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Articles

The Compressed Tetragonal CuF_6^{4-} Complex in $KAlCuF_6$: An Angular Overlap Treatment of the Electronic Structure and Magnetic Exchange Coupling

**Michail Atanasov,[†] Michael A. Hitchman,[*,‡] Rudolf Hoppe,[§] Keith S. Murray,[‖]
Boujemaa Moubaraki,[‖] Dirk Reinen,[⊥] and Horst Stratemeier[‡]**

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria, Chemistry Department, University of Tasmania, Box 252C, Hobart, Tasmania 7001, Australia, Institut für Anorganische Chemie, Justus-Liebig Universität, Heinrich-Buff-Ring 58, D-6300, Giessen, Germany, Chemistry Department, Monash University, Clayton, Victoria 3168, Australia, and Fachbereich Chemie and Zentrum für Materialwissenschaften, Philipps Universität, Hans-Meerwein Strasse, D-3550 Marburg, Germany

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The electronic spectrum and temperature dependence of the magnetic susceptibility of powdered $KAlCuF_6$ is reported and shown to be consistent with the compressed tetragonal geometry of the CuF_6^{4-} groups in this compound. Angular overlap bonding parameters are derived and used to estimate the magnetic coupling between the Cu^{2+} ions, which are linked in chains via the axial fluoride ligands. Good agreement is obtained with the observed exchange coupling constant $J = -60$ cm^{-1}, and it is shown that this coupling is expected to be strongly dependent on the CuFCu bridging angle.

I. Introduction

The compound $KAlCuF_6$ is unusual in containing a copper(II) ion with a compressed tetragonal coordination geometry.[1] Such a geometry has been reported previously for other mixed copper(II) fluorides, for instance K_2CuF_4,[2] but subsequent investigations[3–5] showed that here each copper is in fact surrounded by the more normal elongated tetragonal array of fluoride ligands. The ferromagnetic behavior of K_2CuF_4 at low temperature is also consistent with an elongated octahedron.[6] The compressed tetragonal geometry of the CuF_6^{4-} units in $KAlCuF_6$ has been confirmed by a study of the $^2E(xz, yx) \leftarrow {}^2A(z^2)$ electronic transition[7] and the purpose of the present work is to extend these studies by measuring the electronic spectrum of the compound over the complete visible and near-infrared range, as well as its magnetic behavior and EPR spectrum. The magnetic properties are of particular interest, since the Cu^{2+} ions are linked via the axial fluoride ligands, which—because of the $^2A(z^2)$ ground state—should provide a ready pathway for magnetic superexchange.

II. Experimental Section

The preparation and characterization of $KAlCuF_6$ has been described previously.[1]

Electronic reflectance spectra were measured at room temperature and ~5 K against a standard of freshly sintered MgO using a Zeiss PMQ II spectrophotometer. The extent of diffuse reflexion was transformed into intensity data log (k/s) (k and s being absorption and scattering coefficients, respectively) using the theory of Kubelka-Munk. EPR spectra were recorded both with a Varian spectrometer at Q-band frequency, at 298 and ~130 K, and with a Bruker X-band spectrometer at 298 and 4.2 K. The magnetic susceptibility was measured using a Quantum Design Model MPMS SQUID magnetometer at a field of 1 T. The sample was contained in a calibrated gelatin capsule, loaded in a nitrogen-filled glovebag, and transferred rapidly to the sample chamber of the instrument.

III. Results and Discussion

A. The Geometry of the CuF_6^{4-} Polyhedra. The Cu^{2+} ion in $KAlCuF_6$ (space group *Pnma*) is situated 0.10 Å above a planar array of four fluoride ions[1] at bond distances of 2.123 Å, with much shorter axial bonds to slightly inequivalent fluoride ions (Cu–F(1,1′): 1.875, 1.881 Å) which bridge two copper(II) ions forming a kinked chain (Figure 1). The copper site symmetry is C_s.

