treated with diarsine in dioxane, the pale blue-gray complex $UCl_4(diars)_2$ precipitated. This complex appears to be the first eight-coordinate diarsine complex of a nontransition element and the first complex of an actinide element with coordinated diarsine. Uranium tetrachloride did not react with ethylenebis(diphenylarsine) in tetrahydrofuran.[28]

As well as the expected broad charge-transfer bands at energies above 25 kK (Table II), the complex shows a series of sharp bands in its diffuse reflectance spectrum at energies between 4 and 22 kK (Table V[29]). Tentative assignments of the spectrum, based on a comparison with the spectra of hexahalo complexes of uranium(IV) and energy level calculations for octahedral uranium(IV),[30] are included.

TABLE V

ABSORPTION MAXIMA (kK) IN THE DIFFUSE REFLECTANCE SPECTRUM OF $UCl_4(diars)_2$ BETWEEN 4 AND 22 kK[a]

21.93	$^3P_2$	10.86	$^3H_6$
(21.66)		8.84	$^3F_3$, $^3F_4$
19.72	$^1I_6$	8.31	
18.82		(7.94)	
16.92	$^3P_1$	(6.61)	$^3H_5$
15.79	$^1D_2$, $^1G_4$, $^3P_0$	6.38	
(15.75)		4.40	$^3F_2$
14.97			
14.69			
14.34			
(13.94)			

[a] The tentative assignments are transitions from the $^3H_4$ state. Shoulders are enclosed in parentheses. The complex also shows sharp absorptions at (5.87), 5.74, 5.42, and approximately 4.0 kK. Absorptions are found at similar energies in the diffuse reflectance spectra of all diarsine complexes, and they have been assigned to vibrational overtone and combination bands of the diarsine ligands.[29]

The room-temperature effective magnetic moment of the complex is 2.74 BM. Many other eight-coordinate complexes of uranium(IV) have magnetic moments of approximately 3 BM,[28,31] but the expected value is very sensitive to the stereochemistry of the complex, and the magnetic moment does not appear to have been calculated for dodecahedral or square-antiprismatic complexes. The magnetic moment of an f^2 ion in a cubic ligand field is predicted to be 2.83 BM.[32]

Acknowledgments.—We acknowledge financial assistance granted by the Department of Education and Science in the form of a Commonwealth postgraduate award (to R. L. D.).

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Superexchange Interaction in Anhydrous Copper(II) Formate

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The magnetic susceptibilities of two modifications of anhydrous copper(II) formate were determined in a temperature range of 4.2–300°K. The energy of exchange interaction between copper ions within a two-dimensional lattice was evaluated as $J/k = -42°K$ (J, exchange integral) for the blue modification and 9.9°K for the royal blue modification. An antiferromagnetic transition accompanied by parasitic ferromagnetism was found at about 20°K in the blue modification. A contact shift was observed in the broad-line pmr spectrum of either form of copper(II) formate. Carbon atoms in the formate groups of these compounds carry a negative spin density. Two types of exchange mechanism are involved in the superexchange interaction through formate groups. A path through π orbitals predominates in the blue form, whereas in the royal blue form, contribution from a σ path masks the antiferromagnetic interaction associated with the π path.

Introduction

The magnetic susceptibility of copper(II) formate tetrahydrate has been determined in a wide temperature range.[1-3] The results indicate the presence of a strong superexchange interaction due to anti–anti bonding arrangements (see Figure 1) of Cu–O–C–O–Cu links in a two-dimensional lattice.[4] Martin and Waterman[1] have prepared three modifications of anhydrous copper(II) formate (blue, royal blue, and turquoise blue modifications) and determined their magnetic susceptibilities between 80 and 300°K. The blue modification is presumed to have crystal structure resembling that of the tetrahydrate.[1,5] The Weiss constant amounts to about −175°K. On the other hand, a small positive Weiss constant has been found for the royal blue form. The X-ray crystal analysis of the royal blue form has indicated that anti–syn bridging arrangements (see Figure

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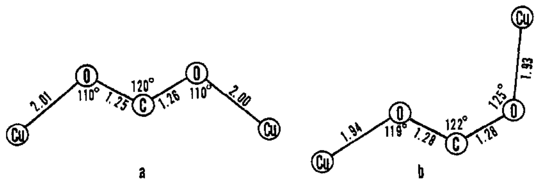

Figure 1.—(a) Anti–anti bonding arrangement of a Cu–O–C–O–Cu link in the crystal of copper(II) formate tetrahydrate. (b) Anti–syn bridging arrangement of a Cu–O–C–O–Cu link in the royal blue modification of anhydrous copper(II) formate.

1) of Cu–O–C–O–Cu links exist in the crystal.[6] It is noteworthy that two anhydrous salts are significantly different from each other in their magnetic properties despite the presence of Cu–O–C–O–Cu links in both compounds.

