nuclear mixed ligand complexes to account for the consistent observation of just one ^{113}Cd NMR signal for each individual species in the various equilibrium mixtures.

A remarkable feature of the ^{113}Cd NMR spectra of each series of mixed-ligand complexes $[Cd(EPh)_x(E'R)_{10-x}]^{2-}$ is the small range of the incremental shifts $\Delta\delta_{Cd}$ produced by incremental change in x. This is quite evident in Figures 1–3. The full ligand environment of the Cd_4 core averages at a rate fast on the NMR time scale (see above), and the near-statistical distribution of individual species (see above) suggests no marked preference of any of the ligands studied for either terminal or bridging positions. From the values of $\Delta\delta_{Cd}$(av) (i.e. with the crude approximation[27] made that $\Delta\delta_{Cd}$ does not depend on x in $[Cd_4(EPh)_x(E'R)_{10-x}]^{2-}$) values of δ_{Cd} can be estimated for some of those parent complexes for which direct spectral data were inaccessible. These are included in Table II, together with the data that could be measured directly, and values of δ_{Cd} for the corresponding mononuclear complexes, $Cd(ER)_4^{2-}$. Except for the cases where $E'R = SBu$, there is close agreement between the δ_{Cd} values of $Cd(ER)_4^{2-}$ and the corresponding results for $[Cd_4(ER)_{10}]^{2-}$, considering that data for different solvents, temperatures, and concentrations are compared in some instances. Therefore, we conclude that δ_{Cd} shows little sensitivity to the terminal or bridging nature of the ligand bound to cadmium. The same conclusion has been reached by Kurtz and co-workers[8] from the solid-state ^{113}Cd NMR spectra of salts of $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$. At present we cannot account for the discrepancy found for the SBu complexes, but even in this case a relatively small change, 16 ppm or less, is projected for one terminal to bridging conversion.

Substitution of Zn for ^{113}Cd in $[^{113}Cd_4(SPh)_{10}]^{2-}$ produces a shielding of 0.46 ppm/Zn, confirming the assumption of Armitage

and co-workers[1] that the ^{113}Cd NMR spectral result of such a change is small. The distribution of species in $2*-[Zn_4(SPh)_{10}]^{2-}$ mixtures is not statistical, though: the equilibrium (5) lies well

$$2[^{113}CdZn_3(SPh)_{10}]^{2-} \rightleftharpoons$$
$$[^{113}Cd_2Zn_2(SPh)_{10}]^{2-} + [Zn_4(SPh)_{10}]^{2-} \quad (5)$$
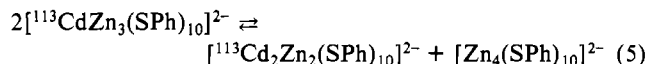
to the right. The instability of the $CdZn_3$ species may have its origin in a mismatch of the sizes of the $(PhS_t)Cd(SPh_{br})_3$ and $(PhS_t)Zn(SPh_{br})_3$ groupings.[4,5] However, models show no evidence for a severe misfit in the $CdZn_3$ cluster, and $[Zn_4(SPh)_{10}]^{2-}$ apparently contains no unusual steric features;[5] in addition, we note that CdS and ZnS are miscible over the whole range of composition.[28] Whatever the origin of the effect, our results for the model heterometallic clusters resemble those found for Zn,Cd-MT, in that no ^{113}Cd NMR evidence was found[1] for the $CdZn_3$ combination in the four-atom cluster of the protein either. For the protein, the absence of the zinc-rich clusters $CdZn_3$ and Zn_4 has been attributed to increased steric hindrance between the residues when the smaller zinc ions predominate.[1]

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(27) Using the assumption that $\Delta\delta_{Cd}$ is linearly dependent on x, to allow for possible curvature of the plot of δ_{Cd} vs. x, produces little change in the extrapolated values.

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EPR Spectrum of Tetragonally Compressed CuF$_6^{4-}$: Ligand and Metal Hyperfine Parameters

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Received April 29, 1985

The metal and ligand hyperfine splittings observed in the low-temperature EPR spectrum of ~1% copper(II) doped into single crystals of K_2ZnF_4 are reported. The splitting parameters of the axial ligands in the compressed tetragonal CuF$_6^{4-}$ guest species are ~2.5 times those of the in-plane fluorines. The overall unpaired spin density on the metal is ~0.77, the bulk of which resides in the $3d_{z^2}$ orbital, though with a minor contribution, ~0.03, in the metal 4s orbital.

