1,2,4-Triazole Complexes, IV *

Magnetic properties of manganese (II) \((\text{1,2,4-triazole})_2\text{(NCS)}_2\), a two-dimensional Heisenberg antiferromagnet

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Z. Naturforsch. 33a, 848—854 (1978); received March 31, 1978

Magnetic susceptibility measurements on single crystals of Mn(II)(trz)\(_2\)(NCS)\(_2\) in the temperature range 1.8—300 K are reported. The compound has two-dimensional structural and magnetic properties. The data from susceptibility measurements are accounted for by considering the material to be a quadratic-layer, \(S = \frac{1}{2}\) Heisenberg antiferromagnet. From the comparison of the data with predictions from series expansions the intralayer exchange constant was found to be \(J/k = -0.25\) K. A transition to the antiferromagnetic state is observed at \(T_N = 3.29\) K with the \(b\) axis being the preferred axis. Magnetization measurements at 1.8 K along the \(b\) axis reveal a spin-flop transition at 10.8 kOe. The occurrence of a second discontinuity in the magnetization curve at 15.6 kOe is explained by assuming that the spin system goes to the spin-flop state via an intermediate spin arrangement, as is suggested by the presence of tilted MnN\(_6\) octahedra. From pulsed-field magnetization measurements at 1.17 K, a saturation field \(H_s = 74\) kOe is found which also leads to \(J/k = -0.25\) K. With the aid of neutron powder diffraction at 1.2 K, the magnetic space group was determined to be \(\text{A}_{\text{b}}\text{b}'\text{a}'\text{2}'\). Preliminary results from heat capacity measurements on the corresponding Fe(II), Co(II), Ni(II) and Cu(II) compounds are reported.

Introduction

Recently, a new series of complexes with composition \(\text{M(II)}(\text{trz})_2\text{(NCS)}_2\) has been reported [1] which show two-dimensional structural and magnetic properties [2]. Here \(\text{M}\) are first row transition metal ions and trz is 1,2,4-triazole.

As part of a research program on the physical properties of these compounds we have investigated the magnetic properties of Mn(II)(trz)\(_2\)(NCS)\(_2\) by susceptibility and magnetization measurements on single crystals, and by neutron diffraction experiments on powders. The X-ray powder diffraction pattern shows the material to be isostructural with the corresponding Co(II) complex [1], both compounds crystallizing in the orthorhombic system, space group \(\text{Aba}_2\) with \(Z = 4\) and for the Mn(II) complex at 1.2 K \(a = 7.890\) Å, \(b = 16.263\) Å and \(c = 10.135\) Å.

The structure of the Co(II) compound clearly is two-dimensional in character [2, 3]. Very recently, X-ray diffraction experiments on single crystals of the corresponding Cu(II) and Zn(II) complexes have been performed. Their space groups are \(\text{P2}_1/\text{in}\) and \(\text{Phen}\) respectively, and their structures show a striking similarity to that of the Co(II) complex [3]. All these structures exhibit the same essential

features, namely triazole bridged layers with tilted \(\text{M(II)}\text{N}_6\) octahedra. We therefore believe that the structures of the Co(II), Mn(II), Fe(II) and Ni(II) compounds, being all powder isomorphous, do not differ essentially.

The structure is depicted in Figure 1. Mn(II) ions occupy \((0, 0, 0)\), \((0, \frac{1}{3}, \frac{1}{3})\), \((\frac{1}{3}, 0, \frac{1}{3})\) and \((\frac{1}{3}, \frac{2}{3}, 0)\) positions. They are octahedrally coordinated by two N\(_2\) and two N\(_4\) nitrogen atoms originating from triazole rings and by two nitrogen atoms from the NCS groups. The Mn(II)N\(_6\) octahedra are tilted in the \(a-b\) plane, the angle between the (SC)\text{-N-}-Mn-N(CS) axis and the \(b\) direction being 31°. The planes of the triazole molecules are almost parallel to the \(b\) axis and by coordinating via their \(N2\) and \(N4\) atoms a two-dimensional layered structure is formed.

