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Dynamic Behavior of the Adduct of Copper(II) Bis(hexafluoroacetylacetonate) with a Bidentate Complex Ligand

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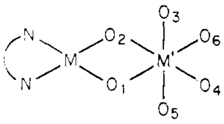
The single-crystal EPR and electronic spectra of $Ni(prp)_2enCu(hfa)_2$ have been recorded between 4.2 K and room temperature. Both have been found to be temperature dependent. In particular the EPR spectra show increasing g and A values on lowering the temperature from 295 to 77 K. At lower temperatures the spectra become much broader, with no copper hyperfine structure resolved, and have a different pattern of g values. The data have been interpreted on the basis of a pseudo-Jahn–Teller distortion. The low-temperature data have been tentatively related to the effects of strong cooperative interactions.

Introduction

The base adducts of copper(II) bis(hexafluoroacetylacetonate), $Cu(hfa)_2$, have attracted a large interest in the last few years[1-8] since in several cases dynamic behaviors attributable to Jahn–Teller or pseudo-Jahn–Teller effects have been detected even when the parent symmetry is much lower than octahedral.[1,2,5]

Fackler has shown how in the EPR spectra of the cis bis(pyridine) adduct the g values are temperature dependent when it is doped into the zinc lattice.[2] Since in the latter the ZnO_4N_2 chromophore is tetragonally compressed,[1] while CuO_4N_2 is elongated, the dynamic behavior was attributable to the effect of axial compression on the copper ion, apparently produced by crystal-packing forces. A similar behavior was observed also in the 1,1′-bipyridine adduct[5] $Cu(hfa)_2bpy$, and Hathaway suggested the possibility of some fluxional behavior in the tris chelate $(C_{14}H_{19}N_2)Cu(hfa)_3$.[9]

Recently we became interested[10,11] in the magnetic resonance spectra of bis(hexafluoroacetylacetonato)[*N,N′*-ethylenebis(2-hydroxypropiophenoniminato-*N,O*(2−))M(II)]M′(II),[3] $M(prp)_2enM'(hfa)_2$ (M = Cu, Ni; M′ = Cu, Ni, Co, Mn). In these dinuclear complexes the metal M is in a square-planar environment, while the M′ metal is in a distorted octahedral coordination[3]



In one sense these complexes can be considered as adducts of $M'(hfa)_2$ with the bidentate complex ligand $M(prp)_2en$.[12]

We have found that the EPR and the electronic spectra of $Ni(prp)_2enCu(hfa)_2$ are temperature dependent and wish to report here the results of an investigation of the spectral properties of single crystals in the range 4.2–300 K with the aim of relating the observed temperature dependence with structural variations.

Experimental Section

$Ni(prp)_2enCu(hfa)_2$ was prepared as previously described.[3] $Ni(prp)_2enZn(hfa)_2$ was prepared following the same procedure. Single crystals were grown by slow evaporation of dichloromethane/methanol solutions.

The crystals have been characterized crystallographically with a Philips PW 1100 automatic diffractometer.

EPR spectra at X- (9 GHz) and Q-band (35 GHz) were recorded with a Varian E-9 spectrometer equipped with a variable-temperature accessory. X-band spectra at 4.2 K were obtained with an Oxford Instrument ESR 9 continuous-flow cryostat.

Results

Although in the preparation of the complexes we followed the procedure previously described,[3] we were not able to obtain crystals that conformed to the reported crystal structure. As a matter of fact, we obtained crystals that were found to belong to the space group $P1$, with cell dimensions a = 12.946, Å, b = 12.646 Å, c = 11.062 Å, α = 109.4°, β = 91.4°, and γ = 97.1°, while the cell dimensions previously reported were a = 10.484 Å, b = 12.446 Å, c = 13.766 Å, α = 91.00°, β = 92.60°, and γ = 110.73°. Although the two cells have almost the same volume, they cannot be transformed one into the other, as checked with standard crystallographic programs, so that it must be concluded that they are different.