The equatorial F^- ligands have only Al^{3+} neighbors. The FCuF angles involving the more distant fluoride ions deviate substantially from 90°, one being 120° and the remaining three 80°. One axial Cu–F bond is approximately normal to the plane containing the longer Cu–F bonds, while the second axial Cu–F bond is bent by ~10° from the normal to this plane toward the bisector (x axis) of the 120° FCuF angle. The Cu^{2+} ion is thus surrounded by a highly distorted compressed tetragonal array of fluoride ions. The structure is of the pyrochlor-type, modified by an ordered distribution of Al^{3+} and Cu^{2+} over the octahedral sites and a significant local distortion of the CuF_6 polyhedra. The unit cell parameters are indeed close to those of the cubic structure, as may be seen if a and b are multiplied by $\sqrt{2}$ (a = 6.73 Å, b = 7.04 Å, c = 9.79 Å).

Since, as far as we are aware, $KAlCuF_6$ is the only example of a copper(II) compound involving just one ligand type in which the Jahn–Teller distortion unambiguously takes the particular form of an axial compression,[8] it is of interest to consider how

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[†] Bulgarian Academy of Sciences.
[‡] University of Tasmania.
[§] Justus-Liebig Universität.
[‖] Monash University.
[⊥] Philipps Universität.

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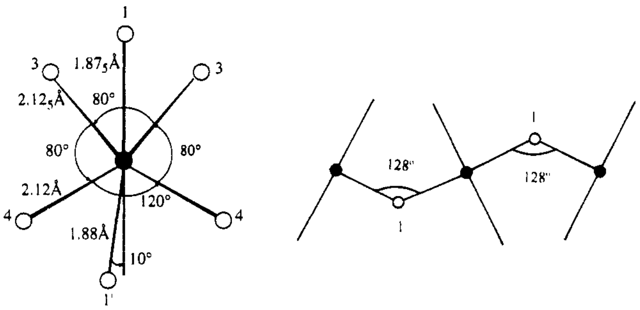

Figure 1. Local geometry of the CuF_6 polyhedron in $KAlCuF_6$ (left) and illustration of the interconnection between these polyhedra via the F(1) and F(1′) ligands (right). The molecular *z* axis follows the Cu–F(1) bond direction, while the *x* axis bisects the F(4)–Cu–F(4) angle.

the geometry compares with that in a typical compound exhibiting the more usual tetragonally elongated geometry. The radial distortion parameter ρ, defined in eq 1 with Δr_i being the deviations

$$\rho = \{2(\Delta r_x^2 + \Delta r_y^2 + \Delta r_z^2)\}^{1/2} \qquad (1)$$

of the Cu–F spacings from the average (2.04 Å), is 0.285 Å, which is significantly smaller than that of the elongated octahedra in K_2CuF_4, for example (0.38 Å). Comparison with the ZnF_6 polyhedron in cubic $KAlZnF_6$ [1.94 Å (F(1)), 1.96 Å (F(2)), 2.06 Å (F(3)), 2.11 Å (F(4))], which possesses a similar but distinctly less compressed geometry (ρ = 0.165 Å[9]) suggests that a significant linear vibronic coupling occurs in the copper compound. The deviations from a regular octahedral geometry observed in the Zn–F distances suggest that lattice strain effects favor a compressed tetragonal coordination in $KAlCuF_6$. It has been proposed[10] that a strain of this kind stabilizes such a geometry for the CuF_6^{4-} guest complexes formed when Cu^{2+} is doped into K_2ZnF_4[11] and Ba_2ZnF_6.[12] Higher order vibronic coupling terms, which include the $4s-3d_{z^2}$ interaction, are small for ionic fluorides and can easily be dominated by lattice strain effects.[8] Despite the fact that the deviation of the CuF_6 geometry from D_{4h} symmetry is rather large, we believe that the above interpretation is valid, and the AOM calculations described below support this conclusion. Though the thermal ellipsoids of the fluoride ions provide no definite indication of this,[1] it cannot be excluded that a bond length difference in the plane of the long Cu–F spacings may be present, possibly as a dynamic effect at room temperature. There are examples where only the average ligand position has been revealed by an X-ray structure determination, due to the relatively small scattering power of the anions.[10] An underlying orthorhombic distortion component of this kind would enhance the ρ parameter.