The strongest exchange between Mn(II) ions in the same \(a-c\) layer will take place via the bridging triazole molecules. In this way the Mn(II) ions in the planes \(y = 0\) and \(y = \frac{1}{3}\) can be considered to comprise quasi-quadratic lattices since each Mn(II) ion is connected equivalently to four nearest magnetic neighbours. The superexchange paths between next-nearest neighbours within the layers are highly unfavourable. Furthermore, as regards interlayer couplings, structural evidence is present for hydrogen bonding between a S atom in one layer and a H atom connected to a N1 atom of a triazole ring in a neighbouring layer [3]. This would

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result in the exchange path

\[ \text{Mn} - \text{N} - \text{C} - \text{S} \ldots \text{H} - \text{N1} - \text{N2} - \text{Mn} \].

Thus a total number of six non magnetic atoms will be involved in this bridging, so that the corresponding interlayer interaction is expected to be very much weaker than the intralayer exchange. This explains the observed two-dimensional character.

Experimental

Single crystals of Mn(II)(trz)2(NCS)2 were grown by slow evaporation at room temperature of an aqueous solution of the complex prepared according to Haasnoot et al. [1]. Crystals obtained in this way have a very pale green colour and are usually quite flat and diamond-shaped. By means of X-ray diffraction it was established that the \( b \) axis is perpendicular to the flat surface and that the diamond shape corresponds to the pattern of the Mn(II) ions in the \( a-c \) plane. Several crystals with a total mass of about 30 mg were mounted with Apiezon grease into a small delrin cube, which was fixed to the sample rod of a vibrating sample magnetometer equipped with a superconducting magnet supplying fields up to 56 kOe [5]. Measurements from 80 to 300 K were taken on powdered samples using the Faraday method [6]. Susceptibilities were corrected for diamagnetism using a value of \(-156(5) \times 10^{-6}\) e.m.u./mole as found for the Zn(II) complex. Magnetization measurements up to 100 kOe were carried out in pulsed magnetic fields at the Kamerlingh Onnes Laboratorium using a set-up as described previously [7]. Neutron diffraction patterns were collected at 300 K and 1.2 K at the powder diffractometer at the Petten nuclear reactor. For the analysis of the data Rietveld’s profile method was used [8]. Atomic form factors for Mn(II) were taken from Watson and Freeman [9]. The following neutron scattering lengths have been used: \( b_{\text{Mn}} = -0.387 \), \( b_{\text{C}} = 0.665 \), \( b_{\text{N}} = 0.904 \), \( b_{\text{S}} = -0.374 \) and \( b_{\text{S}} = 0.285 \), in units of \( 10^{-12} \) cm.

Results and Discussion

a) Susceptibility Measurements

Magnetic susceptibilities along the three orthorhombic axes were measured at a field strength of 5.57 kOe. They are depicted in Fig. 2 and show the broad maxima characteristic of a two-dimensional antiferromagnet. The \( b \) axis clearly is the easy axis of antiferromagnetic alignment, and the \( a \) and \( c \) axes are the perpendicular directions. No evidence for canting could be seen in these measurements. The broad maxima occur at 4.3(2) K with \( \chi_{\text{max}}(b) = 0.31(6) \) e.m.u./mole. The transition temperature is estimated to be 3.2(2) K from the point of maximum slope of the \( \chi_b \) versus \( T \) curve. The susceptibilities become isotropic (within experimental error) above 8 K and do not display any discontinuities up to 300 K. Heat capacity measurements corroborate
the two-dimensional character and yield a more accurate value of 3.29 K for $T_N$ [10].

The value of the exchange constant $J/k$ can be obtained in a number of ways. Firstly we use the theoretical estimates for the quadratic Heisenberg lattice with $S = 5/2$ as given by De Jongh [11]:

$$kT(\chi_{\text{max}})/J S(S + 1) = 2.05(1),$$

$$\chi_{\text{max}} |J|/N g^2 \mu_B^2 = 0.0551(1).$$

In these equations $\chi_{\text{max}}$ is the observed susceptibility maximum, $T(\chi_{\text{max}})$ is the temperature at which this maximum occurs, and the other symbols have their usual meaning. Substituting $T(\chi_{\text{max}}) = 4.3(2)$ K and $\chi_{\text{max}} = 0.331(6)$ e.m.u./mole we obtain $J/k = -0.24(1)$ and $-0.249(7)$, respectively (taking $g = 2.00$). Secondly, a fit of the data in the range 80—300 K to the prediction from the series expansion for $\chi$ of Dalton and Wood [12] gives $J/k = 0.25(1)$ K (with $g = 2.00$). As can be seen from Fig. 2 this value yields a good fit even at fairly low temperatures.