On the other hand, we obtained also monoclinic crystals, which were found to belong to the $P2_1/c$ space group, with cell dimensions a = 13.548 Å, b = 20.077 Å, c = 12.504 Å, and β = 97.96°. From comparison of these values with those reported for other complexes in the series,[3] namely, M = Ni, M′ = Co, Ni and M = Cu, M′ = Co, Ni, Cu, it is apparent that our crystals are isomorphous with all the others and presumably also isostructural.

The polycrystalline powder EPR spectra of $Ni(prp)_2enCu(hfa)_2$ are shown in Figure 1. The spectra obtained by grinding the triclinic crystals are, within experimental error, identical with those of the monoclinic crystals. The room-temperature spectra, although not unexpectedly rather broad, show a well-resolved copper hyperfine splitting. The spin Hamiltonian parameters are $g_1 = 2.37$, $A_1 = 89 \times 10^{-4}$ cm^{-1}, $g_2 = 2.13$, and $g_3 = 2.07$. When the temperature is lowered to $T \sim 140$ K, the spectra sharpen up and also the spin Hamiltonian parameters vary, being $g_1 = 2.39$, $A_1 = 118 \times 10^{-4}$ cm^{-1}, $g_2 = 2.09$, and $g_3 = 2.06$. Decreasing further the temperature determines again a severe broadening of the lines and washes out the copper hyperfine splitting. At 4.2 K a broad spectrum is observed that can be interpreted with $g_\parallel$ = 2.08, and $g_\perp$ = 2.27.

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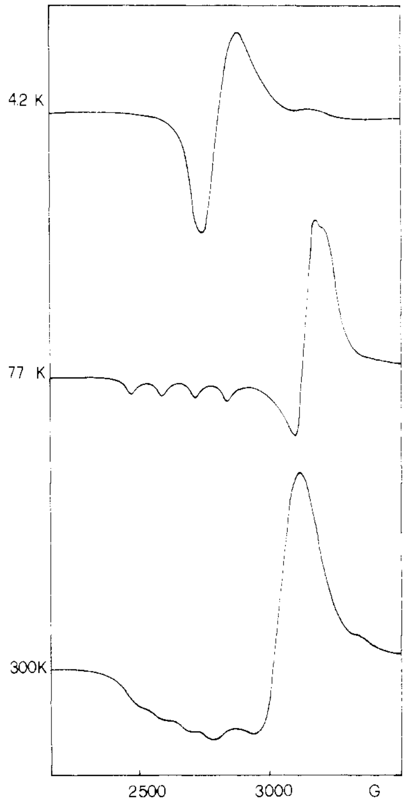

Figure 1. Polycrystalline powder EPR spectra of Ni(prp)$_2$enCu(hfa)$_2$ at various temperatures.

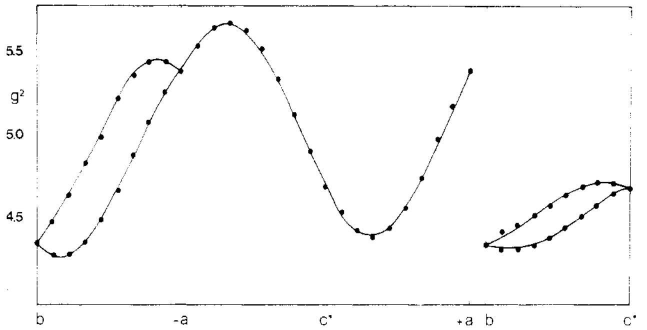

Figure 2. Angular dependence of the g^2 values in single crystals of the monoclinic form of Ni(prp)$_2$enCu(hfa)$_2$.

The X-band spectra are similar to the Q-band ones, although the lines appear to be much narrower in the former case.

