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Characterization of the Antiferromagnetism in Ag(pyz)$_2$(S$_2$O$_8$) (pyz = Pyrazine) with a Two-Dimensional Square Lattice of Ag^{2+} Ions

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The chemistry of 4d ion Ag^{2+} (4d^9, $S = {}^1/_2$) differs considerably from that of its 3d analogue Cu^{2+} (3d^9, $S = {}^1/_2$) in that, contrary to the case of Cu^{2+}, coordination compounds of Ag^{2+} are generally unstable in solution and in the solid state unless the ion is protected against reduction to Ag$^+$ (4d^{10}, $S = 0$) by suitable ligands.[1] Numerous two-dimensional (2D) antiferromagnets of Cu^{2+} ions exist, but there is no proven 2D antiferromagnet of Ag^{2+} ions. Lewis bases such as pyridine (py),[2] 2,2′-bipyridine (2,2′-bipy),[2] and 1,4,8,11-tetraazacyclotetradecane[3] are known to stabilize Ag^{2+} ions in the solid state. Ag(py)$_4$(S$_2$O$_8$) apparently consists of square planar Ag^{2+} ions surrounded by the nitrogen atoms of four py ligands although it is unclear whether the S$_2$O$_8$$^{2-}$ anion is also coordinated.[2] A promising candidate for a 2D antiferromagnet of Ag^{2+} ions is Ag(pyz)$_2$(S$_2$O$_8$) (pyz = pyrazine)[4] reported nearly four decades ago. The magnetic properties of this compound measured above 83 K indicated an antiferromagnetic (AFM) exchange interaction, and its IR spectrum suggested the presence of square-planar Ag^{2+} cations linked through pyz ligands. In this communication we show that Ag(pyz)$_2$(S$_2$O$_8$) is indeed a 2D antiferromagnet on the basis of the crystal structure determination, magnetic property measurements, and density functional theory (DFT) electronic structure calculations.

Dark red-brown Ag(pyz)$_2$(S$_2$O$_8$) was synthesized in nearly quantitative yield using the procedure described in ref 4. The IR spectrum of the resulting product reproduced the previously reported data.[4] The crystal structure of Ag(pyz)$_2$(S$_2$O$_8$) was determined by combining synchrotron X-ray powder diffraction with *ab initio* methods (see Figure S1).[5] The crystal structure of Ag(pyz)$_2$(S$_2$O$_8$) differs from the postulated one[4] in that it consists of octahedral AgN$_4$O$_2$ units that are linked by bridging pyz and S$_2$O$_8$$^{2-}$ to form a three-dimensional (3D) network.

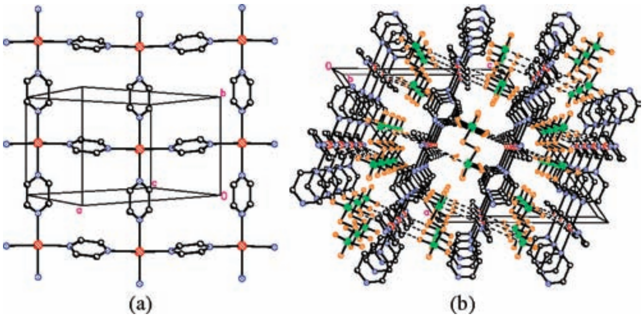

Figure 1. Crystal structure of Ag(pyz)$_2$(S$_2$O$_8$): (a) 2D square sheet made up of Ag^{2+} ions and pyz ligands. (b) 3D network made up of [Ag(pyz)$_2$]$^{2+}$ sheets and (S$_2$O$_8$)$^{2-}$ ions with dashed lines indicating long Ag1−O1 bonds. Hydrogen atoms have been omitted for clarity. Atoms correspond as follows: red = Ag, blue = N, black = C, yellow = O and green = S.