Thirdly, from heat capacity measurements [10] the total magnetic energy $E_{\text{mag}}/R$ was determined to be 6.2(2) K. From this result $J/k = -0.23(1)$ K is calculated from the formula given by spin-wave theory:

$$E_{\text{mag}} = -N |J| z S^2 (1 + e(z)/z S).$$

In this formula $z = 4$ (the number of nearest magnetic neighbours) and $e(z) = 0.632$ (from Keffer [13]).

Fourthly, from the Curie-Weiss temperature $\theta$ using the molecular field (MF) relation:

$$\theta = 2z JS(S + 1)/3k.$$  

With $\theta = 6.0(2)$ K as obtained from the data in the temperature range 80—300 K, we find $J/k = -0.25(1)$ K, in agreement with the results obtained so far.

b) Magnetization Measurements

A magnetization measurement in pulsed field parallel to the $b$ direction is shown in Figure 3. The saturation field $H_s = 74(1)$ kOe and the spin-flop field $H_{sl} = 10.3(5)$ kOe. From these data the exchange field $H_E$, the anisotropy field $H_A$ and the exchange parameter $J/k$ can be calculated with the aid of the MF relations:

$$H_{sl} = (2 H_E H_A - H_A^2)^{1/2},$$

$$H_s = 2 H_E - H_A,$$

$$g \mu_B H_E = 2z |J| S.$$
Inserting the abovementioned values of $H_{sf}$ and $H_c$ we find $H_A = 1.43(5)$ kOe and $H_B = 38(1)$ kOe, yielding a value of 0.038(2) for the anisotropy parameter $\alpha = H_A/H_B$. From Eq. (7) a fifth value of $J/k = -0.25(1)$ K is found, agreeing well with the four values determined by other methods. An independent determination of the anisotropy parameter is possible by means of the MF relations

$$\chi_a = \chi^0_a / (1 + \frac{1}{2} \alpha z),$$

$$\chi_b = \chi^0_a / (1 - \frac{1}{2} \alpha z).$$

for $H > H_{sf}$, where

$$\chi^0_a = N g^2 \mu_B^2 / 4 z |J| .$$

At $H > 16$ kOe, $\chi_a/\chi_b = 1.043$ is calculated from the magnetization curves in Fig. 4 (see below), resulting in $\alpha = 0.042(4)$.

The perpendicular susceptibility can now be calculated using the relation given by spin-wave theory:

$$\chi^0_\perp = \chi^0_\parallel / \left[ 1 + \frac{1}{2} \alpha z \left( 1 - \frac{\Delta S(z)}{S} - \frac{e(z)}{S} \frac{1}{2 + z} S \right) \right].$$

$\chi^0_\perp$ is calculated from Eq. (10) with $z = 4$ and $J/k = -0.25$ K, for $e(z)$ the already mentioned value of 0.632 was taken and $\Delta S(z) = 0.121$ (from Lines [14]). Thus $\chi^0_\perp(0) = 0.345$ e.m.u./mole is calculated, which is in good agreement with the value of 0.35(1) found by extrapolating the $\chi_a$ and $\chi_c$ vs. $T$ curves to $T = 0$. The small difference between these curves may be due to a small orthorhombic inplane anisotropy, caused by the

local environment of the Mn(II) ions. Further evidence for a more complicated situation is given by the magnetization curves at lower field strength as displayed in Figure 4.

The spin-flop transition SF1 is now observed at 10.8(3) kOe.

An unusual second transition SF2 is observed at a field of 15.6(3) kOe. This second transition cannot be ascribed to misorientation effects as it was observed on different sets of crystals. SF2 was also observed in the pulsed-field measurements, which were carried out on a larger single crystal, although this is hardly visible on the scale of Figure 3. The occurrence of SF2 may be explained by assuming that the spin system reaches the spin-flop state via an intermediate spin arrangement (Figure 5). This possibility is suggested by the presence of tilted octahedra as shown in Fig. 6, so that there may be a contribution to the anisotropy due to the local environment of the Mn(II) ions. A more quantitative indication towards this relationship can be obtained.

