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Experimental determination of single-ion anisotropies in two nickel complexes

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Abstract

Motivated by the Haldane conjecture, the powder susceptibilities of two nickel complexes (**1**: $NiCl_2L_2$, with $L = P(CH_2CH_2CN)_3$; **2**: bis(propiolato)tetraaquonickel(II)) have been investigated as part of a search for new $S = 1$ antiferromagnetic linear chains. The effective moments of both complexes correspond to high-spin $S = 1$ Ni(II) ions at room temperature but decrease rapidly below 20 K. Analysis of the data showed the decreases to correspond to the effects of single-ion anisotropy and not magnetic exchange. The susceptibilities of **1** and **2** can be described as resulting from single-ion anisotropy parameters $D/k = 7$ and 8.5 K, respectively, with the $m_s = 0$ single state low for both complexes. Neither **1** nor **2** can be considered a magnetic linear chain.

Introduction

The magnetic properties of integer spin antiferromagnetic linear chains have recently been shown to differ strongly from those of half-integer spin chains. Haldane [1] first conjectured that the ground state of an integer spin Heisenberg antiferromagnetic chain (HBAF) is a non-magnetic singlet, separated by an energy gap, ΔE, from the first (magnetic) excited state. No such gap exists for chains of half-integer spin ions. Since the size of the gap is predicted to decrease sharply for $S > 1$, experimental investigations [2] of the Haldane conjecture have concentrated on nickel chains for which the d^8 Ni(II) ions have $S = 1$.

Nickel(II), however, is well known to possess single-ion anisotropy (SIA), in which the $m_s = \pm 1$ sublevels are split away from the $m_s = 0$ sublevel. This splitting introduces an energy gap D, unrelated to the co-operative Haldane gap ΔE. More extensive calculations [3] have been performed on $S = 1$ HBAF chains using the Hamiltonian in eqn. (1), in which both magnetic exchange (J) and single-ion anisotropy (D) are present.

$$\mathscr{H} = -2J\sum_i S_i S_{1+1} + D\sum_i (S_i^z)^2 \qquad (1)$$

These calculations confirmed the existence of the Haldane gap, even in the presence of the single-ion term, and gave detailed predictions for the dependence of ΔE on both J and D.

The best studied example of an $S = 1$ HBAF linear chain is $Ni(en)_2NO_2(ClO_4)$, NENP [4]. NENP has a strong intrachain exchange constant, $2J = -50$ K (33 cm^{-1}), and a ratio of interchain to intrachain coupling of $\approx 10^{-4}$; no transition to a state of long-range order appears above 1.2 K. The single-ion anisotropy parameter is now considered to be near 12 K [2]. Experimental studies on NENP [2, 5–7] have established the existence of the gap and shown its magnitude, $\Delta E \approx 0.4|2J|$, to be consistent with Haldane's original prediction.

Verification of the predicted dependence of the Haldane gap upon both J and D requires a series of studies on compounds of various J/D ratios. To this end, we have begun investigations of the magnetic properties of nickel compounds which may serve as further model systems. We report here on the first results of these studies.

The blue phase of **1**, $NiCl_2L_2$, where $L = P(CH_2CH_2CN)_3$, consists of linear polymers of Ni(II) ions [8]. The structure of **1** is shown in Fig. 1. The octahedrally coordinated nickel ions are coordinated to two *trans* chloride ions (Ni–Cl; 2.406 Å) and two *trans* phosphorus atoms (Ni–P; 2.438 Å) in the plane,

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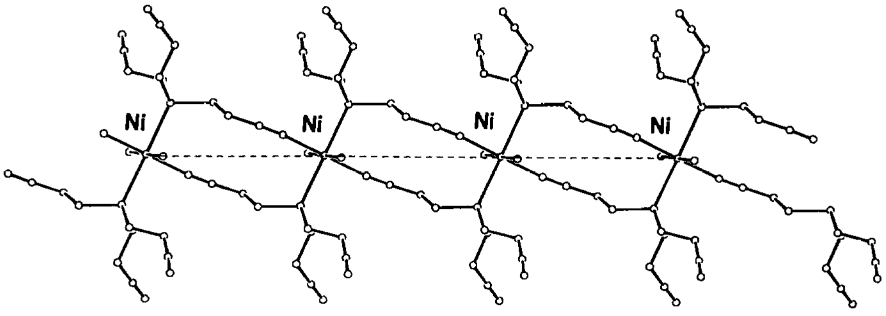

Fig. 1. The linear polymeric chain in **1**, $NiCl_2L_2$, $L = P(CH_2CH_2CN)_3$.

while the axial sites are occupied by nitrogen atoms from the cyano groups (Ni–N; 2.098 Å). The polymeric structure is achieved through one of the three cyanoethyl chains which links adjacent nickel ions into linear chains (Fig. 1). The resulting Ni–Ni distance is 7.699 Å. The remaining two nitrile moieties are uncoordinated. The angles around the metal ion correspond to nearly perfect octahedral coordination (Cl–Ni–N = 89.5°; P–Ni–N = 89.4°; P–Ni–Cl = 92.0°).