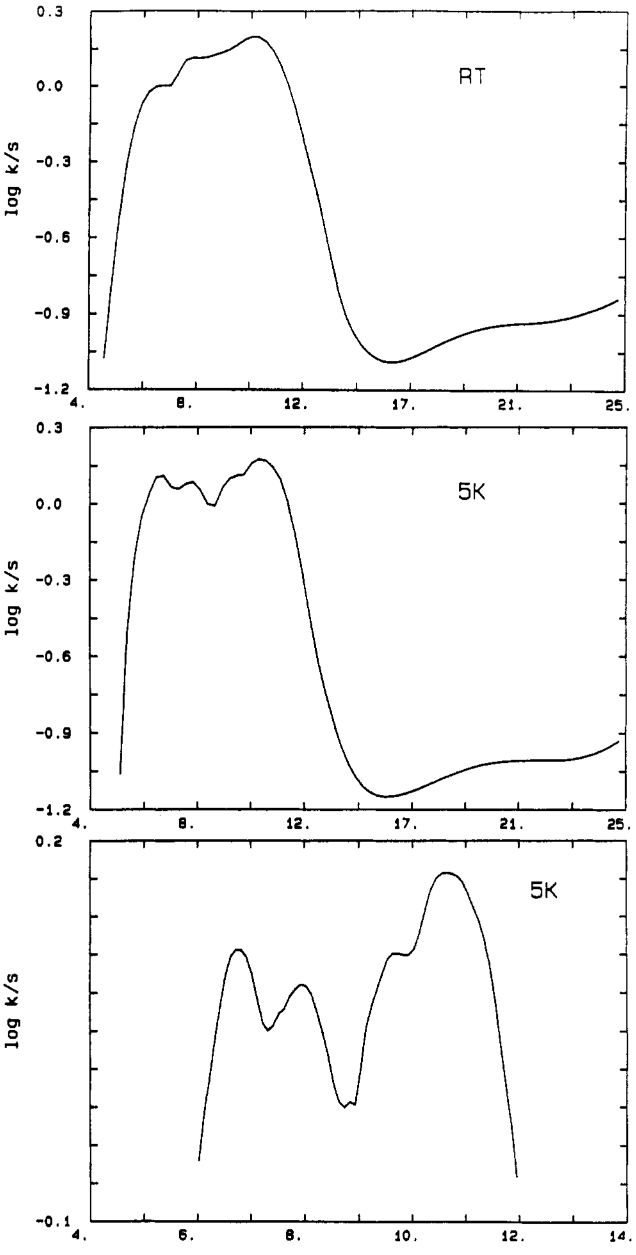

Figure 2. Diffuse reflectance spectra of $KAlCuF_6$ at room temperature (RT) and 5 K. The latter spectrum is also shown in higher resolution.

B. Electronic Spectrum and metal-ligand Bonding Parameters. The electronic reflectance spectrum of $KAlCuF_6$ over the range 5000–25 000 cm^{-1} at room temperature and ~5 K is shown in Figure 2. As expected for a system lacking an inversion center, the intensity does not alter significantly with temperature. At low temperature, a pair of bands centered at 6700 and 8100 cm^{-1} are resolved, together with a band centered at 10 800 cm^{-1} having a shoulder at ~9400 cm^{-1}. The energies of the two central bands agree well with those reported by Finnie *et al.* (8000 and ~9400 cm^{-1}),[7] which were assigned to transitions to the split components of the ^2E_g state. The band positions are quite similar to those reported for the tetragonally compressed CuF_6^{4-} complexes formed when Cu^{2+} is doped into K_2ZnF_4[4b,13] and Ba_2ZnF_6.[14] In the former, band maxima were observed at ~6000, 8200, 9300, and 10 700 cm^{-1}.[4b,13] It is interesting to note that the lowest energy band was not resolved in the single-crystal spectrum,[13] but was observed in the reflectance spectrum, with an energy that altered from 5200 to 6600 cm^{-1} as the mole fraction of Cu^{2+} increased from 0.01 to 0.40.[4b] The band assignments in $KAlCuF_6$ are expected to be similar to those in the other compressed tetragonal complexes, the lowest energy peak being to the $^2B_{1g}(x^2 - y^2)$ state, the middle pair of bands to the components of the $^2E_g(xz, yz)$ state and the highest energy band to the $^2B_{2g}(xy)$ state. It should be noted that the magnetic interaction present in $KAlZnF_6$ (see following section) is not expected to affect the d–d transition energies significantly—for instance, the electronic spectrum of copper(II) acetate monohydrate is very similar in this region to that of other complexes with analogous local ligand stereochem-