Fig. 4. Magnetization curves at lower field strength, recorded at $T = 1.8$ K. The discontinuities occurring in the $b$ direction are indicated. Measurements along the $c$ axis nearly coincide with those along the $a$ axis and have therefore been omitted.
that the magnetic lattice is no longer A-centred. In this case 3 possible groups have to be considered, namely [1] (i) $\text{A}_p\beta a'2$, (ii) $\text{A}_p\beta a'2'$ and (iii) $\text{A}_p\beta b'a2'$. Of these (i) can be ruled out immediately as in this space group the $c$ axis would be the preferred direction, which is in contradiction with other experimental findings. Possible spin arrangements are shown in Fig. 7. (Note that both space groups allow hidden canting.)

From Fig. 7 it is clear that a magnetic structure with antiferromagnetic layers in the planes $y = 0$ and $y = \frac{1}{2}$ and with the $b$ axis as the preferred axis can only be realized in space group (iii). Moreover, it was found that a satisfactory description of the observed magnetic intensities could only be obtained with space group (iii). It should be clear now that a canted spin structure is symmetry allowed. However, its presence would require $M_x$, the $x$ component of the magnetic moment of the Mn(II) ions to differ from zero in a significant way and within the accuracy of the diffraction data this could not be established. The best fit to the data was obtained with $M_x = M_z = 0$ and $M_y = 4.9(2)$ B.M. The final discrepancy indices for the nuclear and magnetic structures were $R_{\text{nuc}} = 17\%$ and $R_{\text{magn}} = 26\%$ respectively.

The value of $R_{\text{nuc}}$ seems fairly high for a structure whose essential features are claimed to be well known and this requires some additional comment. During the refinement process the positional parameters as found for the isomorphous Co(II) complex were used. Although we believe the
structures of the Co(II) and Mn(II) complexes not to differ essentially as we have argued already, there are apparently some small differences, which are reflected in the high $R_{\text{nucel}}$ value. Therefore, in order to extract the maximum amount of information contained in the neutron diffraction data, a X-ray single crystal study of the Mn complex will be undertaken.

d) Deviations from the Ideal Two-Dimensional Behaviour

Finally we will make a comparison between Mn(II)$\text{trz}_2$(NCS)$_2$ and other two-dimensional Mn compounds as regards deviations from the ideal two-dimensional Heisenberg antiferromagnet. Such deviations usually show up as an increase of $T_N/\theta$, the relative transition temperature [11]. Using our experimental determination of $J/k = -0.25$ K we have $T_N/\theta = 0.56$ for the title compound. This value is quite a bit higher than those found for other two-dimensional Mn compounds, which are in the range $0.38$ (BaMnF$_4$) $- 0.44$ (Rb$_2$MnF$_4$) [11]. This implies that in our case there is a significant departure from the ideal behaviour. This deviation may be caused by interlayer couplings.

However, an estimate of the interlayer coupling $J'$ can usually not be obtained experimentally in the present case. Therefore we have tried to estimate $J'$ from the interlayer dipolar coupling, ignoring the effect of interlayer exchange whose influence will be very small as has already been pointed out in the discussion of the crystal structure. Dipolar interaction energies were calculated numerically by Blöte [16]. The results of these calculations are as follows: Mn(II) ions in the plane $y = 0$ contribute $E_{\text{dip}}/R = -0.0737$ K. For a plane $y = \pm \frac{1}{2}$ the contribution is $-0.0068$ K. Sufficient convergency was reached with a circle of radius 100 Å. The contribution of other planes appeared to be negligible since a value for $E_{\text{dip}}/R = 0.0873$ K was obtained for a sphere of radius 50 Å.

The ratio $E_{\text{dip}}/R(y = \pm \frac{1}{2})/E_{\text{mag}}/R = 2 \times 10^{-3}$ seems to provide a reasonable estimate for $|J'/J|$, and a similar value was found indeed from preliminary calculations on the metamagnetic transition in the isomorphous Co(II)$\text{trz}_2$(NCS)$_2$ [17]. Comparing this value for $|J'/J|$ with our experimental result $H_A/H_E = 0.04$, we expect that the anisotropy is probably the most important parameter in determining the value of $T_N/\theta$.