Each Ag^{2+} cation is equatorially coordinated to four N-donor atoms from pyz ligands [Ag−N1a = 2.239(9), Ag−N1b = 2.230(7) (×2), and Ag−N2a = 2.253(9) Å] and two axial O-atoms from the S$_2$O$_8$$^{2-}$ anion at much longer distances of 2.62(3) Å. Thus, each Ag(pyz)$_2$O$_2$ layer of Ag(pyz)$_2$(S$_2$O$_8$) is made up of corner-sharing axially elongated AgN$_4$O$_2$ octahedra. The Ag−N bond distances observed in Ag(pyz)$_2$(S$_2$O$_8$) agree with those found in related systems, e.g., Ag(2,2′-bipy)$_2$(NO$_3$)$_2$[2] and Ag(L_4)(NO$_3$)$_2$ (L = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclo-tetradecane).[6] Another Ag^{2+} compound, (1,4,7,10,13,16-hexathiacyclooctadecane)-silver(II) perchlorate, shows a trigonal distortion of the AgS$_6$ chromophore.[7] The AgN$_4$O$_2$ octahedron of Ag(pyz)$_2$(S$_2$O$_8$) is distorted such that the N−Ag−N′ bond angles deviate slightly from 90° [88.2(2)°−91.8(2)°] whereas the O−Ag−N and O−Ag−O′ bond angles are 80.5(3)° and 161.0(7)°, respectively, which deviate significantly from their ideal angles of 90° and 180°, respectively. The molecular structures of the pyz ligand[8,9] and the S$_2$O$_8$$^{2-}$ anion[10] agree well with those observed in other compounds.

Ag(pyz)$_2$(S$_2$O$_8$) consists of 2D square nets (Figure 1a) in which AgN$_4$O$_2$ octahedra are linked through pyz bridges with Ag−pyz−Ag distances of 7.11(2) and 7.15(2) Å along the (−101) and (010) directions, respectively. These 2D nets pack approximately along the (201) direction and are linked by bridging S$_2$O$_8$$^{2-}$ anions to form a 3D polymeric network (Figure 1b).

Isofield and isothermal magnetization measurements were carried out for a polycrystalline sample of Ag(pyz)$_2$(S$_2$O$_8$) using vibrating sample magnetometry and pulsed-field techniques.[11] Our results are shown in Figure 2a. The magnetic susceptibility χ vs T gradually increases as the temperature is lowered, reaching a broad maximum at $T_{\max} = 49$ K. The relatively high $T_{\max}$ value suggests the presence of significant AFM interactions in each 2D square lattice of Ag^{2+} ions. A least-squares fit of $1/\chi$ vs T in the region $150 \leq T \leq 300$ K to a Curie−Weiss law led to $g = 2.011(1)$ and $\theta = -66.8(1)$ K, which signifies a dominant AFM interaction between adjacent Ag^{2+}

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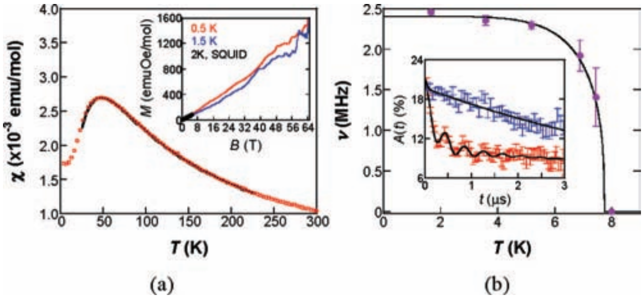

(a) (b)

Figure 2. (a) χ vs T (○) for polycrystalline Ag(pyz)$_2$(S$_2$O$_8$) using a probe field of 0.1 T where the solid line (—) represents the result of the QMC simulation. Inset: Magnetization measured at 0.5, 1.5 (pulsed fields) and 2 K (SQUID). (b) T-evolution of the single muon precession frequency ν. Inset: Muon decay asymmetry $A(t)$ measured at 1.7 (red) and 10 K (blue).