In order to have a check of the spectra of Ni(prp)$_2$enCu(hfa)$_2$ in a diamagnetic lattice, we also prepared Ni(prp)$_2$enZn(hfa)$_2$ and doped it with the Ni–Cu complex. The EPR spectrum at room temperature in this case is dominated by a species with $g_{\parallel} = 2.18$, $g_{\perp} = 2.07$, $A_{\parallel} = 200 \times 10^{-4}$ cm^{-1}, $A_{N\parallel} = 17 \times 10^{-4}$ cm^{-1}, and $A_{N\perp} = 17 \times 10^{-4}$ cm^{-1}. The g and A values and the nitrogen hyperfine clearly show that some Cu(prp)$_2$enZn(hfa)$_2$ complex was also formed. Similar results had previously been reported for Co(SAL)en and Cu(hfa)$_2$.[6] The spectrum at 4.2 K is different, the main features corresponding to $g_1 = 2.40$, $A_1 = 118 \times 10^{-4}$ cm^{-1}, $g_2 = 2.10$, and $g_3 = 2.06$. The room-temperature spectrum is still present, but its relative intensity is not more than approximately 10–12% of the other.

The single-crystal spectra could not be recorded at room temperature since the lines are too broad to be detected in small crystals. At 77 K the spectra are sharp enough and the data were collected for both the triclinic and the monoclinic crystals. The angular dependence of the g^2 values for the monoclinic form is shown in Figure 2. The principal g and A values were obtained with the usual Schonland analysis.[13]

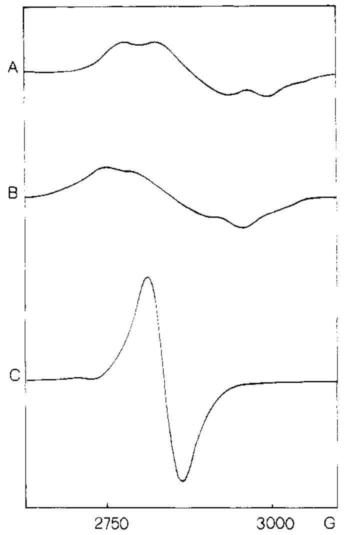

Figure 3. Representative spectra of Ni(prp)$_2$enCu(hfa)$_2$, triclinic form at 4.2 K. All the spectra refer to the rotation along the y laboratory axis: A, $\alpha = 40°$; B, $\alpha = 70°$; C, $\alpha = 130°$.

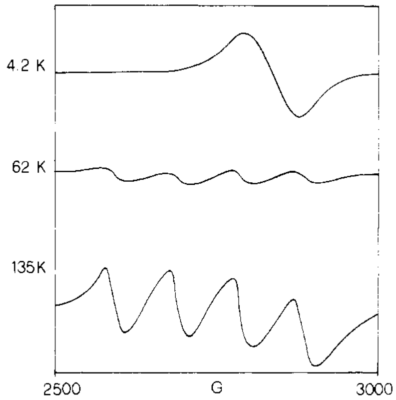

Figure 4. Temperature dependence of the single-crystal EPR spectra of Ni(prp)$_2$enCu(hfa)$_2$, monoclinic form.

At 4.2 K only disappointingly broad signals were detected, and it was impossible to record Q-band spectra for both the triclinic and the monoclinic crystals. Also at X-band frequency it was not possible to analyze the spectra meaningfully. Some representative spectra are shown in Figure 3. There is some evidence that more than one site is formed even for the triclinic crystal. In some orientations the signal sharpens up a bit and in this case one g value of 2.28 is seen.

The temperature variation of the single-crystal spectra of the monoclinic crystal is shown in Figure 4. The angular setting corresponds to the direction along which the maximum g value is observed in the rotation around the y laboratory axis. At high temperature the lines are reasonably narrow, the peak-to-peak width being 3 mT, with $g = 2.35$ and $A = 10$ mT. On cooling the lines broaden and below about 30 K one signal at $g = 2.27$ appears, showing no hyperfine splitting, whose peak-to-peak width is 85 mT. At 4.2 K the signal shows some splitting, and also a satellite at lower field shows up clearly. A similar behavior is observed on warming the crystal.