The present investigation has been undertaken in an attempt to derive some conclusion on the nature of superexchange interaction in copper(II) formate. In order to obtain further information about the magnetic properties of the anhydrous salts, we have extended magnetic susceptibility measurements to liquid helium temperature (4.2°K). Since superexchange interaction operates between copper atoms through formate groups, one may expect unpaired electrons diffusing into ligands. This effect would be revealed by studying Fermi contact shifts in nmr spectra.[7,8] Therefore, we have recorded the broad-line pmr spectra of the compounds and evaluated spin densities on carbon atoms in formate groups.

Experimental Section

The blue and royal blue modifications of anhydrous copper(II) formate were prepared by methods described by Martin and Waterman.[1] We tried to prepare the turquoise blue modification also but obtained samples showing some fluctuations in pmr spectra and magnetic data. In addition, no structural information is available for the turquoise blue modification. Therefore, the blue and royal blue modifications were subjected to magnetic measurements.

Magnetic susceptibilities were determined in a temperature range of 4.2–300°K using magnetic balances described in our previous paper.[9] Pmr spectra were recorded at 24° by means of a Model JNS-B broad-line nmr spectrometer from Jeolco (Japan Electron Optics Laboratory Co.) operating at 35.45 MHz.[8] Water was employed as an external standard.

Results

The magnetic susceptibilities of the blue and royal blue forms observed at room temperature agree with values reported in the literature.[1] The molar susceptibilities were corrected for diamagnetic contributions (in 10^{-6} emu/mol) from copper(II) ions (-11)[10] and formate groups (-20).[11] The temperature-independent paramagnetism was assumed to be equal to 60×10^{-6} emu/mol.[12] The reciprocal susceptibilities are plotted against the temperature in Figures 2 and 3.

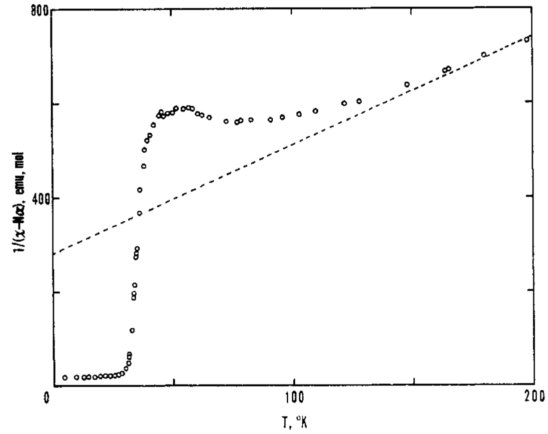

Figure 2.—Reciprocal magnetic susceptibility of the blue modification of anhydrous copper(II) formate plotted against the temperature. The broken line was calculated with the Curie constant and the Weiss constant evaluated from high-temperature data.

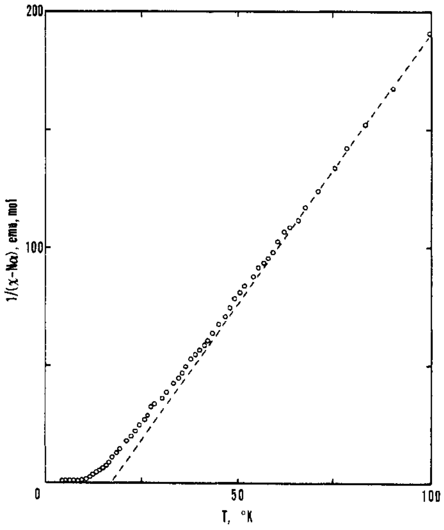

Figure 3.—Reciprocal magnetic susceptibility of the royal blue modification of anhydrous copper(II) formate plotted against the temperature. The straight line shows the Curie–Weiss law.

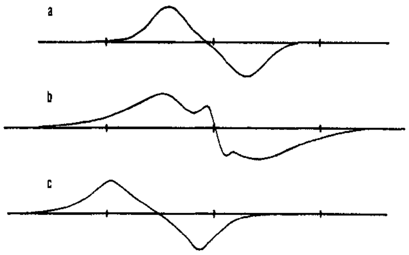

Figure 4.—Broad-line nmr spectra of (a) the blue modification, (b) the tetrahydrate, and (c) the royal blue modification of copper(II) formate.

The crystalline powder of the blue form shows a simple pmr absorption derivative curve with a small low-field shift as shown in Figure 4. The royal blue form gives rise to a single absorption shifted to the low-field side to a considerable extent. Observed contact interaction shifts are given in Table I along with other data developed in Discussion.

