Unusual Magnetic Properties of Binuclear Copper(II) Complexes with Both Hexafluoroacetylacetone and N-Substituted Salicylaldimine in Crystals

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Abstract: A number of new binuclear copper(II) complexes of the form [$Cu_2(hfac)_2(N\text{-R-sal})_2$] were prepared, where hfac and *N*-R-sal represent hexafluoroacetylacetonate and *N*-salicylidenealkylaminate, respectively. The complex with R = *tert*-butyl was found to undergo a phase transition accompanied with drastic changes in properties at ca. −100°; in the high-temperature phase, it is brown and strongly antiferromagnetic (210 cm^{-1}), and, in the low-temperature phase, it turns green and has weak intra- and intermolecular spin-exchange interactions. Its powder ESR spectrum at 4.2°K, in which hyperfine structures were well resolved, was of a triplet-state type with the zero-field splitting due dominantly to dipolar interaction between the copper(II) pairs. The complexes with the other *N*-alkyl groups, which all have the same green color, showed various types of powder ESR line shapes according to the *N*-alkyl groups and temperature. The differences in ESR line shape were interpreted in terms of the relative energy values of zero-field splitting (~0.06 cm^{-1}) and intermolecular spin-exchange interaction. The possible structures of these binuclear complexes were discussed.

During the ESR studies of the mixed-ligand complexes of copper(II) in solution,[1] we found that a new kind of binuclear copper(II) complexes is unexpectedly formed merely by mixing bis(fluorinated-β-diketonato)copper(II) and bis(*N*-salicylidenealkylaminato)copper(II) complexes in toluene.[2] All these binuclear complexes showed triplet-state ESR spectra with the zero-field splitting due dominantly to dipolar interaction between the copper(II) pairs.[3-5] Further investigations of these systems have revealed that crystalline products are easily isolated from the concentrated equimolar mixtures of bis(hexafluoroacetylacetonato)copper(II) and any of the Schiff base complexes of the above-mentioned kind in toluene or benzene. All these products have been identified to be binuclear complexes similar to those in toluene mentioned above. This group of complexes in magnetically undiluted crystals has been found to be unusual especially in magnetic behavior, most of them having the property of undergoing phase transition at low temperatures.

Experimental Section

Materials. Bis(hexafluoroacetylacetonato)copper(II), $Cu(hfac)_2$, and ten kinds of bis(*N*-salicylidenealkylaminato)copper(II) complexes, $Cu(N\text{-R-sal})_2$, with R = H, methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl, and *n*-amyl were prepared and purified by standard methods available in the literature.[6,7]

Preparation of New Complexes. New complexes separated out as green crystals immediately after both the concentrated toluene solutions of $Cu(hfac)_2$ and $Cu(N\text{-R-sal})_2$ were mixed equimolarly. Only crystals of the complex with R = *tert*-butyl, however, were brown. Although only $Cu(N\text{-H-sal})_2$ is insoluble in toluene, the same green crystals could be isolated by stirring this insoluble complex with the concentrated toluene solution of the excess of $Cu(hfac)_2$ for several hours. All these crystalline products were identified as [Cu(hfac)(*N*-R-sal)] by elemental analysis (Table I).

Physical Measurements. Powder ESR spectra were run on a Hitachi 771 X-band ESR spectrometer in the temperature range 350–77°K and at 4.2°K. An improved insertion-type liquid helium dewar designed and constructed in our laboratory was used for ESR measurements at 4.2°K.[8] Magnetic susceptibility determinations were made by the Gouy method in the temperature range 300–90°K. Susceptibilities were corrected for diamagnetism using Pascal's constants.[9] The visible absorption spectra of the complexes in crystals were measured at room temperature on a Cary 14 spectrometer by the opal glass method using the liquid-paraffin or oily silicone suspensions of their fine powders.[10]

Results and Discussion

General Properties. Crystals of the new complexes except **9** have the same green color. Crystals of **9** are brown above ca. −100° and green below it. The visible absorption spectra of **1** and **9** in crystals at room temperature are shown in Figure 1, together with those of their starting complexes. The data of λ_{max} indicate that the energy of λ_{max} for each of the complexes, except for **9**, is between those for its starting complexes (Table I).

Of the effective magnetic moments observed at room temperature (Table I), only the one of **9** is obviously subnormal. The temperature dependence of χ_M determined for **9** (Figure 2) shows that a phase transition accompanying a break in the plot occurs at ca. −100°. The color change mentioned above was observed at this point. Figure 2 shows that **9** is apparently paramagnetic below the temperature and antiferromagnetic above it. The solid curve in the figure gives the theoretical values of χ_M calculated from the Bleaney–Bowers equation using $-2J = 210\ cm^{-1}$, $g = 2.20$, and $N\alpha = 6 \times 10^{-5}$ cgs emu.[11] This result points out that **9** in the high-temperature phase adopts a structure suitable for the copper(II) pairs to couple magnetically in a strong degree.

