observed at -20.9 ppm, which is a typical value for low-spin iron(III) tetraphenylporphyrin derivatives.[9,10] A broad resonance for coordinated ammonia is detected at 240.6 ppm in the proton NMR spectrum. This peak is assigned by its appearance in the pyrrole and deuterated (ammonia)iron porphyrin product (Figure 1b).[11] Integration of the ammonia and pyrrole proton signals yields an 8:6 intensity pattern. Hence, the product is assigned as a bis(ammonia)-ligated low-spin iron(III) porphyrin derivative, (TPP)Fe(NH$_3$)$_2$SO$_3$CF$_3$, on the basis of the NMR spectroscopic results. Ammonia ligand exchange is slow on the 55-MHz deuterium NMR time scale ($k_{ex} < 6 \times 10^4$ s^{-1}), as judged by appearance of both coordinated and free ammonia signals.

A plot of pyrrole proton chemical shift vs $1/T$ shows a straight line from 193 to 308 K with an intercept of 15.0 ppm and correlation coefficient of 0.999. Plots of ammonia and phenyl ortho, meta, and para proton resonances vs $1/T$ also exhibit linearity from 206 to 308 K. This suggests that the signals are from a single species. However, in the proton NMR spectrum at 318 K, a minor pyrrole resonance for a high-spin iron(III) complex is observed at 75 ppm. When the solution temperature is lowered back to 298 K, the 75 ppm peak disappears. Hence, a ligand dissociation reaction occurs in solution at higher temperature to presumably yield a mono(ammonia) complex.

Relative line widths support the far-downfield and near-upfield assignment for respective ammonia and pyrrole proton NMR signals. Under the assumption of dipolar relaxation for protons, the line widths should be proportional to r^{-6}, where r is the iron-proton distance.[12] The pyrrole proton is located 5.1 Å from the iron center, and on the basis of standard bond distances, the ammonia proton would be 3.0 Å from the metal center.[13-15] The 57-Hz line width pyrrole proton signal would predict a 1380-Hz ammonia signal. This value is similar to the 1450-Hz line width value observed in Figure 1a for the coordinated ammonia ligands.

When the relaxation mechanism for a nucleus is limited to that from an unpaired metal spin, the line width is predicted to be proportional to the square of the gyromagnetic constant for the nucleus (γ).[16] Hence, the proton line width could in principle be 42 times as broad as the deuterium line width. Respective proton and deuterium line widths for the ammonia signal in Figure 1 are 154 and 1450 Hz. The 9.4 ratio for these two line widths is considerably less than the possible $(\gamma_H/\gamma_D)^2$ value of 42 and presumably reflects a sizable contribution from quadrupolar relaxation by the deuteron.

The solution magnetic moment for (TPP)Fe(NH$_3$)$_2^+$ is 2.3 ± 0.1 μ_B[17] at 298 K as obtained from the Evans method.[18] This value is in accord with the reported value for the bis(imidazole)-ligated low-spin iron(III) porphyrin complex.[19]

The Mossbauer spectroscopic results for the ammonia adduct of (TPP)FeSO$_3$CF$_3$ also support formulation of a low-spin iron(III) complex. The recrystallized solid material exhibits an isomer shift of 0.21 mm/s (iron metal reference) and a quadrupole splitting of 1.4 mm/s at 80 K. An analogous bis(imidazole) complex exhibits a 0.23 mm/s isomer shift and 2.23 mm/s quadrupole splitting at 77 K, whereas the pyridine complex shows respective values of 0.16 and 1.25 mm/s at the same temperature.[20]

An interesting feature of the ammonia-iron(III) porphyrin complex is the observation of a strong g_{max} type EPR spectrum. The spectrum for a frozen dichloromethane solution of (TPP)Fe(NH$_3$)$_2$SO$_3$CF$_3$ at 5.2 K exhibits a prominent signal at $g = 3.75$, a broad feature at $g = 2$, and no clear evidence of another component up to 6000 G. The strong g_{max} type spectrum is observed for the axially symmetric bisligated low-spin iron(III) porphyrin complexes such as those with pyridine, 3- or 4-substituted pyridine, or 2-methylimidazole complexes.[14,21,22]

In summary, the electronic properties of the first well-characterized ammonia complex of an iron(III) porphyrin largely parallel those of known bis(amine) complexes. The lack of earlier reports on this subject is seemingly a consequence of the competitive hydrolytic chemistry of iron(III) porphyrins in the presence of the basic ammonia ligand. The demonstrated affinity of ammonia for iron porphyrins is of relevance to the coordination chemistry of nitrogen species in turnover of the nitrite reductase enzyme.[23]

Acknowledgment. The financial support of National Science Foundation Grant CHE-8705703 is gratefully acknowledged.