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istries,[15] although the magnetic coupling between the Cu^{2+} ions is considerably greater than that in $KAlZnF_6$. It is possible that the weak absorption maximum at ~19 000 cm^{-1} in the spectrum of $KAlZnF_6$ (Figure 2) is due to a double electron excitation, in which the absorption of one photon excites electrons simultaneously on two Cu^{2+} ions, as it occurs at approximately twice the d–d transition energies and excitations of this kind have been observed in compounds containing magnetically coupled transition metal ions.[16] However, without more detailed evidence, such as could be provided by a single-crystal study using polarized light, such a conclusion is highly speculative.

The transition energies of the complex were calculated using the computer program CAMMAG, developed by Gerloch and co-workers.[17] Here, the metal–ligand interaction is parametrized within the framework of the angular overlap model[18,19] by assigning each independent ligand σ- and π-antibonding parameters e_σ and e_π, the geometry of the complex being defined using the crystal structure of the compound. The small difference in bond length between the axial ligands was ignored and the π-bonding was assumed to be isotropic about the Cu–F bond axis. In the following discussion symmetry labels appropriate to the D_{4h} point group are used.

It is now well established that in complexes of tetragonal symmetry the $a_{1g}(3d_{z^2})$ orbital is depressed in energy compared with simple theoretical predictions. Evidence for such an effect is now available for complexes with tetragonal symmetry ranging from square planar[20b,c] through tetragonally elongated[21] and compressed[11] geometries to those with linear stereochemistry.[22] This effect has been explained alternatively in terms of the interaction of the $a_{1g}(3d_{z^2})$ orbital with the coordination "voids" left when the complex departs from cubic symmetry,[21] or by configuration interaction between this orbital and the copper(II) $a_{1g}(4s)$ orbital.[20] In a copper(II) complex with a compressed tetragonal geometry, the effect is to decrease the energy difference between the $^2A_{1g}$ ground state and the excited $^2B_{2g}$, ^2E_g, and $^2B_{1g}$ states by ΔE_{z^2}). Using an e_σ/e_π ratio of 4, as has been observed in other fluoro complexes,[23] satisfactory agreement with the experimental transition energies is obtained using the following set of bonding parameters, all in cm^{-1}:

$$e_\sigma(z) = 6000,\ e_\pi(z) = 1500,\ e_\sigma(xy) = 2000,\ e_\pi(xy) = 500,\ \Delta E_{z^2} = 1200 \quad (2)$$

An effective spin–orbit coupling coefficient of 700 cm^{-1} was used in the calculation, corresponding to a decrease of 15% from the free ion value, consistent with the covalency deduced from the EPR spectra of the CuF_6^{4-} ion.[11] Variations of the e_σ/e_π ratio to 1:5 and 1:3.5 had relatively little effect on the results. The calculated (observed) transition energies in cm^{-1} were 6950 (6700), 8300 (8100), 9100 (9400), 10 600 (10 800). Calculations were also carried out using an idealized compressed tetragonal geometry, and it was found that the substantial angular distortions have surprisingly little effect on the bonding parameters producing optimum agreement with experiment. Presumably, the substantial opening of one equatorial FCuF angle is counterbalanced by the closing of the opposite angle (Figure 1).