The powder ESR spectra of the new complexes are of particular interest, since this group of complexes in magnetically undiluted crystals shows some peculiarities in both ESR line shape and its temperature dependence, and since these peculiarities are related to a unique kind of triplet-state dicopper(II) system, as will be demonstrated below. The new complexes listed in Table I, accordingly, must actually be of the formula [$Cu_2(hfac)_2(N\text{-R-sal})_2$], bis(hexafluoroacetylacetonato)bis(*N*-salicylidenealkylaminato) dicopper(II). This is consistent with the susceptibility result of **9** mentioned above.

Powder ESR Spectra of Triplet-State Dimers. Representative powder ESR spectra for several complexes, which well cover all the powder ESR spectral patterns observed in this work, are shown in Figures 3–5. In addition, an ESR spectrum of the toluene solution of **2** at 77°K is given in Figure 4a for comparison.

The ESR spectra of **2** in toluene at 77°K and in crystals at room temperature, which are shown in Figures 4a and 4b, respectively, are similar in line shape, except for hyperfine structures. The magnetic parameters were determined

Table I. New Complexes of the Empirical Formula [Cu(hfac)(*N*-R-sal)]

R	% found (calcd) C	H	N	μ_{eff} at 20° (BM)	$\lambda_{max}{}^{a}$ (nm)	Type of powder ESR spectrum[b] 293°K	77°K
1 H	37.10 (36.89)	1.80 (1.81)	3.67 (3.59)	1.71	615 (590 sh)	AB	B
2 Methyl	38.77 (38.57)	2.07 (2.24)	3.57 (3.46)	1.75	630 (600 sh)	A	B
3 Ethyl	40.37 (40.15)	2.75 (2.65)	3.09 (3.35)	1.78	635 (600 sh)	C	C
4 *n*-Propyl	41.84 (41.62)	3.27 (3.03)	3.09 (3.24)	1.79	640 (600 sh)	B	C
5 Isopropyl	41.91 (41.62)	2.88 (3.03)	3.10 (3.24)	1.79	630 (620 sh)	C	C
6 *n*-Butyl	43.30 (43.01)	3.11 (3.38)	3.26 (3.14)	1.80	635 (600 sh)	C	C
7 Isobutyl	43.25 (43.01)	3.28 (3.38)	3.24 (3.14)	1.77	640 (600 sh)	BC	C
8 *sec*-Butyl	43.26 (43.01)	3.21 (3.38)	3.33 (3.14)	1.79	650 (620 sh)	AB	B
9 *tert*-Butyl	43.20 (43.01)	3.52 (3.38)	3.01 (3.14)	1.58	800 (750)		A
10 *n*-Amyl	44.53 (44.30)	3.70 (3.72)	2.95 (3.04)	1.72	645 (600 sh)	B	BC

[a] The λ_{max} value of Cu(*N*-R-sal)$_2$ is given in parentheses (sh = shoulder); 675 nm for Cu(hfac)$_2$. [b] The ESR spectra of Figures 4b, 4c, and 5d (corresponding to types A, B, and C, respectively) were chosen as standards for comparison. Furthermore, AB, for example, represents an intermediate between A and B in a qualitative sense.

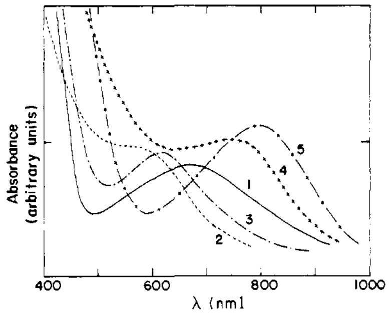


Figure 1. Visible absorption spectra in a polycrystalline state: (1) Cu(hfac)$_2$; (2) Cu(*N*-H-sal)$_2$; (3) **1**; (4) Cu(*N*-*tert*-butyl-sal)$_2$; (5) **9**.