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Spectroscopic Verification of a Tetragonal Compression in an Octahedral Copper(II) Compound

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It is well established that six-coordinate copper(II) complexes preferentially adopt a tetragonally elongated geometry although there are several examples of doped Cu(II) crystals having a compressed geometry.[1] Six-coordinate copper(II) complexes are susceptible to tetragonal distortions, as this is the Jahn-Teller active coordinate in the parent octahedral complex. In this work, a series of CuF$_6^{4-}$ complexes has been used to study the spectroscopic implications of such tetragonal distortions.

The crystal structure of the pure K$_2$CuF$_4$ compound was originally described as containing compressed octahedra,[2] but magnetic[3] and spectroscopic[4] studies were incompatible with this geometry. Subsequently, it has been established that the structure of K$_2$CuF$_4$ has an "antiferrodistortive" order where elongated octahedra are orthogonally aligned perpendicular to the tetragonal axis of the crystal.[3]

Recently an X-ray diffraction study has shown that crystals of KCuAlF$_6$ contain compressed CuF$_6^{4-}$ octahedra.[5] A spec-

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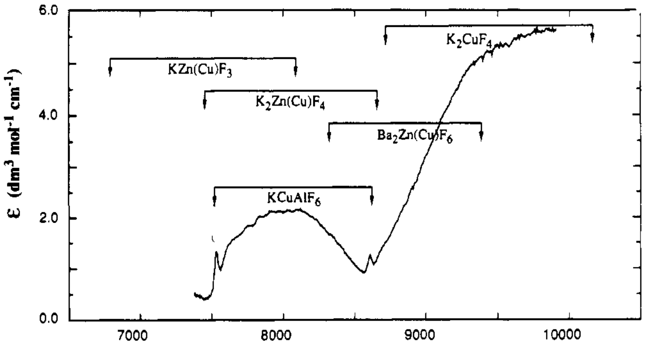

Figure 1. Unpolarized single-crystal absorption spectrum of KCuAlF$_6$ at 15 K. The energies of the origins of other CuF$_6^{4-}$ complexes are indicated by arrows.

Table I. Magnetic Dipole Origins Observed in CuF$_6^{4-}$ Complexes[a]

complex	transitions	energy/ cm^{-1}	ΔE/ cm^{-1}	ref
K$_2$CuF$_4$	$\Psi(x^2 - y^2) \rightarrow \Psi_3$	8764		
	$\rightarrow \Psi_2$	10214	1450	9
Cu(II)/KZnF$_3$	$\Psi(x^2 - y_2) \rightarrow \Psi_3$	6829		
	$\rightarrow \Psi_1,\Psi_2$	8129	1300	8
Cu(II)/K$_2$ZnF$_4$	$\Psi(z^2) \rightarrow \Psi_3$	7497		
	$\rightarrow \Psi_1$	8704	1207	8
KCuAlF$_6$	$\Psi(z^2) \rightarrow \Psi_3$	7531		
	$\rightarrow \Psi_1$	8604	1073	this work
Cu(II)/Ba$_2$ZnF$_6$	$\Psi(z^2) \rightarrow \Psi_3$	8370		
	$\rightarrow \Psi_1$	9438	1068	10

[a] The three Kramers doublets (Ψ_1, Ψ_2, Ψ_3) of the $^2T_2$ multiplet are defined in the text.

troscopic study of KCuAlF$_6$ was undertaken to determine if it was consistent with the reported crystal structure.

Experimental Section

A flawed single crystal of KCuAlF$_6$ contained a fragment of dimensions 0.2 × 0.15 × 0.1 mm^3, which was suitable for absorption measurements. The polarization properties of the orthorhombic crystals were not measured because of the very small dimensions. Light from a 150-W tungsten-halogen lamp was dispersed by a 1-m Spex 1704 monochromator fitted with a 600 line/mm grating blazed at 1.6 μm. The sample was cooled to 15 K in a helium gas flow tube. Light was focused on the sample with Beck reflecting objectives and detected with a liquid-nitrogen-cooled ADC Model 403 germanium photodetector. The signal was collected with lock-in techniques and accumulated on an IBM PC/AT clone (Cleveland 286).