Introduction

Analysis of the hyperfine coupling between electronic and nuclear spins provides a powerful method of investigating the ground-state wave function of a transition-metal complex.[1] The interaction with the metal nucleus depends upon the unpaired spin density in the metal d and s orbitals, the latter contribution apparently varying significantly as a function of the stereochemistry of the complex and the nature of the ground state.[2,3] The superhyperfine coupling involving ligand nuclear spins on the other hand allows the covalency of a complex to be quantified and this has provided a reasonably self-consistent picture of the unpaired spin density transferred to the ligands in a wide range of octahedral fluoride complexes.[4]

Recently, we reported the powder EPR spectra of copper-(II)-doped K_2ZnF_4, this lattice being unusual because at low Cu^{2+} concentrations the comparatively rare tetragonally compressed geometry is stabilized for the guest CuF$_6^{4-}$ species.[5] The g shifts and temperature dependence of the g values suggest that while the d_{z^2} orbital is the most important component of the ground-state wave function, vibronic coupling causes significant admixtures of $d_{x^2-y^2}$ at higher temperatures and this aspect is the subject of a separate publication.[6] At low temperature, the spectra show

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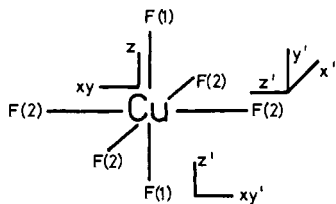†University of Tasmania.
‡Philipps-Universität.

Figure 1. Coordinate systems used to define the copper (unprimed) and fluorine (primed) hyperfine tensors. For the metal and F(1) ions the tensors are axially symmetric.

extensive structure due to coupling involving the metal and two different types of fluorine nuclei, and this is the subject of the present paper, the unusual nature of the ground state making comparison with other systems of particular importance.

Experimental Details and Analysis of Spectra

The preparation of the doped crystals has been described elsewhere.[5] The tetragonal unit cell of K_2ZnF_4 contains a single molecule in the asymmetric unit, with four equivalent Zn–F bonds lying along $\langle 100 \rangle$, $\langle \bar{1}00 \rangle$, etc. and two remaining bonds parallel to $\langle 001 \rangle$.[5] Though the bond lengths differ by less than one standard deviation, an anisotropy is imposed on the ZnF_6^{4-} units by the fact that while the equatorial fluorides connect two Zn^{2+} octahedra via common corners, the axial ones only participate additionally in the K^+ coordination and thus form slightly stronger Zn–F bonds than the equatorial ligands. The local axis systems used to define the metal and ligand hyperfine tensors are shown in Figure 1. EPR spectra of several crystals containing $\sim 1\%$ Cu^{2+} were measured at X-band frequency on a Varian E-15 spectrometer at ~ 6 K for rotations of the magnetic field B in the (100) and (001) crystal planes; typical spectra are shown in Figure 2A. The crystals were mounted on the flat side or base of a specially made quartz rod and aligned to better than $\sim 2°$ by using a polarizing microscope. Measurements were made by using 100 K modulation frequency, with a modulation amplitude of ~ 250 and width of ~ 1 G, at a power level of ~ 2 mW.