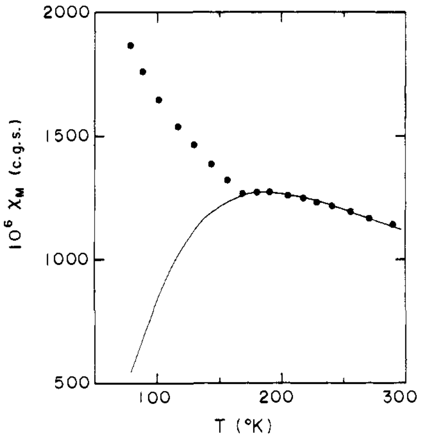


Figure 2. Temperature dependence of χ_M for **9**: ●, experimental susceptibility; solid line, calculated susceptibility.

to be $g_D = 2.170$, $|D| = 0.0642$ cm^{-1}, $|A_\perp| = 0.0073$ cm^{-1}, and $|A_\parallel| = 0.0060$ cm^{-1} in Figure 4a and $g_D = 2.18$ and $|D| = 0.064$ cm^{-1} in Figure 4b. Somewhat similar ESR spectra also have been observed for the triplet-state dimers of various Schiff-base complexes of copper(II) with $-2J \sim 2$ cm^{-1} in solutions.[4,5] Accordingly, it is characteristic of this kind of spectra that zero-field spitting is due dominantly to dipolar interaction between two copper(II) ions. The copper–copper distance, *r*, of **2** in crystals was estimated to be ~3.6 Å from the equation of $r = (0.650 g_D{}^2/D)^{1/3}$ derived by the use of a point dipole model.[3,4] The fact of $|A_\perp| > |A_\parallel|$ in Figure 4a means that the dipolar principal axes do not coincide with those of *g* and *A* tensors.[4,12] Combined with this fact, the estimated *r* value makes us predict that the copper(II) pairs of **2** in crystals are similar in structure to those of the dimers of Cu(*N*-methyl-sal)$_2$ in γ-form crystals.[13]

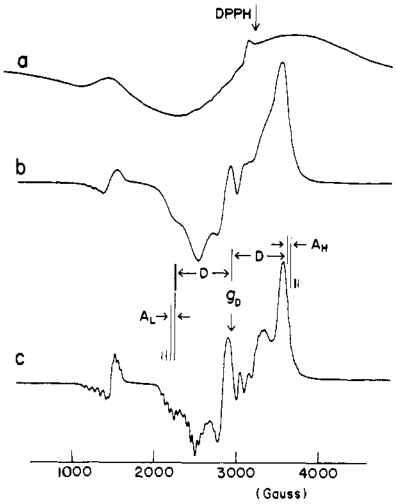


Figure 3. X-Band powder ESR spectra of **9**: (a) at 293°K; (b) at 77°K; (c) at 4.2°K.

When we consider an equilibrium of $CuA_2 + CuB_2 \rightleftharpoons 2CuAB$, the mixed-ligand complex, CuAB, has been reported to be intermediate in most properties between CuA$_2$ and CuB$_2$, where A and B represent different bidentate ligands.[1] This point of view is reminiscent of the experimental fact that all the present green complexes are intermediate in the λ_{max} value between their starting complexes. Since most of the starting complexes do not dimerize in toluene and do not adopt dimeric structures in crystals,[12,14] it is reasonably considered that the mixed-ligand complexes of the form [Cu(hfac)(*N*-R-sal)] have the ability to dimerize easily. We conclude, therefore, that **2** and the other green complexes are parallel planar copper(II) dimers of these mixed-ligand complexes, as schematically shown in Figure 6a.

The powder ESR spectra of **9** at various temperature are quite peculiar, as shown in Figure 3. The spectrum at 77°K (Figure 3b), in which hyperfine structures were slightly resolved, is similar in line shape to Figure 4a. On cooling to 4.2°K, **9** showed well-resolved hyperfine structures because of the narrowing of line width (Figure 3c). Such a phenomenon is quite rare for copper(II) complexes in magnetically undiluted crystals. Figure 3c is of a complicated and unusual type in line shape, especially in the $\Delta M = 1$ spectrum. No triplet-state ESR spectra of such a type have been analyzed by computer simulation methods with a reasonable degree of accuracy. Judging from the results so far obtained

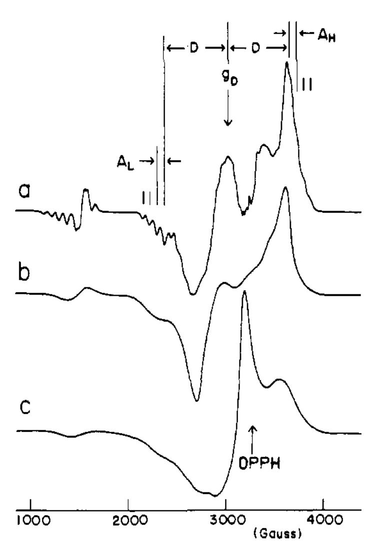


Figure 4. X-Band ESR spectra of **2**: (a) in toluene (0.01 *M*) at 77°K; (b) in polycrystals at 293°K; (c) in polycrystals at 77°K.