Results and Discussion

The absorption spectrum of KCuAlF$_6$ is shown in Figure 1. The spectral resolution is <6 cm^{-1} in the region of the sharp origins, which have an intrinsic line width of $\sim$30 cm^{-1}. The energies of the sharp zero-phonon electronic origins are given in Table I together with those observed in four other CuF$_6^{4-}$ complexes. The polarization properties of the latter show that the origins are magnetic dipole allowed. Although we have not established the intensity mechanism for the origins in KCuAlF$_6$, this information is unnecessary for our argument based on energy considerations. Furthermore, the second argument, based on intensity, relies heavily on vibronic reduction factors, which apply to both electronic and magnetic transition dipoles.

The Energy Argument. Within the angular overlap model (AOM), the tetragonal splitting of the $^2T_{2g}$ ($t_2{}^5e^4$) multiplet is determined by the π-bonding interactions of the ligands. The energies of the three Kramers doublets are shown in Figure 2 as a function of the tetragonal field Δ_t and are given by

$$\begin{aligned} \Psi_1(\Gamma_6)&: \ \tfrac{1}{3}\Delta_t + \tfrac{1}{2}\lambda \\ \Psi_2(\Gamma_7)&: \ -\tfrac{1}{6}\Delta_t - \tfrac{1}{4}\lambda + C \\ \Psi_3(\Gamma_7)&: \ -\tfrac{1}{6}\Delta_t - \tfrac{1}{4}\lambda - C \end{aligned} \qquad (1)$$

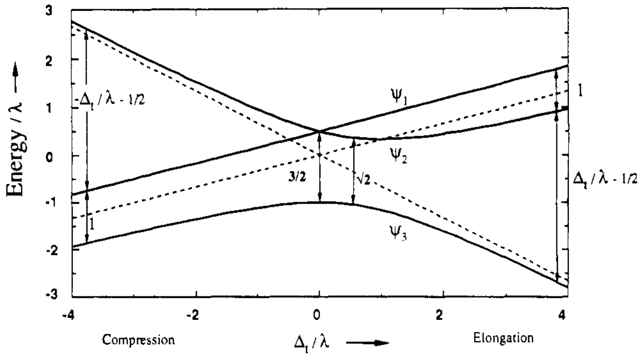

Figure 2. Variation of the energies of a $^2T_{2g}$ multiplet as a function of the tetragonal field Δ_t as defined by eq 1. The spin–orbit coupling, λ, is assumed to be isotropic. The dotted lines indicate the energies when $\lambda = 0$. This figure is also appropriate to the $T_{2g} \otimes \epsilon$ Jahn–Teller problem with spin–orbit coupling (see text). The limiting energy separations for large $|\Delta_t|$ are indicated.

where $\Delta_t = 2(\pi_\perp - \pi_\parallel)$ and $C = [(^1/_2\Delta_t - {^1/_4}\lambda)^2 + {^1/_2}\lambda^2]^{1/2}$. The symbols $\pi_\parallel$ and $\pi_\perp$ represent the AOM π-bonding parameters of the axial and equatorial ligands, respectively, and Δ_t is the one-electron tetragonal splitting of the t_{2g} orbitals $E(xy) - E(xz,yz)$. Such an energy diagram is closely related to the $T \otimes \epsilon$ Jahn–Teller problem,[6] where the tetragonal field Δ_t is replaced by $^3/_2c_tQ_\theta$. Here Q_θ is the tetragonal component of the octahedral ϵ_g vibration and c_t is the Jahn–Teller coupling constant defined[7] as $\langle t_{2\zeta}|\partial V/\partial Q_\theta|t_{2\zeta}\rangle = -2/\sqrt{3}(\partial\pi/\partial R)$. In crystals of cubic symmetry, the harmonic potential of CuF$_6^{4-}$ would be added at the origin of Figure 2. It has been shown[8] that in this case the spin–orbit coupling is large enough to quench the $T \otimes \epsilon$ Jahn–Teller effect so that the origin of the Ψ_3 state is at an octahedral geometry. However, in a crystal of lower symmetry with an intrinsic (static) tetragonal contribution to the ligand field, the harmonic potential is added at a nonzero value of $Q_\theta(\Delta_t)$, and the resulting minima in the potentials will be determined by the slopes of the energy levels at the value of $Q_\theta(\Delta_t)$ appropriate to the tetragonal distortion.

