05 \pm 0.02$.

Introduction

The chemistry of silver complexes and compounds is largely the chemistry of silver(I).[1] There exists, however, an interesting class of paramagnetic silver(II) complexes. The stability of the Ag^{2+} ion is strongly enhanced by coordination with aromatic nitrogen-containing heterocycles such as pyridine and its derivatives,[2–5] and a substantial number of complexes of silver(II) have been characterized.[6–14] The rather unfamiliar Ag(II) ion is analogous to copper(II); its electronic configuration is $4d^9$, and room-temperature magnetic susceptibility measurements of silver(II) complexes have confirmed the presence of one unpaired electron.[6–8,15]

Banerjee and Ray[6–8] initially reported preparation of a series of pyridinecarboxylic acid complexes of Ag(II) and suggested (on the basis of X-ray powder diffraction studies) that the structures of the nicotinic and isonicotinic acid complexes of bipositive silver were either dimeric or polymeric. Magnetic susceptibility measurements in the temperature range 80–300°K performed by Fowles, Matthews, and Walton[15] on several silver(II) pyridinecarboxylates revealed that, with the exception of bis(pyridine-3-carboxylato)silver(II), all the complexes studied exhibited Curie or Curie–Weiss behavior with $\Theta \leq 10°$. Bis(nicotinato)silver(II) showed evidence of antiferromagnetic interactions. The Weiss constant of 52° is quite large, and the moment of 1.68 BM at room temperature was reported to drop to 1.42 BM at 83°K. (No maximum in susceptibility was observed, however.) The only published account[16] of susceptibility measurements at low temperatures of a silver(II) complex deals with $[Ag(py)_4]S_2O_8$, which has been shown to follow Curie behavior to 1.6°K.

As part of a general investigation of magnetic exchange in polymeric transition metal complexes, a detailed study of the magnetic susceptibility of bis(nicotinato)silver(II) in the temperature range 4.2–275°K was undertaken. The object of this research was to determine unambiguously the nature and extent of the antiferromagnetic interactions postulated by Fowles et al.[15]

Experimental Section

Stable complexes of silver(II) are obtained by a general procedure.[2] Solutions of Ag(I) in the presence of an excess of ligand are oxidized by means of $K_2S_2O_8$ or $(NH_4)_2S_2O_8$. The basic redox reaction is[17]

$$2Ag^+ + S_2O_8^{2-} \rightarrow 2Ag^{2+} + 2SO_4^{2-}$$

The method described by Banerjee and Ray[6] was employed to produce bis(nicotinato)silver(II). Three grams of nicotinic acid was dissolved in 50 ml of warm water and the solution was stirred at room temperature with a solution made up of 1.4 g of $AgNO_3$ in 20 ml of water. A white precipitate of silver(I) nicotinate formed immediately. With the resulting slurry still stirring, a concentrated solution of $K_2S_2O_8$ (~6 g in 25 ml of H_2O) was added dropwise to it, and the mixture was stirred at 0° overnight. An insoluble cinnamon red powder of $Ag(nic)_2$ resulted. The powder was collected by filtration, washed with cold water, and dried in vacuo at room temperature. Anal. Calcd for $Ag(C_6H_4NO_2)_2$: C, 40.94; H, 2.29; N, 7.96. Found: C, 40.74; H, 2.57; N, 7.94. About 1 g of product was recovered.

All magnetic susceptibility measurements in the temperature range 4.2–275°K on a powder sample of $Ag(nic)_2$ were recorded at a field strength of 10000 G on a P.A.R. Foner-type vibrating-sample magnetometer[18] calibrated with mercury tetrathiocyanatocobaltate(II).[19,20] Temperatures were measured with a calibrated gallium arsenide diode. Susceptibility data were corrected for the diamagnetism of substituent atoms using Pascal's constants.[21] Electron paramagnetic resonance spectra of powdered samples of $Ag(nic)_2$ were determined with a Varian Model E-3 spectrometer at X-band using diphenylpicrylhydrazine as an internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 421 recording spectrometer.

Results and Discussion

The experimental magnetic susceptibilities and moments determined for $Ag(nic)_2$ at high temperatures (>77°K) appear to be in excellent agreement with the results reported by Fowles et al.;[15] however, a Curie–Weiss fit of our data in the 100–275°K range furnishes the antiferromagnetic Weiss constant of 42°, with a calculated $\langle g \rangle = 2.09$. A plot of the inverse susceptibility *vs.* temperature for the high-temperature region, along with the best-fit Curie–Weiss curve, is presented in Figure 1.