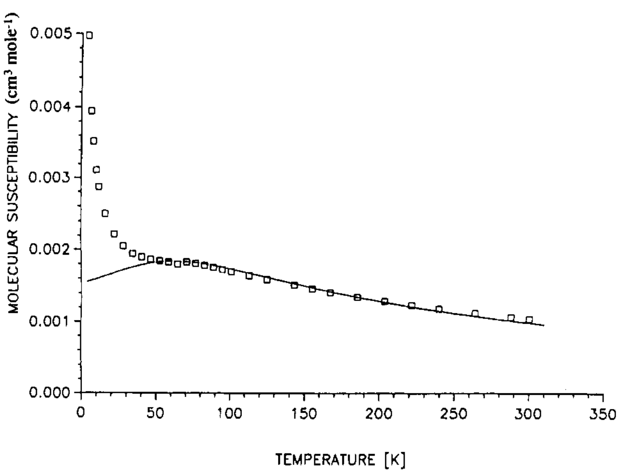

Figure 3. Temperature dependence of the molecular susceptibility. The solid line is the best-fit-calculated using a linear chain model without incorporating a monomer fraction (see text).

The above parameters suggest that the more closely bound axial F^- ions interact with the d-orbitals about 3 times more strongly than the in-plane ligands. Theory predicts[24] that over short changes in the bond length r the d-orbital splitting in an octahedral complex should vary as $\sim r^{-5}$ and this has been confirmed experimentally.[25] Such a relationship suggests that the metal-ligand bonding parameters of the axial fluorides (r = 1.877 Å) should be about double those of the more weakly bound in-plane ligands (r = 2.123 Å). A similar result is obtained when overlap integrals are used to estimate the $e_{\lambda(xy)}/e_{\lambda(z)}$ ratio (λ:σ,π) from the Cu–F bond distances.[26] It thus appears that in $KAlCuF_6$ the metal–ligand interaction changes considerably more steeply than is predicted by the above relationship. However, it must be born in mind that the axial and in-plane ligands are not strictly comparable, since the former bridge to neighboring Cu^{2+} ions, while the latter bond to Al^{3+}. The high positive charge and small size of Al^{3+} may act to reduce the donor-capacity of the in-plane ligands towards copper(II). It is also possible that a dynamic distortion component (see Section IIIA) may lead to an underlying local geometry with Cu–F spacings which differ more markedly than in the 298 K structure.

Calculation of the linear Jahn–Teller coupling constant from the ground state splitting $4E_{JT}$ using the expression[8]

$$E_{JT} = {}^1\!/_2|V_e^{\text{eff}}|\rho \quad (3)$$

yields V_e^{eff} = ~12 000 cm^{-1} Å^{-1}, which is considerably larger than that generally derived for CuF_6 polyhedra (~9000 cm^{-1} Å^{-1}).[8,27] Possibly, the apparent high value of V_e^{eff} is caused by an underestimate of ρ due to an underlying dynamically averaged orthorhombic distortion component, as discussed above.

C. EPR and Magnetic Results. The EPR spectra of three different powder samples of $KAlCuF_6$ were measured at room temperature, 77 and 4.2 K, but only very weak signals were observed. No two samples gave similar signals, so that it seems likely that the resonances were due to trace amounts of impurity. The "EPR silence" is presumably related to the strong antiferromagnetism ($J \cong -60$ cm^{-1}; see below), which indicates significant magnetic interactions along the bent Cu–F(1)–Cu chains (Figure

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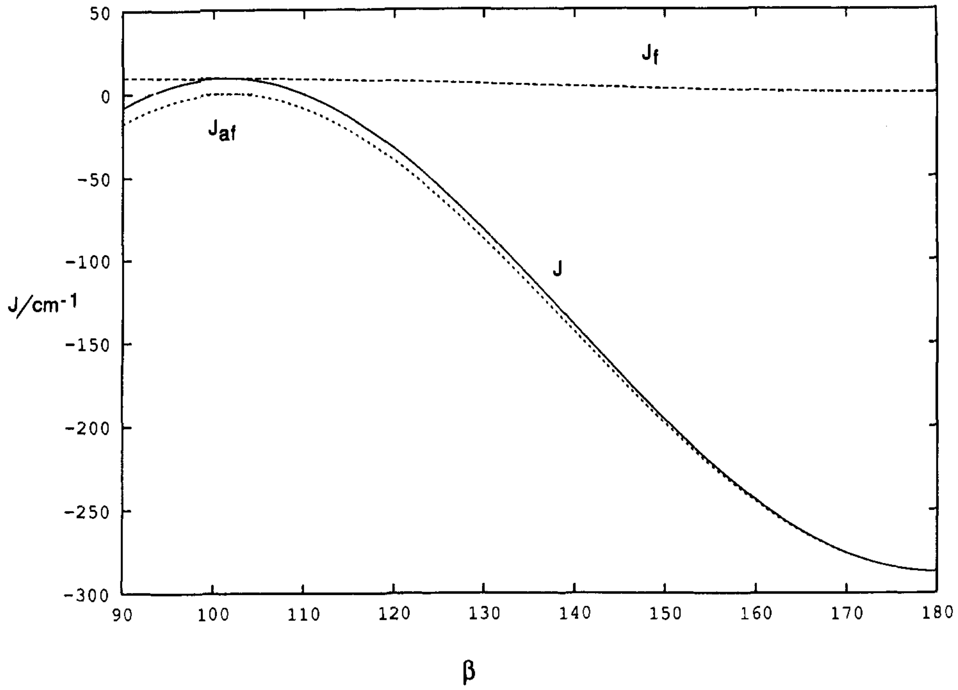