In these cases, the Q_θ coordinate becomes totally symmetric in the D_{4h} point group and the relative coupling constants of states within the T_{2g} multiplet are not symmetry determined.

Because of the different displacements of the potential energy surfaces, the observed energy separations in Figure 1 can be equated with the vertical energy gaps in Figure 2 only to a first approximation. The intensities, however, are much more sensitive to these displacements.

It will be shown that only two magnetic dipole transitions will have observable intensity, Ψ_1 and Ψ_3 for the compressed case and Ψ_2 and Ψ_3 for the elongated case. The salient features to note from Figure 2 are that for strongly compressed octahedra the energy separation between the two transitions, ΔE, is reduced from $^3/_2\lambda$ and approaches λ, while for elongated octahedra ΔE decreases to a minimum value of $\sqrt{2}\lambda$ for $\Delta_t = {^1/_2}\lambda$ and then increases toward a limiting value of $\Delta_t - {^1/_2}\lambda$ for large Δ_t. The data given in Table I reflect this trend, and on this argument alone, it can be concluded that the CuF$_6^{4-}$ units in KCuAlF$_6$ are almost as compressed as in the Ba$_2$Zn(Cu)F$_6$ system.

The mean energy of the two transitions depends on the ground-state energy, which is strongly dependent on the tetragonal environment. In fact, for an increasing distortion in either a compressed or elongated sense, the mean energy should rise, as is indeed observed in the data of Table I. However, it is only the energy separation between the two transitions that is useful as a criterion for determining the sign of the distortion.

The Intensity Argument. The variation of the intensities of the magnetic dipole origins as a function of the tetragonal field, Δ_t, is shown in Figure 3. These calculations were done by using

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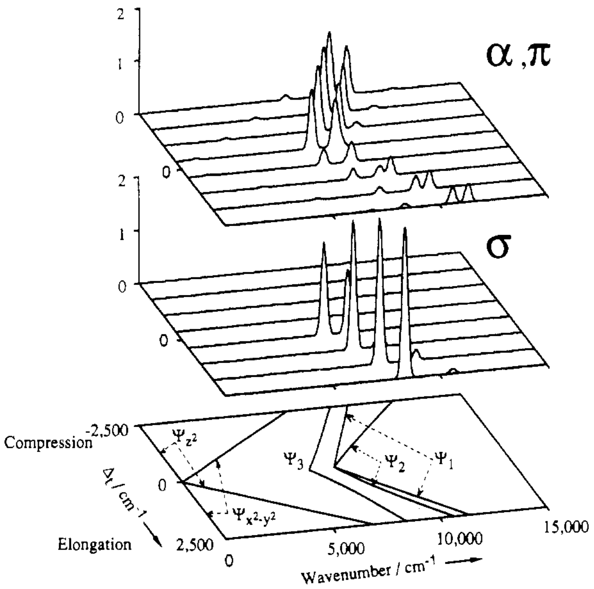

Figure 3. Calculated magnetic dipole strengths as a function of Δ_t for α, $\pi(H\|xy)$, and σ ($H\|z$) polarizations. The "cubic" field is held fixed at $\Delta = 6500$ cm^{-1} and $k = 0.86$. The intensity is given in units of μ_B^2.

methods previously given,[9] with the "cubic" part of the ligand field held constant at $\Delta = 2\sigma_\perp + \sigma_\| + {}^4/_3(2\pi_\perp + \pi_\|)$ and the effect of the tetragonal field on the e_g orbitals given by $\Delta_e = 2(\sigma_\perp - \sigma_\|) \approx 3\Delta_t$. An orbital reduction factor of $k = 0.86$ was used with the reduced spin-orbit coupling constant of $\lambda = 714$ cm^{-1}.