Two important sources of anisotropy are crystal field effects and dipolar anisotropy. In order to determine the contribution from the latter the dipolar energies were calculated assuming two antiparallel sublattices, aligned along the three orthorhombic axes. It was found that:

$$E_{\text{dip}}/R = -0.0304 \text{ K} \text{ (spins//a)},$$
$$E_{\text{dip}}/R = -0.0873 \text{ K} \text{ (spins//b)},$$
$$E_{\text{dip}}/R = +0.1178 \text{ K} \text{ (spins//c)}.$$ 

From these results it is clear that, as far as the dipolar energy is concerned, the $a$ direction is the most favourable one and that the $b$ direction is the next preferred direction. By means of the relation $H = 2E_{\text{dip}}/N g \mu_B S$ a dipolar anisotropy field $H_{\text{A, dip}} = 0.34$ kOe is calculated.

From the fact that this is much less than the experimental value $H_A = 1.43$ kOe, we may conclude that there is a considerable contribution due to crystal field effects, originating from the local environment of the Mn(II) ions. We have tried to determine this contribution by E.S.R. measurements on a Mn(II) doped Zn(II) compound.

The spectrum did not allow an accurate determination of the zero-field splitting $D$, as the distortion of the MnN$_6$ octahedra appears to be mainly tetragonal. $D$ was estimated to be $0.03(1)$ K, yielding $H_A = 2DS/g \mu_B = 1.0(3)$ kOe. This value should be handled with care, as the local environment of the Mn(II) ions in the Zn(II) compound may differ from that in the mother compound.

Nevertheless, we believe that these results indicate that the local environment of the Mn(II) ions is the main source of anisotropy in this compound.

Conclusions

The compound Mn(trz)$_2$(NCS)$_2$ shows two-dimensional properties as is to be expected from its molecular structure. From magnetic measurements the intralayer exchange constant $J/k = -0.25(1)$ K is obtained. Heat capacity measurements yield a slightly lower value $J/k = -0.23(1)$ K. Interlayer couplings will be small and from dipole calculations $|J'/J|$ is estimated to be $10^{-2}-10^{-3}$. For the anisotropy parameter $H_A/H_E$ the rather high value of 0.04 is found and therefore the anisotropy is considered to be most important deviation from the
ideal two-dimensional Heisenberg behaviour. The two main contributions to the anisotropy field $H_A = 1.4 \text{ kOe}$ are shown to be from dipolar interactions (0.3 kOe) and from crystal field effects (1 kOe), the latter due to the local environment of the Mn(II) ions. The tilting of the MnN$_6$ octahedra could be responsible for an anomaly in the magnetization curve measured along the preferred direction below $T_N$ above the spin-flop field. A more rigorous proof of this assumption may be obtained from E.S.R. measurements and from measurements of the angular dependency in the $a$-$b$ plane of the magnetization curve. Such experiments will be performed in the near future.

Acknowledgements

The authors wish to thank Mr. J. F. Strang of the Energie Centrum Nederland for recording the neutron diffraction data, Drs. R. J. Lelieveld for his help with their interpretation, Dr. H. W. J. Blöte for performing the dipole calculations, Drs. J. J. Smit for the pulsed field measurements and Dr. L. J. de Jongh for a critical reading of the manuscript and valuable comments.

Additional Note, by G. M. Nap.

Various properties make the present series of compounds $M(\text{II})(\text{trz})_2(\text{NCS})_2$ very suitable for heat capacity measurements. Apart from the speed with which thermal equilibrium is reached in the actual measurements, the values of $T_N$ are sufficiently low to permit a reasonably accurate separation of the magnetic and lattice contributions to the specific heat. When, as in the present case, a series of isomorphous compounds is studied, the determination of the lattice specific heat will be even more reliable.

It has been found so far that all compounds of the series are antiferromagnets with a two-dimensional character, except for the Cu(II) complex. The Co(II) and Fe(II) complexes both possess a ground state with an effective $S' = \frac{3}{2}$. Their $T_N$ values are 5.70 K and 8.46 K respectively. For the Ni(II) and Mn(II) complexes these quantities are found to be 10.2 K and 3.29 K respectively. In contrast to the above mentioned group of four compounds, the Cu(II) complex appears to behave like a two-dimensional $S = \frac{1}{2}$ Heisenberg ferromagnet, with $T_N \approx 0.8 \text{ K}$ [18].

References