Figure 4. The dependence of the exchange integral J (cm^{-1}) and the ferromagnetic J_f and antiferromagnetic J_{af} components in a Cu^{II}–F–Cu^{II} dimer on the Cu–F–Cu bonding angle β.

1). These interactions are expected both to induce exchange-averaging of the molecular g tensors, and to introduce zero-field splitting effects. However, the situation is somewhat different from that of K_2CuF_4 and Ba_2CuF_6, where internal fields associated with the magnetic ordering lead to unusual EPR spectra at low temperatures[4b,12,28] and the exchange coupling is an order of magnitude smaller. In order to study the local bonding properties an EPR and ligand-field spectroscopic investigation of Cu^{2+} doped $KAlZnF_6$ is in progress.

The magnetic susceptibilities of a powdered sample of $KAlCuF_6$ were measured over the temperature range 4.2–300 K using an applied field of 1 T. As shown in Figure 3, the susceptibility displays a broad maximum at *ca.* 70 K and then increases rapidly below *ca.* 30 K. This rapid increase is probably due to the presence of monomer impurity rather than magnetic ordering. Attempts to fit the data using a simple pairwise Bleaney–Bowers exchange model,[29] incorporating a monomer fraction, were unsuccessful. In particular, the size of χ and the shape of the χ/T plot in the region of χ_{max} were not reproduced when using a J value appropriate to the χ values observed at 300 and at 4.2 K. A Heisenberg linear chain (Fisher[30]) model gave a marked improvement (Figure 3); a monomer fraction was not included in the model but can be estimated to be *ca.* 0.05 by comparison of the χ values at temperatures below 20 K with those expected for a Curie-like Cu^{2+} monomer. The corresponding plot of μ_{eff} against T agrees well with experiment in the region of χ_{max} and diverges only slightly from the observed value in the region 250–300 K. The observed values of the magnetic moment decrease from 1.58 μ_B at 300 K to 0.4 μ_B at 4.2 K. The best-fit parameters were $g = 2.05$ and $J = -60$ cm^{-1}. (N.B. $2J$ is the singlet–triplet splitting.)

D. Magnetic Coupling. It has recently been suggested[31–33] that the AOM may provide a useful method of estimating antiferromagnetic superexchange interactions, and that the interaction will be rather sensitive to the bridging M–L–M angle. The present compound provides a good test of this approach, as the metal ions in the basic dimeric $F_5CuFCuF_5$ unit have just a single unpaired electron in the d_{z^2} orbital pointing at the bridging ligand, with the FCuF bridging angle (128°) deviating substantially from linearity (Figure 1).