A plot of the complete set of experimental susceptibility *vs.* temperature is depicted in Figure 2. The low-temperature susceptibility results reveal a maximum in the susceptibility at about 40°K. Such behavior is evidence of an antiferromagnetic interaction in the complex $Ag(nic)_2$ and is the first positive evidence of an exchange interaction in a silver(II) complex.

One broad resonance centered at $g = 2.08$ was recorded on an EPR spectrum. This value of $\langle g \rangle$ is comparable to published EPR results for other silver(II) complexes,[17,22–25] where $\langle g \rangle$ ranges from 2.08 to 2.12.

The impossibility of growing single crystals of $Ag(nic)_2$ has prevented an X-ray structure determination of the compound, although early X-ray powder diffraction studies[6] suggested a dimeric or polymeric structure for the species. The gross features of the observed magnetism of bis(nicotinato)silver(II) are consistent with such structures, so attempts to describe the magnetic behavior of the complex with model expressions for the magnetic susceptibility of dimeric and polymeric molecules were undertaken.

The Bleaney–Bowers equation[27] for the magnetic susceptibility of antiferromagnetically coupled $S = 1/2$ ions failed to provide an adequate description of the experimental results for reasonable values of g. The best fit to the experimental results for the dimer expression yielded parameters of $g = 2.00$ and $2J = -51$ cm^{-1}. A plot of experimental susceptibility *vs.* temperature along with the best-fit dimer equation curve is shown in Figure 2. The criterion for the best-fit here and in the cases described below was taken to be the minimum value of the parameter

$$P = \sum_{i}^{N} [(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})T_i]^2$$

where N is the number of data. The value of this parameter, P(best dimer fit), was calculated to be 0.014.

Since the failure of the dimer susceptibility expression to account for the magnetic data seems to rule out a dimeric structure for $Ag(nic)_2$, another explanation for the magnetism was sought. The simplest polymeric system is a one-

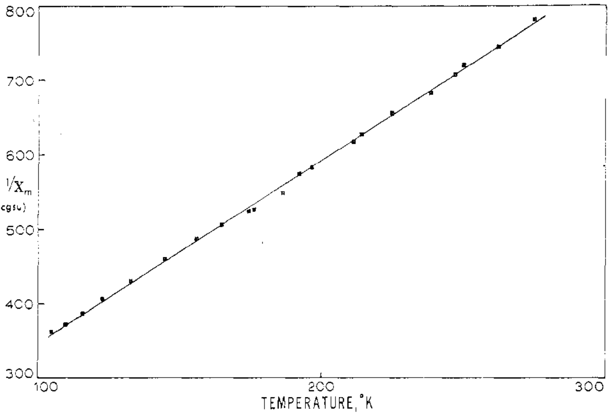


Figure 1. Temperature dependence of the inverse susceptibility of bis(nicotinato)silver(II). Experimental data are depicted as solid squares and the best fit to the Curie-Weiss expression ($\langle g\rangle = 2.09$ and $\Theta = -42°$) is shown as the full line.

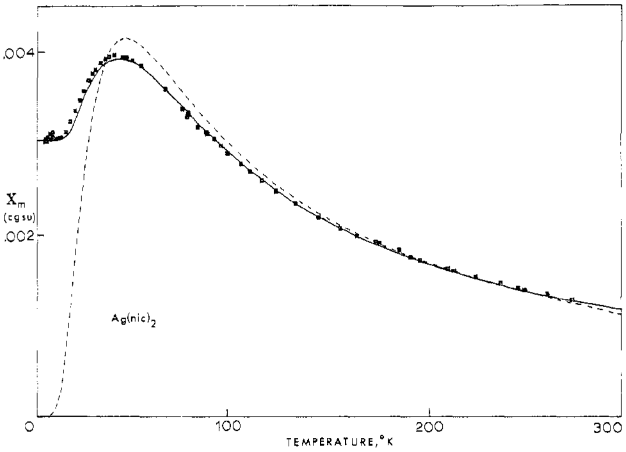


Figure 2. Temperature dependence of experimental susceptibility of bis(nicotinato)silver(II). Susceptibility data are depicted as solid squares. The "best-fit" theoretical dimer expression for exchange-coupled $S = {}^1/_2$ ions is shown as the dashed line. The best fit of experimental results to the Ising chain expressions is depicted as the solid line.

dimensional chain-type structure. The Hamiltonian (1) describes magnetic interaction along a chain of metal ions[28]

$$\mathcal{H} = -J\sum_{i=1}^{N}[S_{iz}\cdot S_{(i+1)z} + \gamma(S_{ix}\cdot S_{(i+1)x} + S_{iy}\cdot S_{(i+1)y})] \qquad (1)$$

where J is the exchange energy and γ can have values ranging from 0 to 1. When $\gamma = 1$, the Hamiltonian (1) yields the isotropic Heisenberg exchange model, while for the limit $\gamma = 0$, the anisotropic Ising model is the result.