To first order, the interaction with the copper nucleus ($I_N = \frac{3}{2}$) gives rise to four equally intense lines, these being split slightly by the different nuclear moments of the two isotopes. Each pair of trans fluorines ($I_N = \frac{1}{2}$) produces a pattern of three lines with relative intensity 1:2:1. When B is parallel to $\langle 001 \rangle$ (Figure 2, $\theta = 0°$), the spectrum consists of eight sets of lines, the center four sets being more intense than the outer four. In this orientation, the splittings are due to A_z for the metal, $A_{z'}$ for F(1), and $A_{y'}$ for F(2), and the overall pattern implies that $A_{y'}$ is small with respect to $A_{x'} \approx 2A_{z'}$. When B is midway between $\langle 100 \rangle$ and $\langle 010 \rangle$, it makes an equal projection on z' and x' of each F(2) and lies in the xy and xy' planes of the metal and F(1) hyperfine tensors. Here, a ten-line pattern is observed, the intensity decreasing steeply on going from the central to the outer lines (Figure 2, $\theta = 90°$, $\phi = 45°$). Such a pattern can only occur if all the metal and fluorine hyperfine splittings are approximately equal. When B lies along $\langle 100 \rangle$, it is parallel to z' for one pair of F(2) ligands and x' for the second pair and is located in the xy' and xy planes of the F(1) and metal hyperfine tensors. The fact that a broad, featureless line is observed in the spectrum (Figure 2, $\theta = 90°$, $\phi = 0°$) provides a significant restraint on the possible values of the parameters. With the above considerations as a starting point a computer program was used to simulate the spectra for various possible values of the hyperfine parameters, and it was found that satisfactory agreement with experiment could only be obtained for a quite narrow range of each of these (a change of $\sim 3 \times 10^{-4}$ cm^{-1} significantly worsened agreement with experiment). Both Gaussian and Lorentzian line shapes were investigated,[7] and the former was found to give marginally better agreement with experiment. Second-order corrections for the positions of the peaks[8] were included. The basic half-width of each line was assumed to increase by a factor of ~ 2 as B rotated from being parallel to z to lying in the xy plane; a relationship between line width and g shift of this kind is generally observed for Cu^{2+} ions diluted in host lattices.[9] The simulated spectra (Figure 2B) agree very well with those observed experimentally except when the magnetic field lies between the molecular z and xy axes ($\theta = 30$, and 60°); agreement for these spectra could be significantly improved by increasing the half-width in the simulation by $\sim 20\%$, but this would have worsened the fit at the other magnetic field orientations.
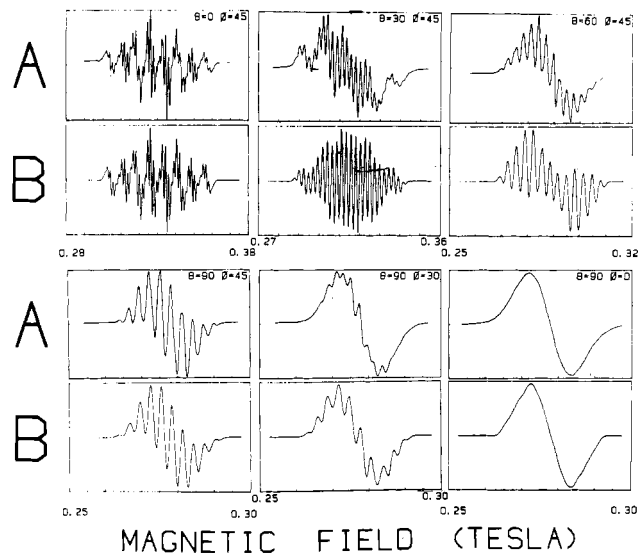

Figure 2. Experimental (A) and computer-simulated (B) EPR spectra of $K_2Zn[Cu]F_4$. The angle between the magnetic field and the [001] crystal axis is represented by θ, while the angle made by the projection of the magnetic field in the (001) plane and the [100] axis is represented by ϕ. The parameters used in the simulation are given in the text, the half-width of each component being given by the expression $\Delta B = (\Delta B_z^2 \cos^2 \phi + \Delta B_{xy}^2 \sin^2 \phi)^{1/2}$ with the best-fit values of ΔB_z and ΔB_{xy} being found to be 5.5×10^{-4} T and 10.0×10^{-4} T, respectively.

tations. The best fit parameters were found to be as follows (cm^{-1} × 10^{-4}): $A_z = 75.8$, $A_{xy} = 30.0$, $A_{z'}(F(1)) = 132.8$, $A_{xy'}(F(1)) = 25.6$, $A_{z'}(F(2))$, $= 48.6$ $A_{x'}(F(2)) = 13.9$, $A_{y'}(F(2)) = 14.0$, the metal hyperfine parameters being quoted for the ^{63}Cu isotope. The g values at 6 K were observed to be $g_z = 2.003$, $g_{xy} = 2.386 \pm 0.002$. During the preparation of this paper we became aware of a similar investigation by Yablokov and co-workers.[10] A single crystal of K_2ZnF_4 doped with $^{63}Cu^{2+}$ with g values $g_z = 2.014$ and $g_{xy} = 2.381$ was studied, which yielded copper and fluorine hyperfine values quite similar to ours (cm^{-1} × 10^{-4}): $A_z = 72.2$, $A_{xy} = 42.3$, $A_{z'}(F(1)) = 123.6$ (123.8), $A_{xy'}(F(1)) = 31.7$ (31.1), $A_{z'}(F(2)) = 33.7$ (48.0), $A_{x'}(F(2)) \approx 6$ (10.9), $A_{y'}(F(2)) = 13.9$ (14.1); values of the ligand hyperfine parameters obtained by calculation are indicated in parentheses.