Following the superexchange theory of Anderson,[34] the overall exchange constant J of the Heisenberg operator $-2JS_1S_2$ applied to the coupled spins S_1, S_2 is approximated by

$$J = J_{af} + J_f = -2b_{\sigma\sigma}{}^2/U + 2(I/U^2)(b_{\sigma\pi}{}^2 + b_{\pi\sigma}{}^2) \quad (4)$$

Here, J_{af} and J_f are the antiferromagnetic and ferromagnetic contributions, respectively, U is the electrostatic energy difference between the on-site and inter-site Coulomb repulsion and I is the interatomic Hund's exchange integral. The parameters $b_{\sigma\sigma}$ and $b_{\sigma\pi}$, $b_{\pi\sigma}$ are the transfer (hopping) integrals of σ–σ and σ–π type, describing the coupling of the two d_{z^2} orbitals via ligand orbitals in the former case, and of the d_{z^2} orbital on one Cu(II) with the d_{xz} orbital on the other Cu(II) in the latter.[31a] Within a recent parametrization of the AOM for extended systems,[31b] which is also applicable to superexchange problems,[31b] J_{af} and J_f are given by

$$J_{af} = -(2/U)[e_\sigma(\mathrm{s}) + \cos\beta\, e_\sigma(\mathrm{p})]^2;\; J_f = (2I/U^2)\sin^2\beta\, e_\pi e_\sigma(\mathrm{p}) \quad (5)$$

Here, β is the CuFCu bridging angle, and e_σ(s) and e_σ(p) represent the AOM contributions to the σ-bonding from the ligand s- and p-orbitals, respectively. For oxide bound to Cu(II) it has been estimated[35] that $e_\sigma(\mathrm{p})/e_\sigma(\mathrm{s}) \approx 5$ and a similar ratio seems reasonable for fluoride, so that for the axial, bridging ligands in $KAlCuF_6$ $e_\sigma(\mathrm{p}) \approx 5000$ cm^{-1}, $e_\sigma(\mathrm{s}) \approx 1000$ cm^{-1}, $e_\pi \approx 1500$ cm^{-1}. Estimates of U and I may be obtained from the relationships[31]

$$U = 146B - 116165/R;\; I = 4B + C \quad (6)$$

where B and C are the Racah parameters, and R is the Cu–Cu separation in Å (3.367 Å, in the present case). Assuming that

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B is reduced to 1000 cm^{-1} from the free ion value[36] of 1240 cm^{-1} and that $C = 4000$ cm^{-1} produces the estimates $U = 111\,500$ cm^{-1} and $I = 8000$ cm^{-1}. Substitution of these values, together with the above AOM parameters, in equations 4 and 5 yields $J_{af} \approx -77$ cm^{-1} $J_f \approx 6$ cm^{-1} producing an overall exchange constant $J \approx -71$ cm^{-1}, in good agreement with the observed value $J = -60$ cm^{-1}.

The above equations imply that the exchange interaction is strongly dependent on the bridging angle β, and the variation of J and the two components J_{af} and J_f as a function of β is shown in Figure 4. Above $\beta \approx 120°$ the exchange interaction is dominated by the antiferromagnetic contribution, increasing in magnitude approximately linearly with β until it reaches a value of $J \approx -300$ cm^{-1} for a linear Cu–F–Cu geometry. Since the energy separation between the spin singlet and triplet states of such a system ($|2J| \approx 600$ cm^{-1}) is considerably greater than kT at room temperature (~ 200 cm^{-1}), a compound involving linear bridges should be effectively diamagnetic below $T \approx 300$ K. The antiferromagnetic contribution vanishes at $\beta \approx 101.5°$ because the contributions from the σ-interaction with the ligand s- and p-orbitals are opposite in sign, and cancel at this angle for the ratio $e_\sigma(p)/e_\sigma(s) = 5$ (eq 5). A simple valence bond picture of the bonding in the complex would ascribe this effect to the orthogonality of s-p hybrid orbitals corresponding to this ratio. The ferromagnetic contribution J_f dominates when β is close to 90°, but is always small, and falls approximately linearly as β increases. However, large ferromagnetic coupling due to a potential energy term have been found in cases of strictly orthogonal magnetic orbitals.[37] It is also noteworthy that the exchange interaction effectively depends on the square of the AOM bonding parameters, which are relatively large for the present compound, as expected from the short bond lengths to the bridging fluoride ligands.

Given the success of the above model in explaining the magnetic behavior of the present complex, and the sensitivity of the calculated parameters to both the bridging angle and metal–ligand bonding parameters, it will be of interest to see how well the model works for other related compounds, and studies of such systems are currently in progress.

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