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Structure and Magnetic Behavior of a New Two-Dimensional Antiferromagnetic Manganese(II)−μ-1,3-Azido System

Albert Escuer,[*,†] Ramon Vicente,[†] Mohamed A. S. Goher,[*,‡] and Franz A. Mautner[§]

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain, Department of Chemistry, Faculty of Science, Alexandria University, Alexandria 21321, Egypt, and Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, A-8010 Graz, Austria

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In this work we present the synthesis, X-ray crystal structure determination, and magnetic behavior of the two-dimensional compound $[\mathrm{Mn(4acpy)_2(N_3)_2}]_n$, (4acpy = 4-acetylpyridine) in which the coordination mode of the azido ligand is end-to-end. The susceptibility measurements for $[\mathrm{Mn(4acpy)_2(N_3)_2}]_n$ are indicative of a moderate antiferromagnetic coupling. EPR and susceptibility data are indicative of magnetic ordering below 28 K. It is relevant to note that these magnetic measurements are the first ones for the manganese−azido(end-to-end) system.

Recently, there has been a growing interest in the synthesis of new magnetic materials of high dimensionality built from inorganic coordination complexes. By using good superexchange bridging groups such as oxalate or cyanide, extended lattices of antiferromagnetic or ferrimagnetic systems which show magnetic order at low temperatures have been achieved.[1] From the point of view of the design of new magnetic systems, the bridging azido ligand shows two key properties: it is a good superexchange pathway (ferromagnetic systems for the end-on coordination and antiferromagnetic for end-to-end coordination) and it frequently leads to nontrivial systems with nuclearity greater than 2. The copper-azido system has been exhaustively studied from synthetic and magnetic points of view,[2] and recently, studies of polynuclear,[3] monodimensional,[4] and bidimensional[5] nickel−azido systems have been reported. At the present, magnetic studies on the manganese−azido-bridged systems have been performed only for the dinuclear compound[6] $(\mu\text{-1,1-N}_3)[\mathrm{Mn(terpy)}]_2\cdot\mathrm{H_2O}$, which shows ferromagnetic coupling ($J/k = +3.5$ K), following the general trends found for analogous Cu(II) and Ni(II) 1,1-azido systems.

$[\mathrm{Mn(4acpy)_2(N_3)_2}]_n$ was prepared by addition of an aqueous solution of sodium azide to an ethanol/water solution of 4-acetylpyridine and $\mathrm{MnCl_2\cdot H_2O}$. The final clear solution was kept in the dark for several days to produce the complex as light yellow crystals. Anal. Calcd (found): C, 44.23 (44.1); H, 3.73 (3.7); N, 29.25 (29.4); Mn, 14.60 (14.3).

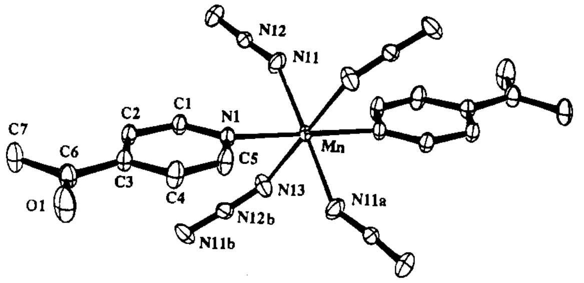

Figure 1. ORTEP diagram with 50% probability ellipsoids and atom-labeled scheme for $[\mathrm{Mn(4acpy)_2(N_3)_2}]_n$.