magnetic moments. To quantitatively extract the spin exchange coupling constant J_{2D} for the 2D square lattice, we performed a quantum Monte Carlo (QMC)[12] simulation of χ vs T for $H = J\Sigma S_i \cdot S_{i+1}$. As shown by the solid line in the main plot of Figure 2a, the simulation agrees very well with the experiment for $20 \leq T \leq 300$ K with $g = 2.0$ and $J_{2D} = 53$ K (under the convention in which a positive spin exchange parameter implies AFM spin exchange). This J_{2D} value is consistent with the value 52.4 K calculated from the expression $J = 1.07 \cdot T_{max}$ for the 2D square-lattice Heisenberg antiferromagnet with $T_{max} = 49$ K and $S = {}^1/_2$.[13] Note that J_{2D} for Ag(pyz)$_2$(S$_2$O$_8$) is significantly greater than those reported for related Cu^{2+} polymers including [Cu(HF$_2$)(pyz)$_2$]BF$_4$ and Cu(ClO$_4$)$_2$(pyz)$_2$.[8,9] The χ vs T data show no indication for 3D magnetic order down to 2 K. Pulsed field $M(B)$ measurements made at 0.5 and 1.5 K (Inset of Figure 2a) show a concave curvature as B rises to 64 T, indicating an effective 2D spin dimensionality of Ag(pyz)$_2$(S$_2$O$_8$).[11] Using eq 2 of ref 11, we estimate the saturation field B_c to be 160 T.

As discussed above, Ag(pyz)$_2$(S$_2$O$_8$) consists of 2D square lattices of Ag^{2+} ions and is a 2D antiferromagnet. Note that 2D square lattices of Ag^{2+} ions are also present in the 2D ferromagnet Cs$_2$AgF$_4$.[14] In the AgF$_4$ layers of Cs$_2$AgF$_4$, however, the corner-sharing AgF$_6$ octahedra are axially compressed [Ag−F$_{eq}$ = 2.291 (×4) Å and Ag−F$_{ax}$ = 2.129 (×2) Å],[14] which is responsible for the ferromagnetic spin exchange between adjacent Ag^{2+} ions.[15]In the CuO$_4$ layers of the representative 2D antiferromagnet La$_2$CuO$_4$, the corner-sharing CuO$_6$ octahedra are axially elongated with the Cu $d_{x^2-y^2}$ orbital being magnetic.[15] By analogy, it is expected that the magnetic orbital of each Ag^{2+} ion in Ag(pyz)$_2$(S$_2$O$_8$) is the Ag $d_{x^2-y^2}$ orbital, and so the spin exchange between adjacent Ag^{2+} ions is AFM. This expectation is borne out from our first principles DFT electronic band structure calculations for Ag(pyz)$_2$(S$_2$O$_8$) (see section 4 of the Supporting Information).

Finally, we examine if 3D magnetic ordering takes place in Ag(pyz)$_2$(S$_2$O$_8$) on the basis of zero-field (ZF) muon-spin relaxation (μ^+SR) measurements. As shown in the inset of Figure 2b, the time dependence of the muon polarization, i.e., the muon decay asymmetry $A(t)$,[17] exhibits oscillations below ~8 K, which indicates that Ag(pyz)$_2$(S$_2$O$_8$) undergoes a transition to 3D magnetic order throughout its bulk.

The extracted frequency ν as a function of temperature is shown in Figure 2b. A power-law fit of the temperature dependence of ν leads to the 3D magnetic ordering temperature $T_N = 7.8(3)$ K. For $T > 8$ K, the observed $A(t)$ spectra show Gaussian relaxation, which is characteristic of the muon ensemble experiencing a static, random array of local magnetic fields.

The low value of $T_N/J = 0.15$ demonstrates that the interlayer interactions are very weak. With this measured value of T_N/J we can use a standard expression for the 2D square lattice Heisenberg antiferromagnet[18] to estimate that the magnetic correlation length at T_N is $\sim 10^3$ lattice spacings, showing that a very large correlated region of spins needs to form before three-dimensional order switches on, larger than is found in the prototypical 2D square lattice Heisenberg antiferromagnet Sr$_2$CuO$_2$Cl$_2$.[19]

To summarize, Ag(pyz)$_2$(S$_2$O$_8$) consists of 2D square nets of Ag^{2+} ions resulting from the corner-sharing of axially elongated AgN$_4$O$_2$ octahedra and, in accord with its structure, exhibits characteristic 2D antiferromagnetism. μ^+SR measurements indicate that the material undergoes 3D magnetic ordering below 7.8(3) K, thus implying that there are weak interlayer spin exchange interactions as mediated by the bridging S$_2$O$_8$$^{2-}$ ligands.

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Supporting Information Available: Figures S1−S5, Table S1, and Experimental and Computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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