probably due to the highly allowed $4f^7$ to $4f^65d^1$ transition which is typical for Eu^{2+} compounds.[9] There are some differences between the spectra of $Eu_{0.99}WO_4$ and the mixed-valence species. For $Eu_{0.99}WO_4$ the main absorption band is split with maxima at about 350 and 470 nm while the bands for the two solid solutions are not. Also the strong absorption falls off much more rapidly at long wavelengths for $Eu_{0.99}WO_4$ than for the mixed-valence compounds. It is possible that these differences are simply due to the different crystal fields at Eu^{2+} in the "pure" Eu^{2+} phases and the mixed-valence phases as the $4f^7$ to $4f^65d^1$ transition is very sensitive to crystal fields.[9] For the mixed-valence phases one would expect a distribution of low-symmetry crystal field components due to the existence of cation vacancies and Eu^{3+} ions in the lattice which would broaden the Eu^{2+} absorption over that for a pure Eu^{2+} phase. Not shown in Figure 4 are the infrared spectra of the Eu_xWO_4 phases which consisted of only three very weak bands at about 1830, 1960, and 2050 nm, which were also found in the spectrum of $Eu_2(WO_4)_3$ and are attributed to the Eu^{3+} ion. These spectra show little unambiguous evidence for mixed-valence absorptions in Eu_xWO_4.

In summary bulk magnetic and optical absorption data on the mixed-valence compounds Eu_xWO_4 show no clear evidence for extensive electron transfer or indeed any degree of electron transfer between Eu^{2+} and Eu^{3+} in spite of crystallographic data[4] which suggests that both ions occupy the same site in the scheelite structure.

Further measurements on these compounds should involve properties such as electrical resistivity and luminescence spectra which are also expected to be quite sensitive to electron transfer in order to determine more precisely the extent of mixed-valence interaction between Eu^{2+} and Eu^{3+}. It is possible that more detailed crystallographic work will reveal slightly different coordination environments for Eu^{2+} and Eu^{3+} in Eu_xWO_4.

However, it is also possible that the application of the Robin and Day criteria to mixed-valence lanthanide compounds is not quite so straightforward as in the case of mixed-valence compounds of the d-group elements. Referring to the notation of ref 5, the matrix element, V, which mixes the wave functions of the two oxidation states on different lattice sites sites will be very much smaller for 4f-group compounds than for d-group compounds owing to very small overlap between the 4f wave functions on adjacent sites compared to that of d wave functions. Thus, a mixed-valence lanthanide compound may exhibit very limited electron-transfer effects in spite of the fact that the two oxidation states are present in nearly equivalent sites, $E_1 \simeq 0$, because the matrix element, V, is also very small.

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Registry No. $EuMoO_4$, 22206-17-3; $EuWO_4$, 13537-12-7; Eu_xMoO_4, 58384-31-9; Eu_xWO_4, 58384-32-0.

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(8) Although it is well-known that the susceptibility of Eu^{3+} can deviate considerably from free-ion behavior, we are justified in ignoring such deviations. This is because the contribution of Eu^{3+} to the total susceptibility is very small, never greater than 6%, for all of the compositions studied in the temperature range of interest. If, for example, the deviation from free-ion behavior is as large as 40% (which is true for Eu_2O_3, the worst case known to us), the uncertainty introduced into the total, theoretical susceptibility is only 2.4% while the experimental uncertainty is estimated at 2–3%.
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Oxygen-17 Superhyperfine Tensor in Copper(II) Acetylacetonate