Interpretation of Data and Comparison with Ligand Superhyperfine Parameters of Other Systems

The interpretation of ligand hyperfine parameters has been discussed in detail by various authors[4,11,13] with particular reference to transition-metal fluoride complexes. The general equations relating the principal hyperfine parameters to the fractional unpaired electron density in fluorine 2s and $2p_{z'}$ and $2p_{xy'}$ orbitals, f_s, f_σ, and f_π, are[4,11]

$$A_{z'} = f_s A_s + 2(f_\sigma - f_\pi)A_p - 2.5K(f_\sigma + 2f_\pi)A_p + 2A_D \quad (1a)$$

$$A_{xy'} = f_s A_s - (f_\sigma - f_\pi)A_p - 2.5K(f_\sigma + 2f_\pi)A_p - A_D \quad (1b)$$

Here, A_s and A_p are the splittings due to unit unpaired spin density in 2s and 2p fluoride orbitals, respectively, A_D is the dipolar splitting due to the unpaired spin on the metal, and the term $2.5K(f_\sigma + 2f_\pi)A_p$ represents the effect of the polarization of the core 1s electrons by the unpaired spin in the fluoride 2p orbitals. Taking into account the different bond lengths to F(1) and F(2) (~ 195 and 207 pm) estimated for the CuF_6^{4-} guest species[5] and the fractional unpaired spin density on the metal (0.77, see below) yields estimates of $A_D = 2.7 \times 10^{-4}$ and 2.5×10^{-4} cm^{-1} for F(1) and F(2), respectively. The magnitude and even the sign of the core polarization parameter are not known with certainty. For the fluorine atom $K = -0.1$,[14] but in CrF_6^{3-}, where the isotropic

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Table I. Fluorine Hyperfine Parameters and Calculated Unpaired Spin Densities for d^9 Complexes Having $^2A_{1g}(d_{z^2})$ Ground States

compd type		fluorine hyperfine parameters × 10^4, cm^{-1}		unpaired spin density, %		
		$|A_z|$	$|A_{xy}|$	f_s	f_p	ref
K$_2$Zn[Cu]F$_4$	F(1)	132.8	25.6	0.46	6.7	a
	F(2)	48.6	14.0	0.19	1.8	a
Zn[Cu]F$_2$	F(1)	121.9	51.5^b	0.56	4.2	13
	F(2)	51.2^b	13.0	0.19	2.1	13
Li[Ni$^+$]F	F(1)	198	53	0.76	9.3	16
	F(2)	25	19	0.16^c	0.0^c	16
				0.00^d	2.5^d	
CuF$_2$	F(1)	102.7	68.7	0.60	1.8	17

^{a} Present work. ^{b} The value for F(1) of A_{xy} = 51.5 × 10^{-4} cm^{-1} is the average of $A_{x'}$ = 55.0 × 10^{-4} cm^{-1} and $A_{y'}$ = 48.0 × 10^{-4} cm^{-1}; the value for F(2) of $A_{z'}$ = 51.2 × 10^{-4} cm^{-1} was derived from the value of 37.4 × 10^{-4} cm^{-1} reported for the situation when the magnetic field makes an equal projection on the z' and x' axes of all F(2) ligands and $A_{x'}$ = $A_{y'}$ = 13 × 10^{-4} cm^{-1} is assumed. ^{c} Calculated by assuming $A_{xy'}$ = 19 × 10^{-4} cm^{-1}. ^{d} Calculated by assuming $A_{xy'}$ = -19 × 10^{-4} cm^{-1}.