The crystal structure of **2**, bis(propiolato)tetraaquonickel(II), has been shown to be strictly isomorphous with the M = Co [9] and M = Zn [10] analogues by powder patterns and Weissenberg photographs. Their structure (Fig. 2) consists of $M(H_2O)_4(O_2CC{\equiv}CH)_2$ monomers linked together by hydrogen bonds as well as by 1,2′-acetylene-acetylene contacts. These short carbon–carbon contacts (3.57 Å in the zinc analog [10]) are believed to be of importance in leading to the solid state reactions found in these compounds. The metal ions are coordinated to six oxygen atoms in a 4 + 2 arrangement, four oxygen atoms from the water molecules and two from the carboxylate groups. Based on the structures of the isomorphous Co and Zn complexes, the expected Ni–O distances should lie in the range 2.05–2.15 Å. The internal oxygen–metal–oxygen angles for the M = Co, Zn complexes are in the range 87.6–89°. The Ni–Ni distance along the 101 direction is 9.15 Å.

Experimental

The two samples were prepared in accordance with published procedures [10, 11]. The magnetic moments of polycrystalline samples of both **1** and **2** were determined between 1.4 and 300 K in a field of one Tesla using a Princeton Applied Research model 155 vibrating sample magnetometer and a custom helium cryostat. The moments at the lowest measured temperature were found to increase linearly with field up to the maximum field of one Tesla. The molar magnetic susceptibilities were calculated as the ratio of magnetic moment to applied field. Corrections for diamagnetism (**1**: -310×10^{-6} emu/mol; **2**: -97×10^{-6} emu/mol) and for temperature independent paramagnetism (100×10^{-6} emu/mol) were made [12]. Sample temperatures were measured using a calibrated carbon-glass resistance thermometer while the applied magnetic fields were determined with a commercial Hall probe. The experimental apparatus has been described elsewhere [13].

Results and discussion

The magnetic susceptibilities χ of the two compounds are qualitatively similar; the results for both **1** and **2** below 70 K are shown in Fig. 3. The susceptibility continues to increase down to the lowest measured temperature. However, Curie–Weiss fits

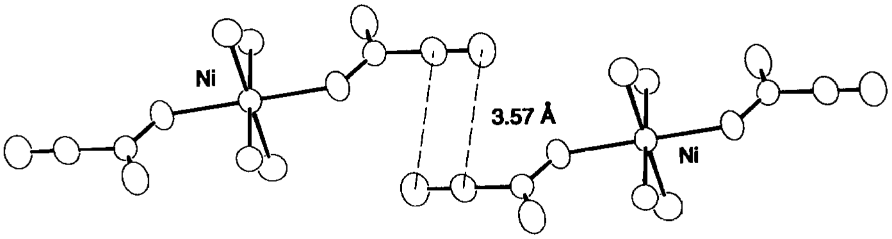

Fig. 2. Pairs of molecules of **2** (bis(propiolato)tetraaquonickel(II)), showing the closest approach of acetylene moieties at a distance slightly larger than the van der Waals separation.

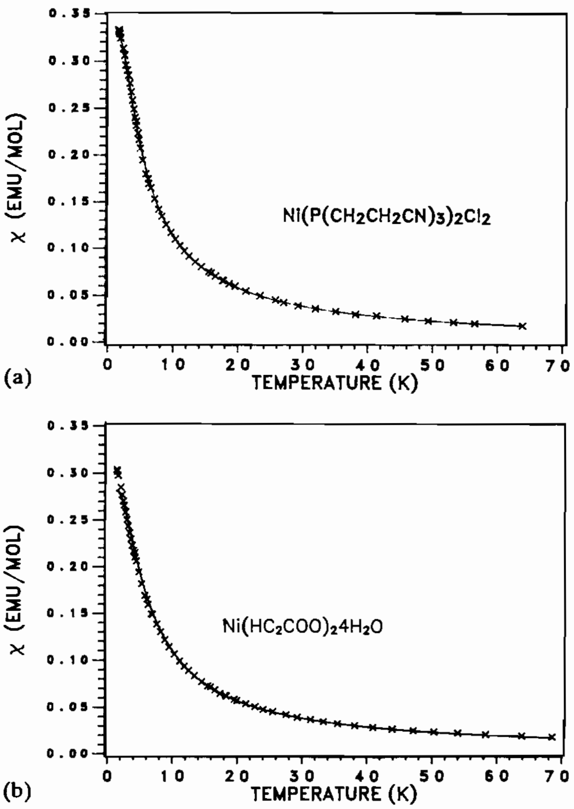

Fig. 3. The powder susceptibility of **1** (a) and **2** (b) plotted vs. temperature. The solid line corresponds to the predictions of the single ion anisotropy model (eqn. (2)) with parameters $D/k = 7.1$ K ($m_s = 0$ state low) and $g = 2.16$ for (a) and $D/k = 8.0$ K ($m_s = 0$ state low) and $g = 2.13$ for (b).