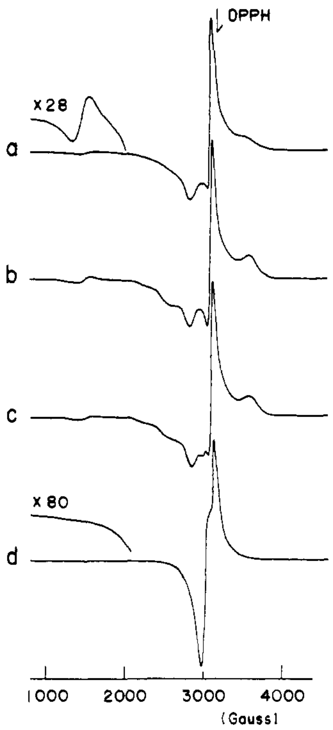


Figure 5. X-Band powder ESR spectra of **4**: (a) at 293°K; (b) at 221°K; (c) at 173°K; (d) below 153°K.

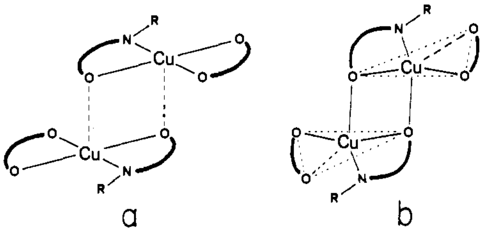
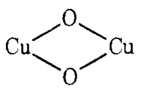


Figure 6. Schematic illustrations of estimated structures: (a) all the green complexes; (b) **9** in the high-temperature phase.

by the usual simulation methods,[3,4] it seems difficult to succeed in such analyses using those methods. The magnetic parameters in Figure 3c are as follows: $g_D = 2.204$, $|D| = 0.0692$ cm^{-1}, $|A_L| = 0.0052$ cm^{-1}, and $|A_H| = 0.0046$ cm^{-1}. The *r* value for this complex was calculated to be 3.57 Å using the point dipole model. From these ESR results and a green color, it is concluded that this complex also has a dimeric structure similar to the other green complexes.

Polycrystals of **9** in the high-temperature phase, which have an antiferromagnetic interaction of $-2J = 210$ cm^{-1}, showed a broad ESR spectrum, as given in Figure 3a. Crystals of this complex are brown; its visible absorption peak appeared at a longer wavelength than those of its starting complexes (Figure 1). As to the interpretation of its magnetic data, it should be mentioned that many binuclear complexes of copper(II) with



bridging structure, which are strongly antiferromagnetic ($-2J > 100$ cm^{-1}),[15,16] show similar broad ESR spectra.[17,18] The representatives of such binuclear complexes are [Cu_2(*N*-R-sal)$_2X_2$] (X = Cl, Br, NO_3, etc.). A five-coordinate complex with the same bridging structure, as is schematically shown in Figure 6b, can be predicted as a most probable structure for **9** in the high-temperature phase; this structure is consistent with all the experimental data. From another point of view, this structure can be regarded to be a distorted trigonal-bipyramidal configuration around copper(II) ions, which has been suggested for [Cu_2(*N*-$(CH_2)_3OH$-sal)$_2Cl_2$].[16] Accordingly, the interconversion between the two largely different structures in Figure 6 is estimated to occur in crystals of **9** at the temperature of phase transition.

Interdimer Spin-Exchange Interaction. The observation of well-resolved hyperfine structures in Figure 3c means that, in crystals of **9** in the low-temperature phase, interdimer spin-exchange interaction is much weaker than the hyperfine interaction and, furthermore, that there is little effect of dipolar broadening on line width in these crystals.[19]

Measurements of powder ESR spectra over the temperature range 300-77°K revealed that many of the green complexes also showed phase transitions at ca. −100° without remarkable color change and with drastic changes in ESR line shape. The temperature dependence of powder ESR spectra for **4** is given in Figure 5 as an example for a demonstration of the phase transition. Polycrystals of **2** also showed a drastic change in ESR line shape below ca. −100°, as shown in Figure 4. When **2** was cooled to 4.2°K, the ESR spectrum at 77°K remained unchanged. This fact indicates $-2J < 4.2$°K for **2** in the low-temperature phase. The difference between Figures 4b and 4c is that, in the latter figure, an additional sharp and intense line is observed at ~3200 G, together with weakening of the intensity of the $\Delta M = 2$ spectrum at ~1500 G.