The structure of the title compound[7] shows that each manganese atom is octahedrally coordinated to four azido ligands and two molecules of 4-acetylpyridine in *trans* arrangement (Figure 1). Each of the four azido ligands bridges two manganese atoms in end-to-end fashion. The Mn atom lies on a crystallographic inversion center. The main bond parameters that involves the manganese coordination polyhedron are as follows: Mn−N(11) 2.192(3) Å, Mn−N(13) 2.214(3) Å, Mn−Mn' 5.997(2) Å, Mn−N(11)−N(12) 151.6(2)°, Mn−N(13)−N(12b) 129.0(2)° and Mn−N3−Mn torsion angle 81.9(2)°. The Mn−N(1) (N atom in pyridine) is 2.291(3) Å. From repetition of this basic unit, the structure consists of a 2D polymer as it is shown in Figure 2A. As a consequence of the long distance between manganese ions in neighboring layers, (minimum interlayer Mn−Mn distance of 11.563(5) Å), the interactions between these atoms can be expected to be completely negligible at high temperature, giving a good example of a local $S = {}^5/_2$ two-dimensional magnetic system.

Taking the widely studied $\mathrm{K_2MnF_4}$ compound as an example,[8] the coordination polyhedra of the Mn atoms show a common apex, and the 4.2 Å Mn−Mn intralayer distance is twice the Mn−F bond distance. $[\mathrm{Mn(4acpy)_2(N_3)_2}]_n$ shows the same connectivity of the 2D lattice with the apex linked by end-to-end azido bridges, which isolates the $\mathrm{MnN_6}$ polyhedra, as is shown in Figure 2B. For the title compound the intralayer Mn−Mn distance is on the order of 6 Å.

Variable temperature solid-state magnetic susceptibility and EPR studies were performed on powdered samples from 290

[†] Universitat de Barcelona.

[‡] Alexandria University.

[§] Technische Universität Graz.

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(7) X-ray structure analysis: STOE four circle diffactometer, μ(Mo Kα 0.79 mm^{-1}, graphite monochromator, $T = 300$ K, Lorentz and polarization corrections (empirical) were made. Data, collection, and refinement: $\bar{\omega}$-scan, solved by direct methods. Anisotropic displacement parameters were only applied to the non-hydrogen atoms in full-matrix least-squares refinements. The H-atoms were included in the final refinement cycles on calculated positions. The programs DIFABS, SHELX-76, SHELX-86, PLATON, and THE XRAY SYSTEM were used for computations. $\mathrm{C_{14}H_{14}MNN_8O_2}$, ($M = 381.26$), monoclinic, space group $P2_1/a$, $a = 8.558(4)$ Å, $b = 8.403(3)$ Å, $c = 11.563(5)$ Å, $\beta = 92.97(3)°$, $V = 830.5(6)$ Å^3, $Z = 2$, $D_{\mathrm{calc}}/D_{\mathrm{obs}} = 1.524/1.53$ g/cm^3, crystal size 0.6 × 0.4 × 0.13, 1450 reflections with $F_o > 3\sigma F_o$, 131 parameters, $R = 0.042$, $R_{\varpi} = 0.042$. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K., on quoting the full journal citation.

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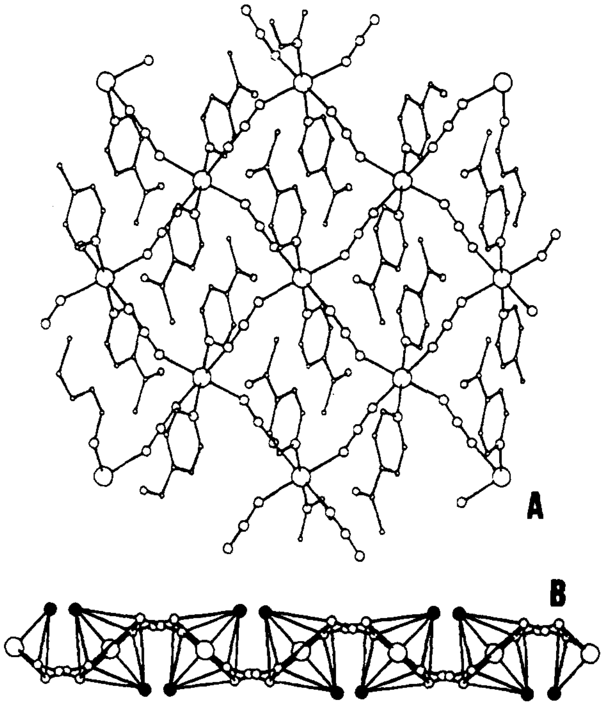

Figure 2. (A) View of a sheet of $[Mn(4acpy)_2(N_3)_2]_n$ along [001] axis. (B) [100] projection of the upper sheet of $[Mn(4acpy)_2(N_3)_2]_n$ showing the coordination octahedra of the manganese atoms linked by azido ligands. Atoms in black correspond to the N atoms of the 4-acetylpyridine ligand.