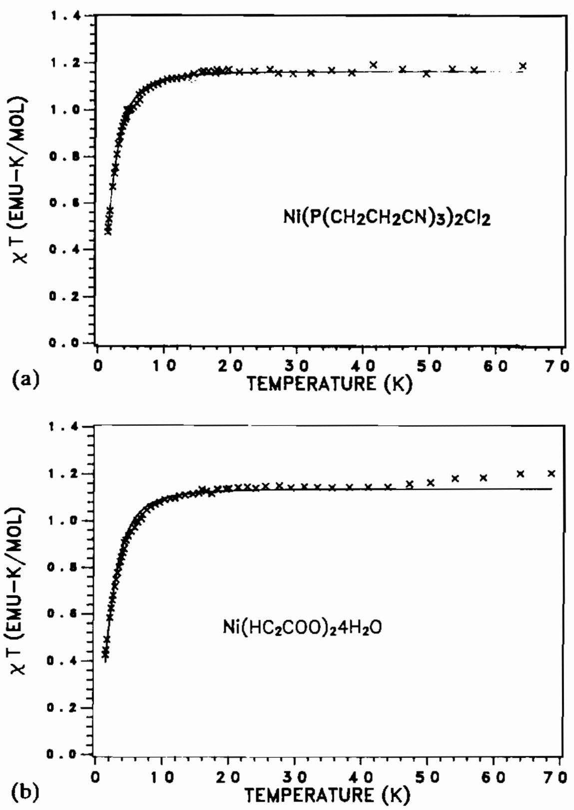

Fig. 4. The powder susceptibility of **1** (a) and **2** (b) plotted as the product $\chi_m T$ vs. temperature. The solid line corresponds to the predictions of the single ion anisotropy model (eqn. (2)) with parameters $D/k = 7.1$ K ($m_s = 0$ state low) and $g = 2.16$ for (a) and $D/k = 8.0$ K ($m_s = 0$ state low) and $g = 2.13$ for (b).

to the high-temperature data (60–300 K) show evidence of deviations from Curie-like behavior. The Curie–Weiss parameters (C, θ) are (**1**: 1.27 emu-K/mol, −6.7 K) and (**2**: 1.29 emu-K/mol, −5.7 K), where the negative sign of θ corresponds to an antiferromagnetic molecular field. The values of the Curie constants imply g factors near 2.26, which is normal for the Ni(II) ion in an octahedral environment [14].

The powder susceptibility data for the two compounds are plotted as the product $\chi_m T$ versus temperature in Fig. 4. As this product is related to the effective moment (in units of Bohr magnetons) through the equation $\mu_{\text{eff}} = \sqrt{(8\chi_m T)}$, it is clear the effective moments of both compounds drop rapidly below 20 K. The room temperature values for each compound, 3.2 BM, are essentially unchanged down to 20 K; below 20 K, the dropoff for **1** is to 2.77 BM at 4 K and to 1.96 BM at 1.4 K. The decline of the effective moment is slightly greater for **2**, reaching a value of 1.85 BM at 1.4 K.

Such a decrease in effective moment can have several origins. Antiferromagnetic interactions between the nickel ions can align their moments antiparallel, causing a decrease in the product $\chi_m T$. Alternatively, single-ion anisotropy with the non-magnetic singlet state low can cause the same effect, as the fraction of nickel ions in the excited magnetic states decreases with temperature. Of course, both antiferromagnetic exchange plus single-ion effects can occur in the same compound.

We have first analyzed the two susceptibility data sets in terms of a model of non-interacting $S = 1$ ions in the presence of a single-ion anisotropy (SIA). The Hamiltonian is that given in eqn. (1) with J held equal to zero. A positive value of the parameter D means the non-magnetic $m_s = 0$ state lies below the $m_s = \pm 1$ states. The derivation of the average magnetic susceptibility of this Hamiltonian has been given elsewhere [13]. It is written as

$$\langle\chi_m\rangle = \frac{2Ng^2\mu_\beta^2}{3kT}\left[\frac{2x^{-1} - 2e^{-x}x^{-1} + e^{-x}}{1 + 2e^{-x}}\right] \qquad (2)$$

where $x = D/kT$. The data sets for **1** and **2** were fit to eqn. (2), allowing both D and g to vary*. Only the more accurate data below 65 K were included. The lowest temperature included in the range of fit was varied, to test the dependence of the parameters on the range. The results for **1** are seen in Fig. 4. The best fit parameters were found to be $D/k = 7.1(2)$ K, $g = 2.16(1)$, independent of the lowest temperature in the fit, provided that temperature was below 5 K. The predicted curve with these parameters is shown as the solid line. The agreement is excellent, except near 5 K where there are slight systematic errors in the data. When the data was restricted to the range above 5 K, the D value was found to be closer to 8 K, but the overall quality of the fit was somewhat worse, due to the poor quality of the data near that temperature.