There now exists a substantial body of evidence which suggests that the anisotropic Ising simplification of exchange along a linear chain is inaccurate[29] for certain systems and that the isotropic Heisenberg model provides a superior description of magnetic substances.[30-32] The Heisenberg model was therefore initially chosen for a one-dimensional exchange model. There are no closed-form expressions available for calculating the susceptibility of a Heisenberg chain antiferromagnet, but the approximate results of Bonner and Fisher[28] for infinite chains of $S = {}^1/_2$ ions where $kT_{\max}/|J| \approx 1.282$ and $|J|\chi_{\max}/g^2\beta^2N \approx 0.07346$ may be fit graphically to experimental data to furnish the magnetic parameters J and g. The best Heisenberg linear chain fit to the experimental data of Ag(nic)$_2$ is plotted (in reduced coordinates) as Figure 3. The presence of paramagnetic $S = {}^1/_2$ impurities, which has been demonstrated to be necessary for the correct description of the properties of some copper chains,[32] was accounted for in the following way. It was assumed that all paramagnetic contributions (from impurities) to the total susceptibility obeyed the Curie law and that the following expression represents the total susceptibility

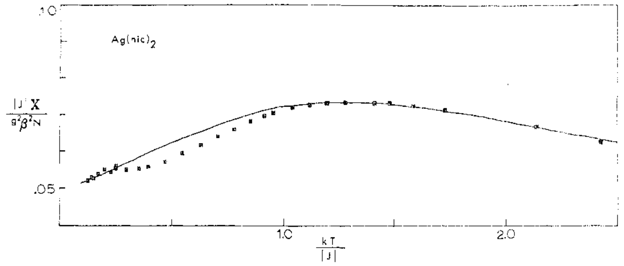


Figure 3. Temperature dependence of experimental susceptibility data, plotted in reduced coordinates. The best fit to the Heisenberg linear-chain model is shown as the full line.

$$\chi_{\text{total}} = (p/100)[Ng^2\beta^2S(S+1)/3kT] + [(1.00 - p)/100]\chi_{\text{Heisenberg}}$$

where p is the weight per cent of the impurities, $S = {}^1/_2$, and g is the EPR-recorded g value. (Owing to the small magnitude of p, χ_{total} is insensitive to minor changes in the g value in the correction term. The best fit to the Heisenberg model yielded the parameters $J = 21.4$ cm^{-1}, $g = 2.10$, $p = 0.2\%$, and P(best Heisenberg fit) = 0.0016. When no correction for a presumed paramagnetic impurity was used, P(best Heisenberg fit) = 0.0024. As can be seen from Figure 3, the fit is excellent at temperatures near and above $T_{\max}$ but is not particularly good for the lower temperature data. The experimental results were then fit to the closed-form expressions (2) and (3) which result from the anisotropic Ising form of the spin Hamiltonian (1).[33]

$$\chi_{\perp} = \frac{Ng^2\beta^2}{8|J|}\,[\tanh(J/kT) + (J/kT)\,\text{sech}^2\,(J/kT)] \qquad (2)$$

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{4kT}\,\exp(2J/kT) \qquad (3)$$

$$\chi_M = {}^1/_3(2\chi_{\perp} + \chi_{\parallel}) \qquad (4)$$

Here J is the exchange energy. The calculated best fit to experimental data from the Ising expressions is included in Figure 2; the parameters $J = -30.8 \pm 1.0$ cm^{-1}, $g = 2.05 \pm 0.02$, and P(best Ising fit) = 0.00015 are obtained. It was not necessary to make a correction for presumed impurities. The Ising description, in this case, appears to provide a good account of the observed magnetism of the silver(II) complex, although the calculated $g = 2.05$ is somewhat less than the experimentally determined $\langle g\rangle$.