On the other hand, Figure 5a for **4** roughly resembles Figure 4c for **2** in line shape. On cooling below ca. −100°, **4** showed Figure 5d, which remained unchanged at 4.2°K. In Figure 5d, the $\Delta M = 2$ spectrum vanishes completely. The powder ESR line shape of Figure 5d is the same kind as those for common mononuclear copper(II) complexes in magnetically undiluted crystals. The same kind of powder ESR line shapes, however, have also been observed for many dimeric copper(II) complexes with a considerably strong intradimer spin-exchange interaction and a weak interdimer one, such as bis(dimethylglyoximato)copper(II)[20,21] and tetrakis(*L*-tyrosinato)dicopper(II).[22] This interdimer interaction, even if weak, has an important effect on the ESR line shape of triplet-state dimers in crystals. Various powder ESR line shapes observed in this work can be arranged in the order of a progressive change, for example, as Figures 4b, 4c (or 5a), and 5d, from a very qualitative point of view. It is possible that this progressive change in line shape may be coherently interpreted in terms of the relative energy values of zero-field splitting (D) and interdimer spin-exchange interaction (J'); namely, $|D| \gg |J'|$ in Figure 4b, $|D| \sim |J'|$ in Figure 4c, and $|D| \ll |J'|$ in Figure 5d, where $|D|$ is of the order of 0.1-0.05 cm^{-1} for the present complexes. The types of powder ESR line shapes for the other green complexes are summarized in Table I using these spectra as standards for comparison. No correlations between the line shape and N-alkyl group, however, can be detected in this table. From the fact that all the green complexes show various ESR line shapes, in spite of their structures being almost the same, it is suggested that drastic changes in ESR line shape for this series of complexes are brought about by small changes in crystal structure, and that these complexes are interesting samples suitable for the investigation of intermolecular spin-exchange interaction in crystals. More quantitative investigations on these problems are now in progress, with the help of crystal structural determinations and single-crystal ESR studies.

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Ground States of Molecules. XXX. MINDO/3 Study of Reactions of Singlet ($^1\Delta_g$) Oxygen with Carbon–Carbon Double Bonds[1,2]

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Received July 29, 1974

Abstract: The reactions of singlet ($^1\Delta_g$) oxygen with carbon–carbon double bonds have been studied using MINDO/3. The compounds examined were ethylene, propene, vinylamine, and 2,3-dihydropyran. The reactions are predicted to take place in steps via peroxirane or zwitterionic intermediates. The results are consistent with the available experimental evidence.

During the past decade, it has been established that singlet ($^1\Delta_g$) oxygen is the reactive intermediate in the photooxygenation of alkenes as well as in oxidations brought about by the hypochlorite–hydrogen peroxide system.[3-5]

Three modes of reaction have been observed with alkenes:[6-10] 1,2-cycloadditions to yield dioxetanes; the ene reaction to form allylic hydroperoxides; and 1,4-cycloadditions with dienes leading to endoperoxides. The mechanisms of these reactions are the subject of much current controversy, the main question being whether the reactions are concerted or involve intermediates.

For a concerted 1,2-cycloaddition, both a ($_\pi2_s + {}_\pi2_s$) and a ($_\pi2_s + {}_\pi2_a$) process have been considered theoretically.[8,11-13] State correlation diagrams[8,11,12] and orbital-phase continuity arguments[13] suggest that the ($_\pi2_s + {}_\pi2_s$) approach should be "forbidden", although it has been proposed[8] that this process might occur in the case of alkenes with particularly low ionization potentials. The ($_\pi2_s + {}_\pi2_a$) approach is classified as symmetry allowed[8,13] and has therefore been considered a likely pathway for dioxetane formation.[13,14]

Stepwise 1,2-cycloaddition could occur via peroxiranes[8,12] or zwitterionic species.[14-16] Experimental evidence for the intermediacy of peroxiranes in the photooxygenation of 2,5-dimethyl-2,4-hexadiene[17] and of 2,2′-biadamantylidene[18] has recently been reported. Correlation diagrams[8,12] and consideration of frontier orbital interactions[19] indicate that peroxirane formation is an allowed process. Zwitterionic intermediates should be important only in the case of electron-rich alkenes such as enamines[16] or enol ethers.[14,15] A recent theoretical study has described the photooxygenation of 2-aminopropene as a "symmetry-forbidden concerted" reaction proceeding via an essentially zwitterionic transition state.[13]

For the ene reaction, most authors favor a concerted mechanism in which the characteristic bond shifts take place via a cyclic transition state with a six-membered ring.[6,20] Others have proposed peroxiranes[21,22] or dioxe-