The diffuse-reflectance spectra of Ni(prp)$_2$enCu(hfa)$_2$ are shown in Figure 5. At room temperature a very broad absorption is present with a maximum at 9100 cm^{-1} and a second peak is at 13 200 cm^{-1}. When cooled to 100 K, the unique band in the near-infrared region splits yielding a maximum at 7400 cm^{-1} and a smaller absorption at 10 200 cm^{-1}, while

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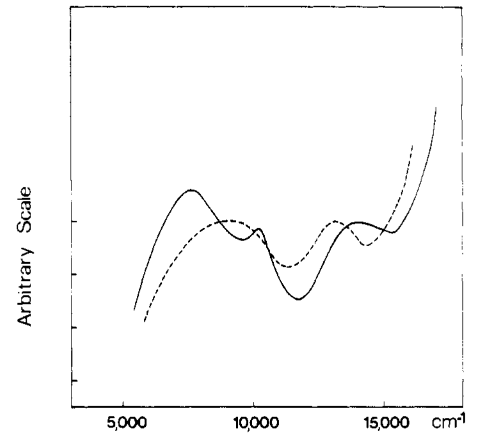

Figure 5. Diffuse-reflectance spectra of $Ni(prp)_2enCu(hfa)_2$ at various temperatures: ---, room temperature; —, 100 K.

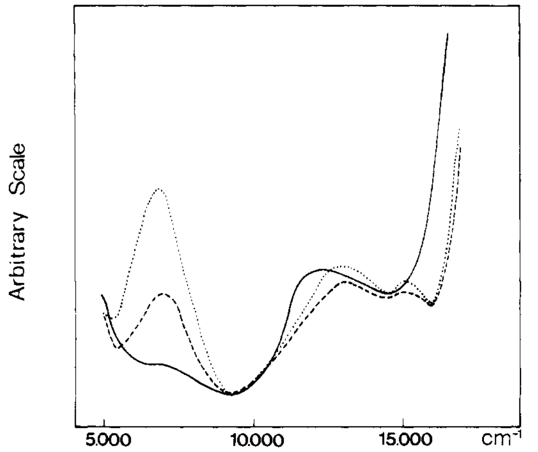

Figure 6. Single-crystal electronic absorption spectra of $Ni(prp)_2enCu(hfa)_2$ at various temperatures: —, room temperature; ---, 77 K; ···, 4.2 K. The incident light is perpendicular to the (010) face.

the higher frequency peak moves to 13 900 cm^{-1}.

We recorded also single-crystal spectra with the incident radiation perpendicular to the (010) face at room temperature and at 4.2 K. They are shown in Figure 6. Also in this case a very broad absorption is present at low frequencies at room temperature with a second peak at 12 500 cm^{-1}. When the temperature is lowered, there is a marked increase in the absorption at 7000 cm^{-1}, while in the higher frequency region two peaks are found at 13 200 and 15 100 cm^{-1}.

Discussion

The temperature dependence of the electronic and EPR spectra is indicative that some distortion is occurring in the coordination sphere of the copper(II) ion. According to the behavior reported for other cis adducts of $Cu(hfa)_2$,[1,2,5] fluxional distortions may be operative as a consequence of pseudo-Jahn–Teller interactions.[14,15] The main difference of the present case with those previously reported is that now the compound under scrutiny is a pure copper complex, while previously fluxional behavior had been noticed only on copper-doped zinc complexes and the fluxionality had been attributed to the axial strain exerted by the zinc lattice in which the metal ion is tetragonally compressed.

Although we were not able to obtain the triclinic crystals for which structural data are available, we are inclined to think that the structure is not much dissimilar from that; i.e., the copper ion is in a distorted octahedral environment. The extent of the distortion is not easy to predict, but again the observed dynamic behavior makes us believe that the room-temperature structural parameters must not be far from those reported for the triclinic crystals. A comparison with the reported structures of cis adducts of $Cu(hfa)_2$ with bidentate complex ligands[3,7,8] shows that in general the $Cu–O_2$ bond corresponds to the longest distance seen in the chromophore (240–250 pm), the second longest being 221–227 pm. The remaining four copper–oxygen bond lengths are similar to each other (average 197–199 pm). In the reported triclinic structure of $Ni(prp)_2enCu(hfa)_2$[3] on the other hand, the longest copper–oxygen bond, $Cu–O_2$, is sensibly longer than the other Cu–O bonds (208 vs. 194–196 pm).