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Superhyperfine interactions, as measured by ESR studies, can in principle reveal details of the electron distribution in the neighborhood of ligand atoms. In practice the number of ligands for which complete hyperfine tensors have been measured is small and most of the published data refer to nitrogen. The low value of $\langle r^{-3} \rangle$ for ^{14}N results in a comparatively small anisotropic tensor and most ^{14}N superhyperfine tensors in the literature are nearly isotropic, with a consequent large uncertainty in the estimated population of the 2p orbital. For ^{14}N atoms which are incorporated in organic ligands the hybridization is usually assumed to be sp^2, whether the full tensor is available or not. Recently the ^{17}O and ^{14}N tensors have been measured in a single-crystal study of copper(II) hydroxyquinolate.[1] The ^{14}N tensor had been studied previously but the anisotropic component of the tensor appears to have been disregarded and the hybridization taken as sp^2. The ^{17}O tensor was not analyzed in terms of orbital populations. Due to a larger gyromagnetic ratio and higher nuclear spin ^{17}O splittings are generally larger and more accurately measurable than corresponding ^{14}N splittings and can provide more reliable estimates of hybridization. Recently ^{17}O superhyperfine interactions have been studied in a transition metal hydrate[2] and in oxide lattices.[3] In the present work we report the results of an ESR study in solution and in frozen solution of copper acetylacetonate enriched to 30 atom % in ^{17}O.

The ESR spectrum of isotopically normal Cu^{II}acac was reported by McGarvey and Maki[4] and the **g** and Cu hyperfine tensors were found to be effectively axial. This is consistent with the near-D_{4h} symmetry of the CuO_4 unit as ascertained by x-ray structure analysis,[5] which gives an O–Cu–O bond angle of 93.5°, for the angle "outside" the chelate ring.

Experimental Section

^{17}O-enriched water was purchased from Yeda (Rehovot, Israel) and ^{63}Cu (99.9 atom %) from Oak Ridge National Laboratory, Oak Ridge, Tenn. Acetylacetone enriched to ~30% in ^{17}O was prepared by exchange with $H_2{}^{17}O$ (~35 atom %) in the presence of ~0.01 M $HClO_4$. Exchange is effectively complete within several minutes at room temperature.[6] Addition of anhydrous copper (^{63}Cu) sulfate was followed by sodium bicarbonate to bring the pH to the alkaline range and by chloroform–toluene (1:1) to extract the complex. The resulting blue solution was dried over sodium sulfate. Spectra, in solution and in frozen solution, were taken at X band with a Varian V-4502 ESR spectrometer equipped with a variable-temperature accessory.

Spectra and Results

Solution. The X-band ESR spectrum of ^{17}O-enriched cupric acetylacetonate in chloroform–toluene (1:1) at room temperature is shown in Figure 1. The strong, and well-known, m_I dependence of the ^{63}Cu hyperfine lines results in a very

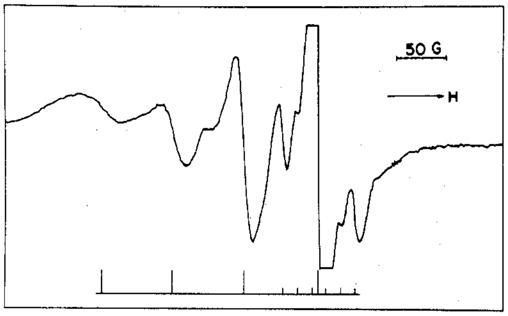

Figure 1. The X-band ESR spectrum of ^{17}O-enriched cupric acetylacetonate in chloroform–toluene (1:1) at room temperature.

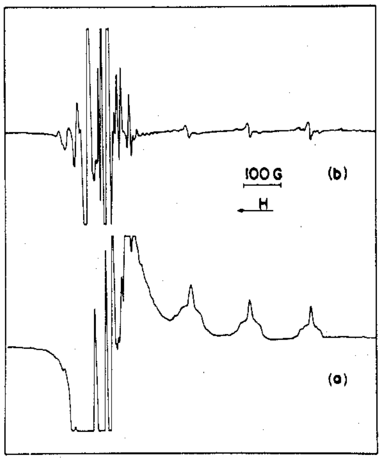

Figure 2. (a) First-derivative X-band ESR spectrum of a frozen solution of ^{17}O-enriched $^{63}Cu^{II}$acac in chloroform–toluene (1:1) solution, at ~−100 °C. (b) Second-derivative X-band ESR spectrum.