ligand hyperfine interaction is thought to be due entirely to this effect, the value K = 0.04 has been estimated.[15] It has therefore been assumed here that K = 0.0, though it should be noted that allowing K to vary over the range ±0.1 would only change the estimated value of f_s by ±15%. In K$_2$Zn[Cu]F$_4$ the only unpaired spin density in orbitals of π-symmetry is that due to the small admixture of d$_{xz,yz}$ into the ground state that occurs via spin–orbit coupling. This affects $A_{y'}$ but not $A_{x'}$ for F(2), and the fact that these are equal to within experimental error confirms the conclusion that such interactions are negligible in systems of this kind.[4] It has therefore been assumed that f_π = 0.0 in the present calculations. The splittings due to the unpaired spin in the fluorine 2s and 2p orbitals, $f_s A_s$ and $f_\sigma A_p$, were calculated on the basis of the above assumptions, both for K$_2$Zn[Cu]F$_4$ and for the other fluoride complexes of d^9 metal ions listed in Table I for comparison. For the fluorine atom A_s and A_p have been reported as 1.764 cm^{-1} and 0.059 cm^{-1}, respectively;[12] somewhat smaller values are expected for the fluoride ion, the reduction factors being estimated as 0.76 and 0.83, respectively.[4] These reduced values yield the values of the unpaired spin densities f_s and f_p listed in Table I.

In K$_2$Zn[Cu]F$_4$ the unpaired spin resides predominantly in d$_{z^2}$ (the contribution of d$_{x^2-y^2}$ to the ground state, ~4% at 6 K, is small). For a pure d$_{z^2}$ ground state—if bond length differences are neglected—the unpaired spin density transferred to F(1) should be 4 times that transferred to F(2), and this ratio should decrease to 3.6, taking into account the d$_{x^2-y^2}$ admixture. The fact that the Cu–F(1) bond is thought to be considerably shorter than Cu–F(2) should accentuate this difference. In practice, the spin density transferred to the 2s and 2p orbitals of F(1) is found to be ~3.7 times that transferred to F(2), the agreement with theory being reasonable. Possible limitations in the present treatment are the neglect of direct overlap between the metal d orbital and the flourine nucleus and the interaction of the fluorine 2p$_{z'}$ orbital with the metal 4s orbital. The former effect is expected to reduce $f_s A_s$, while the latter should reduce $f_p A_p$,[4] both effects being more important for the shorter Cu–F(1) bond.

The present data agree well with that reported[13] for copper-doped zinc(II) fluoride as far as the F(2) ligands go, but the value of $A_{xy'}$ of the F(1) atoms in Zn[Cu]F$_2$ is apparently about twice that in K$_2$Zn[Cu]F$_4$ (Table I). Possibly this is due to the fact that, in contrast to the case of K$_2$ZnF$_4$, F(1) in ZnF$_2$ is a bridging ligand. The ratio of the unpaired spins transferred to F(1) compared with F(2) is considerably smaller in Zn[Cu]F$_2$ than that in K$_2$Zn[Cu]F$_4$. This is expected, as the contribution of d$_{x^2-y^2}$ to the ground state (~9%) is much larger in Zn[Cu]F$_2$. For Ni$^+$ doped into LiF, on the other hand,[16] the f_s and f_p parameters of

the axial fluorines of the center having a predominantly d$_{z^2}$ ground state are ~50% greater than for K$_2$Zn[Cu]F$_4$. Such an increase is expected because of the greater metal–ligand overlap associated with the lower nuclear charge on the metal. The F(2) parameters are anomalous, however, suggesting a negligible spin density in the fluorine p$_{z'}$ orbital if $A_{xy'}$ is positive or a vanishing value of f_s if it is negative. Comparison with the data reported[17] for the linear CuF$_2$ molecule is particularly interesting, as this represents the limiting case of a tetragonally compressed complex with the in-plane ligands removed to infinity. As the Cu–F(1) bonds are expected to be shorter in CuF$_2$ than in K$_2$Zn[Cu]F$_4$, the present simple model predicts that the transferred spin density should be greater in the former compound. In fact, although f_s is slightly larger, f_p is significantly smaller. It seems likely that in CuF$_2$ the metal 4s orbital interacts strongly with the fluorine 2p$_{z'}$ orbital (see discussion of the metal hyperfine parameters), and it may well be that this causes the apparent transfer of σ unpaired spin density to be so low; the anomalously low value estimated for f_σ in a chromium(I) fluoride complex has been interpreted in this fashion.[4]

The overall transfer of unpaired spin to the ligands deduced for K$_2$Zn[Cu]F$_4$ is ~22%, which is similar to that estimated for copper(II) complexes having the more usual d$_{x^2-y^2}$ ground state (values of ~22% and ~25–35% have been estimated for Cu(H$_2$O)$_6^{2+}$[18] and CuCl$_4^{2-}$, respectively[19]). In general terms, the delocalization deduced for K$_2$Zn[Cu]F$_4$ is quite similar to that estimated for the regular octahedral fluoride complexes of other divalent metal ions (e.g. for NiF$_6^{4-}$ $f_s \approx$ 0.53%, $f_p \approx$ 3.1%, a total delocalization of ~22%[4]).

