Silver(II)

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Strong One-Dimensional Antiferromagnetic Interactions of Silver(II) Ions in Silver Sulfate

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The search for new compounds that contain elements in unusual oxidation states is worthwhile, since these compounds often exhibit novel and unconventional chemical and physical properties, for example, those observed in the superconducting $Cu^{II,III}$ oxides.[1] The dominant oxidation state of Ag is +1 and only a few compounds with Ag in higher oxidation states have been synthesized to date. The situation is different for the other coinage metals, in that Cu, the lighter homologue of Ag, can easily adopt the oxidation state +2, whereas the heavier homologue Au is mainly found with the oxidation state +3. Ag^{2+} forms stable complexes with a variety of nitrogen donor ligands, such as pyridine[2] or pyrazine (pyz).[3] Other examples of Ag^{II} compounds are the binary fluoride AgF_2 and its complex salts, for example, Cs_2AgF_4,[4] which has recently attracted great interest since it orders ferromagnetically at low temperatures.[5] Among fluorides, even higher oxidation states of Ag are known, for example, Ag^{3+} and Ag^{4+} in $KAgF_4$[6] and Cs_2AgF_6,[7] respectively. Oxides containing Ag in an oxidation state higher than +1 are very rare. The binary compound AgO is not a Ag^{II} compound, but the diamagnetic mixed-valent compound $Ag^{I}Ag^{III}O_2$.[8] Ag_3O_4 is also a mixed-valent compound as indicated by the formula $Ag^{II}Ag^{III}{}_2O_4$,[9] whereas Ag_2O_3 contains only Ag^{3+} ions.[10]

Malinowski et al.[11] recently reported the synthesis of black $AgSO_4$, which has been obtained by a methathetic reaction of $Ag(SbF_6)_2$ + K_2SO_4 in anhydrous HF at around −80 °C or by the reaction of AgF_2 with H_2SO_4 at −35 °C. According to thermoanalytical studies, the product is metastable and decomposes above 120 °C with evolution of O_2. The triclinic crystal structure of $AgSO_4$ contains planar rectangular AgO_4 units that are connected by SO_4 tetrahedra to form a three-dimensional network (Figure 1). The Ag–O distances within the AgO_4 units range from 2.09 Å to 2.20 Å,[12] as expected for a four-coordinate Ag^{2+} ion,[9] thus suggesting that $AgSO_4$ is indeed a complex Ag^{II} oxide. The two $Ag(1)O_4$ and $Ag(2)O_4$ units are significantly elongated along the twofold axes with O–O distances of 2.62 Å and 2.70 Å for the short edges and 3.30 Å and 3.34 Å for the long edges, respectively. The structural chemistry of the 4d ion Ag^{2+} ($4d^9$, $S = 1/2$) differs considerably from that of its 3d and 5d analogues Cu^{2+} ($3d^9$, $S = 1/2$) and Au^{2+} ($5d^9$, $S = 1/2$). This difference is most obvious when the sulfates are compared. The Ag^{2+} ions in $AgSO_4$ display a rectangular coordination of O atoms, whereas the smaller Cu^{2+} ions in $CuSO_4$ exhibit a distorted octahedral coordination;[13] it is clear that the Jahn–Teller effect is stronger for Ag^{2+} than for Cu^{2+}. In the structure of $AuSO_4$, diamagnetic Au–Au dumbbells with short Au–Au distances of 249 pm are found,[14] thus reflecting the increasing tendency for the occurrence of metal–metal bonding down a group of transition metals.

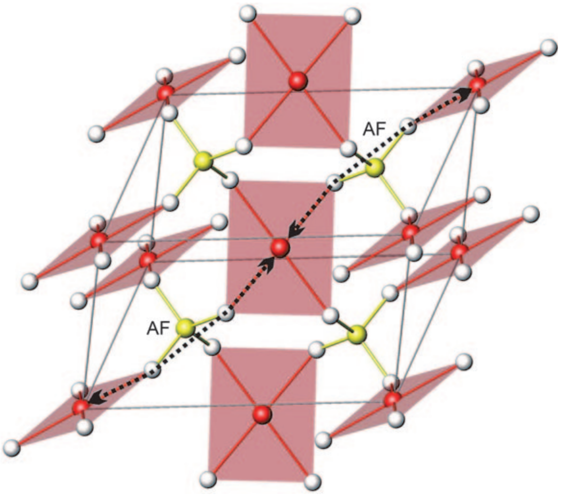

Figure 1. Perspective view of the crystal structure of $AgSO_4$. Ag, S, and O atoms are represented as red, yellow, and gray spheres, respectively. The coordination spheres around Ag and S are graphically emphasized. The path for the 1D antiferromagnetic interaction (AF) in $AgSO_4$ along one distinct diagonal of the triclinic unit cell is indicated by dotted lines.

$AgSO_4$ is also interesting because of its distinct physical properties. IR spectra show that $AgSO_4$ has a band gap of 0.18 eV, and spin-polarized DFT calculations result in nearly the same value for one kind of spin. In contrast, the band gap of $CuSO_4$ calculated in a comparable way is more than ten times larger, namely 2.3 eV.[11] Measurements of the temperature-dependent magnetic susceptibility indicate that the Ag^{2+} ions ($4d^9$, $S = {}^1/_2$) in $AgSO_4$ are strongly antiferromagnetically coupled to the chains within the 3D structure. A fit

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of the data with the so-called Bonner–Fisher model[15] resulted in a very high J value of 217 K for the magnetic superexchange, similar to that observed for various 1D derivatives of Cu^{2+} [16] and the 2D square lattice Heisenberg antiferromagnet $Ag(pyz)_2(S_2O_8)$.[17] For comparison, anhydrous $CuSO_4$ also orders antiferromagnetically below 36 K, however, in this case, the ordering is not low-dimensional.[5] The magnetic exchange path in $AgSO_4$ can take place only through the coupling of two neighboring Ag^{2+} ions through the O–O edges of the SO_4 groups along one of the diagonals of the triclinic unit cell (see Figure 1), since all the angles in the corresponding Ag-O-O-Ag-O-O… chain are close to 180°, which is a requirement for antiferromagnetic interactions. Along all the other chains of AgO_4 units bridged by SO_4 groups, such as along the other diagonals of the unit cell, the Ag-O-O angles are closer to 90° than to 180°. The magnetic exchange path was confirmed by spin-polarized density functional theory calculations using the GGA + U method. The calculated magnetic moments on the Ag atoms in $AgSO_4$ (ca. 0.4 μ_B) are much smaller than those calculated for the Cu atoms in $CuSO_4$ (0.80 μ_B), which likely arises from the fact that the spin density is distributed to a larger extent over the O atoms in $AgSO_4$ as compared to $CuSO_4$.

To summarize, the new Ag^{II} sulfate $AgSO_4$ does not only exhibit an unusual structure with square-planar $[AgO_4]^{6-}$ units, but also shows characteristic 1D antiferromagnetism. The superexchange of the Ag^{2+} ions in title compound can thus be viewed as extraordinarily strong. As suggested by the authors, it would be interesting to investigate partially chemically doped systems based on $AgSO_4$ or the possibility of pressure-induced metallization of $AgSO_4$, especially with respect to the discovery of potential new superconducting materials.

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