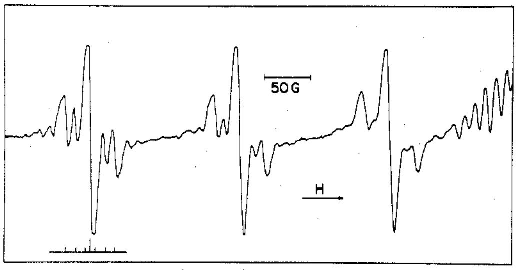

Figure 3. Low-field part of the spectrum in Figure 2(b) at higher gain.

asymmetric spectrum. At higher temperatures the spin-rotational contribution to the line widths becomes dominant, and although the spectrum becomes more symmetrical, the line widths are larger and it is more difficult to identify the ^{17}O satellites. The isotropic ^{17}O splitting a_O was estimated to be 15±1 G.

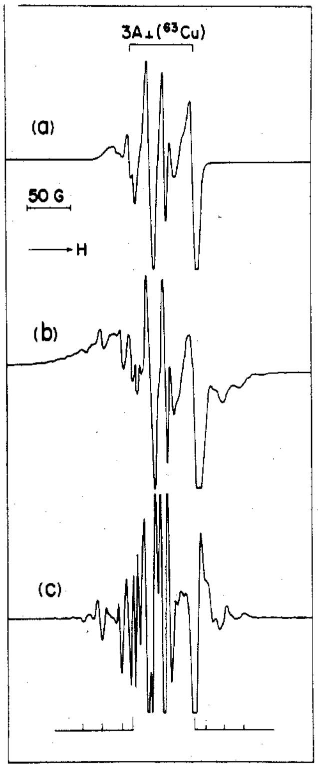

Figure 4. (a) High-field part of the spectrum in Figure 2(a) without ^{17}O enrichment. (b) High-field part of the spectrum in Figure 2(a). (c) Second derivative of the spectrum in Figure 4(b).

Frozen Solution. The first-derivative X-band ESR spectrum of a frozen solution of ^{17}O-enriched cupric acetylacetonate in chloroform–toluene is shown in Figure 2a, and the second-derivative spectrum in Figure 2b. The low-field part of the second-derivative spectrum is shown in Figure 3, in which it can be seen clearly that the hyperfine structure associated with $g_\parallel$ is a superposition of a single line due to isotopically normal molecules and accompanying ^{17}O satellites, as indicated in the stick diagram. ^{17}O satellites are also easily identified in the region of the $g_\perp$ absorption as can be seen from Figure 4. At high gain satellites due to molecules containing two ^{17}O atoms were readily observable. As mentioned above, the **g** tensor is effectively axial and we can thus take the largest principal value of the ^{17}O tensor to be collinear with one of the principal axes of the **g** tensor. The complex is also very nearly planar and we therefore take the other principal values of the ^{17}O tensor to be in, and perpendicular to, the molecular plane. These considerations allow the powder spectrum to be interpreted in a straightforward manner. The ^{17}O splittings associated with $g_\parallel$ can be assigned to $A_z(^{63}Cu)$ where the z axis is perpendicular to the molecular plane. The measured values for the ^{17}O tensor are $A_O(g_\perp) = 24 \pm 1$ G and $A_O(g_\parallel) = 10 \pm 1$ G.

Discussion

The observed powder and solution ^{17}O splittings are compatible with the tensor −24, −10, −10 G where the negative sign is a consequence of the negative gyromagnetic ratio of the ^{17}O nucleus; the error is estimated at ±1 G for all values. Ammeter at al.[1] found $-25.5, -10.9, -10.2 \times 10^{-4}$ cm^{-1} for the ^{17}O tensor in copper(II) hydroxyquinolate. The isotropic splitting measured in the present work unambiguously fixes the relative signs of the tensor element. In both studies the tensors are consistent with unpaired spin in an antibonding σ orbital between copper and oxygen atoms, confirming the usual qualitative description of the bonding. In the hydroxyquinolate the principal axes of the ^{17}O tensor were not collinear with those of the **g** tensor,[1] but the distortion from D_{4h} symmetry is more pronounced than for Cu^{II}acac. Powder spectra do not allow the direct determination of the directions of principal axes, but as stated above we assume near collinearity of the **g** and ^{17}O tensors on the basis of the geometry of the complex.