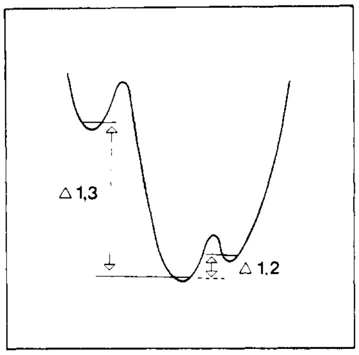

Figure 7. Schematic section of the potential energy surface associated with the three Jahn–Teller valleys in $Ni(prp)_2enCu(hfa)_2$.

If we apply to these complexes the analysis suggested by Ammeter and Burgi,[13] we find that the Jahn–Teller radii, R_{JT}, for $Cu(SAL)enCu(hfa)_2$[7,8] and $Cu(prp)_2enCu(hfa)_2$[3] are 476 and 512 pm, respectively, while it is only 281 pm for $Ni(prp)_2enCu(hfa)_2$. Since it has been suggested, and experimentally verified,[16,17] that R_{JT} should remain approximately constant in different lattices, we feel that the shorter R_{JT} calculated for $Ni(prp)_2enCu(hfa)_2$ is indicative of dynamical Jahn–Teller features.

The structural data suggest that the Jahn–Teller-distorted potential surface shown in Figure 7 may be considered for $Ni(prp)_2enCu(hfa)_2$. The well-known Mexican hat shows three nonequivalent minima, the lowest one corresponding to an elongation along the $Cu–O_2$ direction, the second highest minimum corresponding to an elongation along the $Cu–O_1$ bond. The third minimum, which corresponds to an elongation along the $Cu–O_3$ direction must be at higher energy as shown by the fact that the copper–oxygen bonds along the direction have the same length as in the case of the more distorted chromophores. A similar potential energy curve was suggested for the copper-doped zinc Tutton's salts.[18] The estimated values of $\Delta_{1,2}$ and $\Delta_{1,3}$ were 75 and 450 cm^{-1}, respectively, in this case.

For our triclinic and monoclinic $Ni(prp)_2enCu(hfa)_2$ compounds a similar curve can be suggested on the basis of the EPR and electronic spectra. If the experimental g directions seen in the monoclinic lattice are compared with the molecular coordinates reported for the isomorphous $M(prp)_2enM'(hfa)_2$ complexes, it is found that the two g's, which are temperature dependent, are quite close to the Cu–O bridge directions (see Figure 8). In particular g_1 makes angles of 14.0° and 5.8° with the $Cu–O_2$ and $Cu–O_4$ bond directions, respectively, while g_2 makes an angle of 7.7° with $Cu–O_1$.

The pattern of g and A values is in agreement with an elongated octahedral structure,[19] the preferred elongation axis

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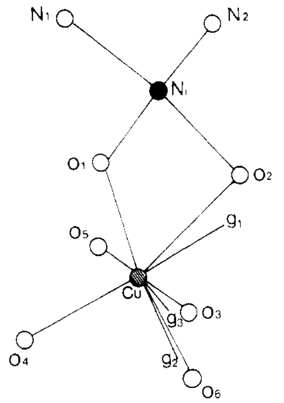

Figure 8. Orientation of **g** in the molecular frame. The molecular coordinates are those of Cu(prp)$_2$enCu(hfa)$_2$.

corresponding roughly to the Cu–O$_2$ direction. The fact, however, that g_1 and g_2 are temperature dependent indicates that at higher temperature the second minimum is populated also. Since g_2 is close to the Cu–O$_1$ direction, the second elongation direction must be along this direction.

From the temperature dependence of the g values it is possible in principle to estimate $\Delta_{1,2}$.[18,20] The data available are not accurate enough for an exact calculation, but a reasonable estimate seems to be 400 ± 100 cm^{-1}. With these figures the ratio of the populations of the two lowest minima at room temperature is 0.15 ± 0.07.