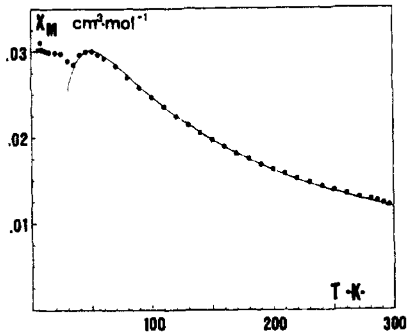

Figure 3. χ_M *vs* T plot for $[Mn(4acpy)_2(N_3)_2]_n$. The solid line shows the best fit obtained (see text). Deviation at low temperatures is due to the long range order of the compound.

to 4 K. The antiferromagnetic interaction is evident from the susceptibility data (Figure 3). The χ_M value increases when temperature decreases reaching a maximum at $T_{max} = 51$ K (3.00×10^{-2} cm^3 mol^{-1}), decrease slightly down to 35 K (2.85×10^{-2} cm^3 mol^{-1}) and then returns to a practically constant value close to 3×10^{-2} cm^3 mol^{-1} between 20 and 4 K. The behavior in the low temperature region agrees with the magnetic properties expected for long-range order in a two-dimensional Heisenberg antiferromagnet. For systems of this kind, the isotropic behavior is maintained just to below the maximum of susceptibility, at which point the system becomes strongly anisotropic: the parallel susceptibility tends to zero whereas the perpendicular susceptibility increases slightly, giving a characteristic polycrystalline plot.[9] In our case the T_c is close to 35 K. High temperature susceptibility data have been fitted to the high temperature expansion series of Lines[9] for an $S = {}^5/_2$ antiferromagnetic layer. The best fit is given by the exchange parameters $J = -3.83$ cm^{-1}, $g = 2.00$ with a reliability factor $R = 7.8 \times 10^{-5}$, defined as $\sum(\chi_M{}^{calc} - \chi_M{}^{obs})^2/\sum(\chi_M{}^{obs})^2$. This coupling between paramagnetic centers placed at distances close to 6 Å demonstrates the good superexchange pathway provided by the azido ligand. For the nickel(II)–azido system, in which the magnetically active atomic orbitals are restricted to d_{z^2} and $d_{x^2-y^2}$, some of the authors have reported[4] a good correlation between the Ni–N–N bond angles and Ni–N–N–N–Ni torsion angles with the superexchange parameter J. This model predicts a negligible coupling for a torsion angle close to 90°, but the relatively strong coupling observed in this manganese compound illustrates the important role of the t_{2g} orbitals of the manganese in the magnetic coupling. The previous model should be extended in the future to explain the magnitude of the coupling in this new system.

The room temperature EPR spectrum shows a sharp intense isotropic signal centered at $g = 2$, (peak-to-peak line width 26 G). Variable temperature spectra show that the peak-to-peak line width is strongly dependent on the temperature,[10] increasing from 100 K down to 28 K, at which temperature the compound abruptly becomes silent to EPR. The line width at 28 K is close to 400 G. This line width is low in comparison with those reported for compounds such as K_2MnF_4,[10] as a probable consequence of the large Mn–Mn distance which minimizes the dipolar interactions in the layers.

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Supporting Information Available: Text giving details of the structure determination and tables of crystallographic data, complete bond lengths and angles, atom coordinates, thermal parameters, and hydrogen atom coordinates (6 pages). Ordering information is given on any current masthead page.

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