Copper Hyperfine Parameters

The metal hyperfine parameters of a copper(II) complex with a d$_{z^2}$ ground state are conventionally interpreted by using the expressions[20]

$$A_z = -PK\alpha^2 + P\left(\frac{4\alpha^2}{7} - \frac{6\mu}{7} + \frac{15\mu^2}{7} \right) \quad (2a)$$

$$A_{xy} = -PK\alpha^2 + P\left(-\frac{2\alpha^2}{7} + \frac{45\mu}{7} - \frac{57\mu^2}{14} \right) \quad (2b)$$

Here, the first term in both equations represents the contact interaction with unpaired spin density in the metal s orbitals, the second term represents the dipolar interaction with that in the d$_{z^2}$ orbital, and the final two terms represent the effect of the orbital angular momentum associated with the d$_{xz,yz}$ orbitals mixed into the ground state by spin–orbit coupling. For K$_2$Zn[Cu]F$_4$ the orbital contribution μ may be estimated[5] as 0.071 from the value g_{xy} = 2.386 by using the relationship $g_{xy} = g_0 + 6\mu - 6\mu^2$, while the above analysis of the fluorine hyperfine coupling suggests the fractional occupancy of the metal orbital $\alpha^2 \approx$ 0.77. The parameter $P = 2g_N\beta\beta N\langle r^{-3} \rangle$, which occurs essentially as a scaling factor, has been estimated as 360 × 10^{-4} cm^{-1} for Cu^{2+}.[21,22] For copper(II) complexes the isotropic contact interaction is considered to be dominated by the polarization of the core s electrons by the unpaired d electron. Calculations suggest K = 0.43 for Cu^{2+} due to this effect,[22] and the hyperfine splitting in relatively ionic copper(II) complexes with d$_{x^2-y^2}$ ground states can be reproduced quite well by using these values.[21,23] However, their substitution in eq 2a,b yields the estimates A_z = 21 × 10^{-4} cm^{-1} and A_{xy} = -41 × 10^{-4} cm^{-1} for K$_2$Zn[Cu]F$_4$ in poor agreement with the experimental values $|A_z|$ = 78 × 10^{-4} cm^{-1} and $|A_{xy}|$ = 30 × 10^{-4} cm^{-1}. Accounting for the small d$_{x^2-y^2}$ contribution to the d$_{z^2}$ ground

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state does not lead to significantly better agreement. On the other hand, for a complex with a $^2A_{1g}$ ground state the direct participation of the metal 4s orbital is allowed by symmetry, and this is expected to have an effect opposite in sign to that of the polarized core electrons.[21] For $K_2Zn[Cu]F_4$ a much better agreement with experiment is obtained with $K = 0.20$, yielding $A_z = 85 \times 10^{-4}$ cm^{-1} and $A_{xy} = 23 \times 10^{-4}$ cm^{-1}. This corresponds to a contribution $K = -0.23$ due to direct 4s participation in the ground state. The calculated value of the isotropic hyperfine splitting due to unit unpaired spin density in a copper 4s orbital is 0.2003 cm^{-1},[12] so that the above estimate of K implies a fractional occupany of the 4s orbital by the unpaired electron of $\sim(0.23 \times 0.77 \times 0.036/0.2003)$ or $\sim 3.2\%$. This is similar to the value derived from the analysis of the metal hyperfine parameters of low-spin cobalt(II) complexes having the more common tetragonally elongated Jahn–Teller distortions in which the unpaired electron occupies a $^2A_{1g}(d_{z^2})$ orbital[24] and also to the 4s mixing coefficient deduced from the energy of the $^2A_{1g}(d_{z^2})$ excited state of planar four-coordinate copper(II) complexes.[25]