The contribution of the oxygen 2s and 2p orbitals to the σ^* orbital is estimated by taking $|\chi_{1s}(O)|^2 = 1660$ G and $2\beta(^{17}O) = 103$ G,[7] which leads to $f_{2s} = 0.009$, $f_{2p} = 0.1$ and $f_{2s}/f_{2p} \approx 1/10$. These figures apply equally to the hydroxyquinolate complex and can be compared with those obtained previously[2] for the $Cu^{II}(H_2O)_6$ complex: $f_{2s} = 0.0085$ and $f_{2p} = 0.047$, averaged over the equatorial oxygens, give $f_{2s}/f_{2p} \approx 1/5$. The distant dipolar contribution was taken into account in obtaining the latter figures but was small and will be smaller in the case of the organic complexes since the spin density on the metal ion is smaller. Thus, although this contribution could increase the ratio 2s:2p (f_{2s}/f_{2p}), we estimate that the maximum value for the ratio is 1/9. The above analysis assumes that the ^{17}O tensor is entirely accounted for by spin in the σ^* antibonding orbital. In principle the ground state will involve admixture of the $3d_{z^2}$ orbital and consequently out-of-plane π bonding can introduce spin into the out-of-plane 2p oxygen orbital. This would result in a deviation from axiality although distant dipolar interaction with the spin on the metal ion can also contribute. Both of these effects are certainly small in our case and we take the 2s:2p ratio to be directly indicative of the hybridization at the oxygen atom.

The strong deviation from sp^2 hybridization is in contrast to the generally accepted approximation. The σ^* orbital contains very little contribution from $2s_O$. If the ^{14}N tensor for copper(II) hydroxyquinolate[8] is analyzed in terms of its isotropic and anistropic parts, a value of 1/10 is found for the 2s:2p ratio, although the authors preferred to use the value of f_{2s} alone, and then assumed sp^2 hybridization to arrive at the values of α^2 and α'^2, the MO coefficients for the σ^* orbital. In $Cu^{II}(H_2O)_6$, the σ^* bond has a smaller relative contribution from $2p_O$.

In the σ^* orbital, the oxygen atoms are therefore represented almost entirely by the $2p_O$ orbital, with a very minor part played by the $2s_O$ orbital. The σ^* bond in the $Cu^{II}(H_2O)_6$ complex is probably less covalent than that in the organic complexes.

For manganese(III) acetylacetonate the measured ^{17}O NMR contact shifts were used[9] to give a maximum value of 0.0059 for f_s, considerably lower than f_s for Cu(acac). However the solution NMR results do not give the $2p_O$ contribution and so a comparison of covalency is not possible.

The observed ^{17}O tensor can be used to derive the coefficients α' and α in the MO containing the unpaired electron.[10] Using the values given by Smith[11] for $p\sigma$–$d_{x^2-y^2}$ metal–oxygen overlap integrals we find $\alpha'^2 = 0.43$ and $\alpha^2 = 0.76$. The value for α^2 is in excellent agreement with that derived from analysis of the **g** and ^{63}Cu hyperfine tensors.[10]

It is interesting to analyze the present results by the method of McMillan and Halpern.[12] Putting $A_\parallel = K + T_\parallel$ and $A_\perp = K + T_\perp$ for the metal ion hyperfine tensor, they wrote the contact term K as

$$K = \alpha^2 K_O + (1 - \alpha^2) K_L \tag{1}$$

where $K_O = \langle \chi_O | \hat{K} | \chi_O \rangle$, $K_L = \langle \chi_L | \hat{K} | \chi_L \rangle$, $\hat{K}$ is the polarization operator, and the antibonding MO containing the unpaired electron is $|\chi\rangle = \alpha|\chi_O\rangle - \beta|\chi_L\rangle$. In our case χ_O is the $3d_{x^2-y^2}$ orbital of copper and χ_L an sp^n hybrid on oxygen, where $n \approx 9$. From an analysis of many ESR data on Cu^{2+} complexes, McMillan and Halpern arrived at the values $K_O = 204$ kG and $K_L = 63$ kG with a standard error of ~22 kG. Using these values and that obtained here for α we find $K = 133$ kG. We now use these figures to obtain estimates of $A_\parallel$ and $A_\perp$ from the equations