Attempts to describe the Ag(nic)$_2$ magnetism with a two-dimensional antiferromagnetic Heisenberg model[34] met with no success. The parameters which were obtained are $J = -23.6$ cm^{-1}, $g = 2.05$, and P(best two-dimensional Heisenberg fit) = 0.0095. The expression fails completely in the low temperature region to account for the magnetic properties. Lines[34] has pointed out that the series expansion for the susceptibility is only an approximation which ceases to be of much quantitative value below $kT \approx 0.9|J|S(S+1)$. If the data below 10°K are excluded from the fitting process, the parameters are $J = -27.0$ cm^{-1}, $g = 2.10$, and P(two-dimensional Heisenberg fit) = 0.00072. Even with this truncation of the data the Ising linear-chain equations fit the data better and it does appear that the structure of Ag(nic)$_2$ must be one that allows for chainlike interaction between the Ag(II) ions of the compound. This is an extremely interesting result since few chains (and none of silver(II), of course) are known to exhibit Ising behavior. This probably cannot be pure Ising behavior since an EPR absorption at $g \approx 2$ was observed.

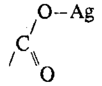
Gerstein et al.[35] have derived expressions for the magnetic susceptibility for a linear chain ($N = 2$, $S = {}^1/_2$) with intermediate anisotropies, as indicated by the value for γ in eq 1. The equations are

$$\chi_{\|} = \frac{Ng_{\|}^2\beta^2}{kT}\,\frac{1}{1 + \exp(-J/kT)\cosh(J\gamma/kT)} \tag{5}$$

$$\chi_{\perp} = \frac{Ng_{\perp}^2\beta^2}{J(\gamma-1)}\,\frac{\exp(J\gamma/kT) - \exp(J/kT)}{\exp(J/kT) + \cosh(J\gamma/kT)} \tag{6}$$

The best mathematical fit of the data for Ag(nic)$_2$ to these equations was obtained with a value of γ outside the range $0.0 \leq \gamma \leq 1.0$ and thus was discarded. Calculations using reasonable values of J, $g_{\|}$, $g_{\perp}$, and γ did not yield good agreement.

Infrared spectra of solid KBr pellet specimens of uncomplexed nicotinic acid and of bis(nicotinato)silver(II) obtained here are in agreement with earlier results;[15] the broad absorption due to the asymmetric carbonyl stretch of the free acid at ~1700 cm^{-1} is shifted to 1630 cm^{-1} in the complex, which is characteristic of silver–carboxylate bonding in the manner[36]



Far-infrared spectra have confirmed the presence of silver–nitrogen bonds,[10] and roughly square-planar coordination about the silver(II) ions of Ag(nic)$_2$ has been postulated on the basis of visible spectroscopy.[10,22]

A structure for Ag(nic)$_2$, incorporating the specific inventory of structural clues listed above and capable of providing a pathway for the observed linear-chain type antiferromagnetic exchange in the complex is difficult to construct. Although Kleinstein and Webb[10] preferred a square-planar coordination for Ag(nic)$_2$, the six-coordinate structure that they proposed, in general, provides a chainlike pathway for magnetic exchange.

Magnetic exchange in complexes of silver(II) is probably not confined to the complex Ag(nic)$_2$. It has been established that magnetic interaction across pyrazine and quinoxaline bridges occurs in the compounds Cu(pyr)(NO$_3$)$_2$ and Cu(quinox)(NO$_3$)$_2$.[30,31] Since nitrogen-donor ligands stabilize the Ag(II) oxidation state, it ought to be possible to synthesize stable pyrazine (and pyrazine derivatives)-bridged silver(II) polymers exhibiting magnetic interaction such as that found for bis(nicotinato)silver(II).

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Notes

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Structural Study of Phosphoryl Bromide by Means of Nuclear Quadrupole Resonance

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The crystal structure of phosphoryl bromide (POBr$_3$) was determined recently by Olie, *et al.*,[1] as orthorhombic, space group $Pn2_1a$. Later, the Templetons[2] reexamined the crystal structure on the basis of the data obtained by Olie, *et al.*, and concluded that there was no reason to reject *Pnma* as the correct space group because their calculations reduced the discrepancy index R below 11.3% in both space groups. Therefore, we investigated this compound by means of nuclear quadrupole resonance (nqr) in order to clarify its crystal structure and to examine the P–Br bond character.

Experimental Section

Phosphoryl bromide was purchased from Katayama Chemical Industries Co., Ltd. The single crystal was prepared by the Bridgman–Stockbarger method. The nqr spectrometer was a superregenerative oscillator with frequency modulation. The magnetic field used for the Zeeman study was provided by a Helmholtz coil with a field strength of about 200 G. The temperature of the sample was set at the desired value by controlling the flow rate of nitrogen gas over the sample.

Results and Discussion

Phosphoryl bromide shows two ^{81}Br resonance lines as seen in Table I. The intensity ratio of the lower line (ν_1) to the