The metal hyperfine parameters $|A_z| = 645 \times 10^{-4}$ cm^{-1} and $|A_{xy}| = 697 \times 10^{-4}$ cm^{-1} of the CuF$_2$ molecule[17] are almost isotropic and far higher than those of $K_2Zn[Cu]F_4$, or almost all other copper(II) complexes, clearly implying a significant unpaired spin density in the copper 4s orbital. The g_{xy} value of 2.601 suggests an orbital contribution $\mu = 0.112$ for CuF$_2$, yielding "best fit" estimates of the hyperfine constants $A_z = 684 \times 10^{-4}$ cm^{-1} and $A_{xy} = 657 \times 10^{-4}$ cm^{-1} using a value of $K = -1.5$. This implies an occupancy of the 4s orbital of $\sim 33\%$, some 10 times that in $K_2Zn[Cu]F_4$. Simple theory suggests that the $3d_{z^2}/4s$ mixing coefficient in tetragonally distorted complexes is proportional to the difference in metal–ligand bonding between the axial and in-plane ligands,[26] so that a significantly greater 4s participation is indeed expected for the linear CuF$_2$ molecule compared with the axially compressed CuF$_6^{4-}$ ion.

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Redox Reactivity of Photogenerated Cr(CO)$_5$ Species: Formation of [Cr^{III}(o-semiquinone)$_3$] Complexes

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The mechanism of the formation of [Cr^{III}(o-semiquinone)$_3$] complexes by complete photochemical oxidative substitution of Cr(CO)$_6$ with o-quinones (o-chloranil, 3,5-di-*tert*-butyl-1,2-benzoquinone) was studied by both stationary and flash photolysis in aromatic hydrocarbon solvents. The photogenerated coordinatively unsaturated Cr(CO)$_5$ species was found to undergo a rapid oxidative addition of the o-quinone molecule, resulting in a strong labilization of Cr–CO bonds and launching a series of very fast reactions that ultimately produce the CO-free Cr(III) complex [Cr(o-semiquinone)$_3$]. The rate of its formation was found to be determined by the rate of the solvent molecule dissociation from the primary photoproduct, the Cr(CO)$_5$(solv) species, producing the reactive Cr(CO)$_5$ intermediate; $k_1 = 1.1 \times 10^{-5}$ s^{-1}. Prospects of oxidative substitutions of group VIB (6) metal carbonyls are briefly discussed.

Introduction

Chromium hexacarbonyl, Cr(CO)$_6$, is a well-known coordinatively saturated and substitution-inert compound, which can be only hardly oxidized or reduced at rather extreme values of electrode potentials: $E_p^{Ox} = +1.53$ V, $E_p^{Red} = -2.66$ V (vs. SCE, measured in tetrahydrofuran), respectively.[1]

Cr(CO)$_6$ is well-known to undergo fast photochemical substitutions with Lewis bases in solution producing, Cr(CO)$_5$L or Cr(CO)$_4$L$_2$ complexes.[2,3] Photosubstitution of more than two CO ligands is very difficult[4] and occurs only with some fluorophosphines under prolonged irradiation[4] (often for several days or even weeks). All hitherto described solution photosubstitutions of Cr(CO)$_6$ take place without any change of the oxidation state of the chromium central atom.

Recently, we have described[5] a photochemical synthesis of [Cr^{III}(o-semiquinone)$_3$] complexes by irradiation of mixtures of Cr(CO)$_6$ and the appropriate o-quinone, particularly o-chloranil, in benzene solution. This reaction represents not only a convenient

preparative method but also a very interesting mechanistic problem. It is a unique process among the huge amount of simple photosubstitutions of one or two CO ligands in Cr(CO)$_6$, as all six CO ligands are very readily replaced by three quinone molecules, which are reduced to corresponding semiquinone radical anions, whereas the Cr(0) central atom is concomitantly oxidized to the oxidation state III. This reaction represents a new type of Cr(CO)$_6$ reactivity, which can be described as a *complete photochemical oxidative substitution.*

Elucidation of its mechanism may thus afford a better understanding of the reactivity of group VIB (6)[42] metal carbonyls which are now often employed as photocatalysts.[6,7]

We have thus undertaken a mechanistic study of the photochemical reaction between Cr(CO)$_6$ and various o-quinones

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