The most striking features of Figure 3 are that there is only a *single* strong origin for elongated octahedra, while there are *two* origins of comparable intensity for compressed octahedra. Again, this is strong evidence that the spectra of Figure 1 are due to tetragonally compressed CuF_6^{4-} complexes. However, it must be emphasized that Figure 3 implies "vertical" electronic transitions. The observed intensity also depends on the overlap of the ground- and excited-state zero-point vibrational functions. This overlap is very sensitive to the relative displacement of the minima. The vibrational functions should be approximately localized about the minima of their respective potentials, and small relative displacements of these minima should greatly affect the relative vibronic reduction factors. It remains to show that these reduction factors strengthen the intensity argument.

For the elongated case, the equilibrium geometry of the ground state should correspond to an elongation greater than that of any of the $^2T_{2g}$ excited states. This follows from the greater effect a tetragonal distortion has on the e_g compared to the t_{2g} orbitals, or more simply $e_\sigma > e_\pi$. The slopes of the energy levels in Figure 2 require that the minima of the states Ψ_3, Ψ_2, and Ψ_1 be increasingly displaced with respect to the ground state. Therefore, relative to the strong origin of Ψ_3, the origins of the Ψ_2 and Ψ_1 states should be even weaker than actually shown in Figure 3. This is exactly what was observed for K_2CuF_4, where the Ψ_2 origin was found to have only $\sim{}^1/_{60}$th of the intensity of the Ψ_3 origin, while the Ψ_1 origin was not even observed.

Similarly, the ground state in the compressed case is expected to have a more compressed geometry than any of the excited states. The energy levels of the two lowest excited states, Ψ_3 and Ψ_1, have a similar slope and therefore have *similar* displacements.

Therefore, for an elongated octahedron, only *one* main origin would be expected when the magnetic vector of the incident light is parallel to the tetragonal axis ($H\|z$) and no origins would be expected for $H\perp z$. Conversely, for a compressed octahedron, no origin would be expected for $H\|z$, while *two* origins of comparable intensity would be expected for $H\perp z$. The mere fact that two electronic origins were observed in the low-temperature absorption spectrum of $KCuAlF_6$ shows that the copper center is in a compressed geometry. The energy separation of these origins gives an estimate of the size of the distortion.

The data in Table I suggest that the CuF_6^{4-} center in $KCuAlF_6$ should have a geometry similar to that found in the doped $Ba_2Zn(Cu)F_6$ system. The Ba_2ZnF_6 compound has the bond lengths[11] 196 (×2) and 205 pm (×4), whereas for $KCuAlF_6$ the reported[5] bond lengths are 187, 188, and 212 pm (×4). This implies that the six-coordinate Cu(II) complexes do not necessarily adopt the exact geometry of the host lattice. Rather, the magnitude of the tetragonal distortion is intrinsic to the Cu(II) ion from the $E \otimes \epsilon$ Jahn-Teller effect, while the role of the crystal lattice is to determine the sign of the distortion. The structure of the analogous $KZnAlF_6$ compound is also compressed[12] with the bond lengths 194, 196, 206 (×2), and 211 pm (×4), and so it appears that the sign of the tetragonal distortion is also determined by lattice forces in undiluted copper(II) compounds.

The size of the Jahn-Teller distortion in the ground state, given by[1] $\rho_0\ [=(\sum_i(r_i - \bar{r})^2)^{1/2}] = 28$ pm, is smaller than that found for K_2CuF_4, $\rho_0 = 33$ pm, which is consistent with simple $E \otimes \epsilon$ Jahn-Teller models where the warping of the "Mexican hat" potential causes ρ_0 to be larger for an elongated compared to a compressed geometry.[13]

Conclusions

The CuF_6^{4-} centers in $KCuAlF_6$ have been shown unambiguously to be compressed octahedra by low-temperature absorption measurements. This is in agreement with the published crystal structure[5] and represents one of the few pure compounds known in which copper(II) adopts a compressed geometry.[5,14] Criteria for spectroscopically distinguishing between compressed and elongated octahedra have been given. Such spectrostructural relationships can be useful in cases where the crystal structure determination may be complicated by twinning or antiferrodistortive ordering.

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Conformation of H_2 on Dinuclear Complexes: Attractive Effect of a Cis Hydride

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The nonclassical coordination of H_2 to mononuclear transition-metal complexes has been established for a number of different metal centers and studied via a variety of experimental and theoretical techniques.[1] However, examples of dinuclear transition-metal complexes involving this novel ligand are relatively rare.[2,3] The aim of this work is to show that the nature of the

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