The actual g and A values seen at 77 K compare quite well with the values reported for other cis adducts of Cu(hfa)$_2$ having CuO$_6$ chromophores.[21] A comparison with the EPR spectra of Cu(hfa)$_3^-$ shows that in the present case g_1 is much larger (2.40 vs. 2.30). Although in that case no copper hyperfine structure was resolved, showing that sizeable intermolecular-exchange interactions are operative, the angle between the elongation axes of the magnetically nonequivalent molecules does not justify such a large decrease in the g values. Therefore, it seems probable that even in that case a dynamical distortion is operative, as previously suggested. Calculating R_{JT} from the reported structural data[22] for Cu(hfa)$_3^-$ one finds 208 pm, which again is much smaller than the values calculated for the fully distorted complexes.

Also the electronic spectra are in agreement with the model of a pseudo-Jahn–Teller distorted chromophore. The increase in intensity of the band at 7000 cm^{-1} on cooling may now be attributed to the increased population of the lowest potential well. For this assumption to be correct, the electronic spectra of the two complexes in the two lowest energy minima must be different, a not unreasonable assumption since in any case the symmetry of the complex is low. The low-temperature spectra can be compared to those[9] of Cu(hfa)$_3^-$, which show a peak at 7000 cm^{-1} which was attributed to the $x^2 - y^2 \rightarrow z^2$ and the 10 200 and 13 900 cm^{-1} bands to the other d–d transitions. The spectra of Cu(prp)$_2$enCu(hfa)$_2$, which is clearly elongated, show absorptions at 8000, 10 200, and 12 900 cm^{-1}.

According to the above assignment, the Jahn–Teller stabilization energy, E_{JT}, of Ni(prp)$_2$enCu(hfa)$_2$ is 1750 cm^{-1}, which compares well with the values reported for other CuO$_6$ chromophores.[14]

The data below 77 K are somewhat more puzzling. The electronic spectra show that the chromophore is not changed. The EPR spectra on the other hand are completely different from the high-temperature spectra. It is apparent that intermolecular-exchange interactions have become more important as confirmed also by the lack of resolved hyperfine splitting.[23]

The intermolecular origin of the spectral changes is confirmed by the EPR spectra of Ni(prp)$_2$enCu(hfa)$_2$ doped into the zinc complex. The spectra of this doped compound at 4.2 K are practically identical with those of the pure complex at 77 K. Unfortunately the presence of Cu(prp)$_2$enZn(hfa)$_2$ did not allow us to follow the temperature dependence in the high-temperature region. Although the structure of Ni(prp)$_2$enZn(hfa)$_2$ is not known, the similarity of the g values to those of Ni(prp)$_2$enCu(hfa)$_2$ shows that there are not large structural differences.

The $g_{\parallel}$ value of Ni(prp)$_2$enCu(hfa)$_2$ is close to the average of g_1 and g_2 as would be expected for pairs of elongated octahedra in antiferrodistortive order[15,24] affected by intermolecular-exchange interactions larger than $(g_1 - g_2)\ \mu_{\mathrm{B}}$. At Q-band frequency this corresponds to ca. 0.15 cm^{-1}. J must not be larger than this limit since the lines are not exchange narrowed as would be expected when $J >> (g_1 - g_2)\ \mu_{\mathrm{B}}$. A confirmation of this comes from the fact that the lines are much broader at Q-band than at X-band frequency.[25] The low-field feature of the powder spectra is 35 mT broad at 35 GHz and 10 mT at 9 GHz.

In principle another possibility of averaging signals is fast hopping between different distortion wells, but this seems to be unfeasible at very low temperatures.

If the above interpretation is correct it is nevertheless unclear how antiferrodistortive order of elongated octahedra can occur. As a matter of fact the EPR data at high temperature show only one site for the triclinic crystals, and for the two sites of the monoclinic crystals the axes of preponderant elongation make angles of about 20°, thus not justifying the low-temperature g values. It can only be conceived that the low-temperature cooperative effects between the elongated octahedra are turned by a phase transition. It should be assumed that the elongation along Cu–O$_1$ is stabilized in the low-temperature phase as compared to the high-temperature phase. In a similarly distorted complex,[16] an apparent inversion of the potential energy curve below and above a phase transition was observed and attributed to cooperative effects.

Acknowledgment. Thanks are due to Professor J. Reedijk for helpful discussion.

Registry No. Ni(prp)$_2$enCu(hfa)$_2$, 69120-35-0.

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