$$\begin{aligned} A_\parallel &= K + (\Delta g + (3/7)\Delta g - 4/7)\Omega\langle r^{-3}\rangle \\ A_\perp &= K + (\Delta g - (3/14)\Delta g + 2/7)\Omega\langle r^{-3}\rangle \end{aligned} \tag{2}$$

where $\Omega\langle r^{-3}\rangle$ is estimated at 1194 MHz. Substituting the experimental g values, we find $A_\parallel = 1.87 \times 10^{-2}$ cm^{-1} and $A_\perp = -0.30 \times 10^{-2}$ cm^{-1}. These predictions can be compared with the experimental Cu hyperfine tensor, $A_\parallel = 1.60 \times 10^{-2}$ cm^{-1} and $A_\perp = 0.19 \times 10^{-2}$ cm^{-1}.

Acknowledgment. We thank the United States–Israel Binational Science Foundation for support.

Registry No. Cupric acetylacetonate, 13395-16-9; ^{17}O, 13968-48-4.

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Mechanism and Equilibrium Constants of the Reaction of Formation of (π-PhCH=CHCOR)Fe(CO)$_3$SbPh$_3$ from (π-PhCH=CHCOR)Fe(CO)$_3$ and SbPh$_3$

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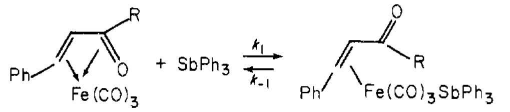
The formation of (π-R'CH=CHCOR)Fe(CO)$_3$L complexes from (π-R'CH=CHCOR)Fe(CO)$_3$ and the ligands L = MR$_3$ (M = P, As, Sb; R = H, Me, Ph) has been reported.[1,2]. Since the first step of the substitution reaction is much slower than the second one,[3,4] this type of reaction was not previously observed for other π-diene complexes. Only for polydentate ligands having well-separated nucleophilic atoms have partial substitution reactions been described.[5]

The present work describes the mechanism of the substitution of the heterodiene ligand in (π-PhCH=CHCOR)-Fe(CO)$_3$ by SbPh$_3$, as shown in reaction 1.



(1)

Experimental Section

The (π-PhCH=CHCOR)Fe(CO)$_3$ (R = H, Me, Ph) complexes were prepared as described in the literature.[6,7] Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer.

Preparation of Complexes. The reaction between (π-PhCH=CHCOR)Fe(CO)$_3$ and SbPh$_3$ leads to considerable accumulation of (π-PhCH=CHCOR)Fe(CO)$_3$SbPh$_3$ but does not go to completion. For L = SbPh$_3$ and temperatures lower than 20 °C, no further reactions were observed during handling. The preparation and purification of the products of reaction 1 were as follows. (π-PhCH=CHCOR)Fe(CO)$_3$ (0.5 g) and SbPh$_3$ (0.5 g) were dissolved in 10 ml of degassed acetone (RS grade, Carlo Erba). After 3 h of standing there was no further reaction. The solution was evaporated to dryness and the residue was chromatographed on neutral Al$_2$O$_3$ using 2:3 (v/v) dichloromethane–n-hexane as eluent. Two colored bands were observed, the faster corresponding to unreacted (π-PhCH=CHCOR)Fe(CO)$_3$ and the other to the product (π-PhCH=CHCOR)Fe(CO)$_3$SbPh$_3$. When the bands were well separated, the chromatography column was broken and the product recovered by extraction with acetone and evaporation to dryness. It was further purified by recrystallization from a dichloromethane–n-hexane mixture at −20 °C. During manipulations the solvents were maintained at <10 °C to avoid re-formation of initial reagent.