Somewhat more variation in the parameters was found for **2**. The best fit parameters were found to vary from $D/k = 8.0(3)$ K, $g = 2.13(1)$ for the temperature range 1.4–65 K, to 8.6 K, 2.14 from 2.6–65 K and 9.7 K, 2.15 for data from 5.2–65 K. The solid curve in Fig. 4 corresponds to the lowest range. The larger value of D found for **2** is consistent with the greater rate of dropoff in the effective moment for this compound. However, the variation of the parameter D with range of fit indicates some deficiency of the model. Subsequently an alternative model was tried.

The second model postulated an antiferromagnetic interaction between nickel ions in a linear chain, with zero single-ion anisotropy. The existence of such interactions is suggested by the close contacts between the acetylene groups in **2** (Fig. 2). The Hamiltonian used was a simplified form of that given in eqn. (1), where now D is held equal to zero. We have used an approximate expression for the susceptibility of this model, as given in ref. 4, with the sole change of multiplying the exchange constant by two, to be consistent with the Hamiltonian in eqn. (1). Both the exchange constant and the g factor were allowed to vary.

When the antiferromagnetic chain model was applied to **2**, the quality of the fit was once again excellent, comparable to that found with the SIA fit. However, the variation of fitting parameters with range of fit was far worse. When only data above 12 K was included, the best fit value to J was -0.33 K; as more data was added, the absolute magnitude of the exchange constant steadily increased, reaching a value of -0.52 K when all data were considered. This sizable variation indicates the failure of the simple antiferromagnetic chain model.

Most of the temperature dependence of the effective moment of **2** is accounted for with a single-ion anisotropy between 8 and 9 K. The slight variation of the value of D with range-of-fit may indicate a small interaction between the nickel atoms; unfortunately there is no model which predicts the dependence of susceptibility on both J and D. However, based on the small size found for J when using the antiferromagnetic chain model to explain the entire temperature dependence of the susceptibility, it is clear that J as a correction to a D near 8.5 K will be much smaller. We conclude that the exchange strength must be less than 0.1 K.

The antiferromagnetic chain model has also been applied to **1** and was found to be even less appropriate. Data above 12 K could be fit with $J/k = -0.11$ K, but the entire data set required $J/k = -0.46$ K. This four-fold variation of the fitting parameter rules out this model.

The absence of magnetic interactions in both **1** and **2** demonstrates that neither structure contains effective superexchange pathways. Such an absence cannot be explained *a priori* as being due to the large separation of the nickel ions, since many examples are known of widely separated metal ions being magnetically coupled [15]. The absence is particularly surprising in the case of **1**, since the unpaired electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals of the Ni(II) ion are oriented directly towards the nitrogen atoms in the axial positions and the set of in-plane chlorine and phosphorus atoms, respectively. It is known [16] that copper dimers bridged by Cl^- ions in the axial position possess strong interaction strengths ($|J|/k \approx 130$ K), so some exchange interaction was anticipated. The absence of any measurable effect means that the superexchange information is unable to propagate through the cyanoethyl chains. The absence of magnetic interactions in **2** is more understandable, since there is no covalently bonded network linking the metal ions in this compound. The short carbon–carbon contacts (≈ 3.5 Å, Fig. 2) are slightly longer than a typical van der Waals separation (3.4 Å), and the magnetic interaction between the propiolate groups is thus quite small. The possible interaction strengths (on the order of 0.1 cm^{-1}) may just as well have their origin in dipolar interactions as in superexchange.

In summary, both **1** and **2** show evidence of single-ion anisotropies with the $m_s = 0$ states low. **1** can be described with $D/k = 7$ K, with no evidence of any spin exchange magnetic interactions. There may be

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*It is recognized that rhombic distortions are present in the crystal fields of the nickel ions in **1** and that these distortions should lead to an additional term in the Hamiltonian. Since the experimental data were collected on powdered samples in which the rhombic contributions will tend to cancel, this term has been ignored.

very weak interactions present in **2**. D/k is less well determined for this compound but is near 8.5 K. Neither **1** nor **2** can be considered a magnetic linear chain.

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