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TABLE I

CURIE CONSTANT C, WEISS CONSTANT θ,[a] EXCHANGE INTEGRAL J, CONTACT INTERACTION SHIFT $\Delta H/H$, CONTACT INTERACTION CONSTANT a_i, AND SPIN DENSITY ρ_i ON CARBON ATOMS OF THE BLUE AND ROYAL BLUE MODIFICATIONS OF ANHYDROUS COPPER(II) FORMATE WITH THE DATA OF COPPER(II) FORMATE TETRAHYDRATE FOR COMPARISON

Modification	C, emu deg/mol	θ, °K	J/k, °K	$\Delta H/H \times 10^4$	a_i, Oe	ρ_i
Blue	0.437	−124	−42	−0.32	0.54	−0.024 (p_π)
Royal blue	0.434	+17	+9.9	−3.42	3.90	−0.023 (sp^2)
Tetrahydrate	0.497[b]	−175[b] −120[c]	−30[d]	∼−0.5	∼0.8	∼−0.035 (p_π)

[a] The Curie constants and Weiss constants of the first two compounds were evaluated from data at temperatures above 200 and 70°K, respectively. [b] Reference 1. [c] Reference 2. [d] Estimated from the temperature of the maximum susceptibility cited in ref 2.

Discussion

The magnetic susceptibility of the blue modification increases with decreasing temperature obeying the Curie-Weiss law above about 200°K and passes through a broad maximum at about 80°K. The susceptibility increases sharply with decreasing temperature between 30 and 40°K, below which it assumes a value almost independent of temperature. The magnetic behavior resembles that of copper(II) formate tetrahydrate, for which Kobayashi and Haseda[2] have observed two maxima at 60 and 17°K in the susceptibility *vs.* temperature curve. These authors have suggested that a strong interaction within a two-dimensional lattice gives rise to a short-range spin ordering at 60°K and an antiferromagnetic ordered state arises at 17°K owing to a weak interaction between layers.

Although no structural information is available for the blue modification, the retension of external crystalline form on dehydration suggests that the layers approach one another without any significant change in the bonding arrangement of Cu–O–C–O–Cu links.[1] Therefore, magnetic interaction within a layer is presumed to be predominant in the blue form of anhydrous copper(II) formate also. No rigorous theoretical calculation has been performed for the susceptibility of a two-dimensional lattice. A fairly good approximation is afforded by the coupled-pair model, which gives the following equation for the total electron spin S of $^1/_2$ above the transition temperature[13]

$$\chi = \frac{Ng^2\beta^2}{4kT}\left[\frac{4}{ze^{-2J/kT} - (z-4)}\right] + N\alpha \qquad (1)$$

where, apart from obvious notations, J denotes the exchange integral between nearest neighbors, g is the electronic g factor, z is the number of nearest neighbors, and $N\alpha$ is the temperature-independent paramagnetism. The high-temperature expansion method gives a rigorous equation when the series converges rapidly. The coefficients have been calculated up to the sixth order for the Heisenberg spin.[14] However, convergence is rather slow in the case of a two-dimensional antiferromagnetic lattice with $S = {}^1/_2$. For a two-dimensional square lattice ($S = {}^1/_2$ and $z = 4$), eq 1 leads to

$$\chi = \frac{Ng^2\beta^2}{4kT}\, e^{2J/kT} + N\alpha \qquad (2)$$

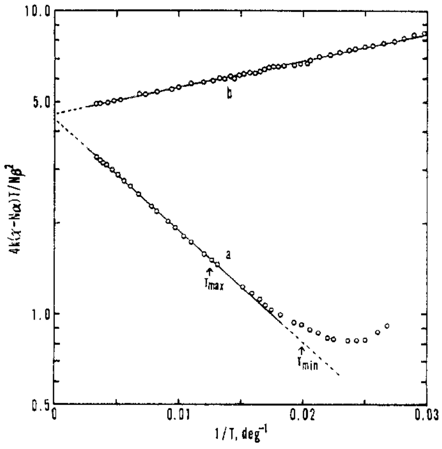

Figure 5.—$4k(\chi - N\alpha)T/N\beta^2$ plotted against $1/T$: (a) blue form; (b) royal blue form.

In Figure 5, observed log $[4k(\chi - N\alpha)T/N\beta^2]$ is plotted against $1/T$. The curve is strictly linear above about 65°K. The intercept of the straight line gives a g value equal to 2.09 in good agreement with 2.16 evaluated from the Curie constant. This indicates that the magnetic behavior can be explained by the two-dimensional coupled-pair model in the high-temperature region. From the slope of the straight line, the exchange integral is obtained as $J/k = -42$°K. Since the value of $2|J|/k$ agrees well with the temperature of the maximum susceptibility as expected from eq 2, the broad maximum at about 80°K can be attributed to a magnetic interaction within the layer.

In the crystal of copper(II) formate tetrahydrate, weak ferromagnetic moments of the same kind as discussed by Dzyaloshinsky[15] and Moriya[16] possibly appear, because the crystal symmetry belongs to $P2_1/a\text{-}C_{2h}{}^5$ having two kinds of nonequivalent (*i.e.*, incapable of being coincided with one another by inversion) copper ions in a unit cell.[4] In fact, Kobayashi and Haseda[2] have measured the magnetic field dependence of the susceptibility below 20°K and found a saturation magnetic moment amounting to about 3% of the saturation value for 1 g-ion of free copper ions. The blue modification of anhydrous copper(II) formate has a possibility of showing parasitic ferromagnetism, if it has a crystal structure analogous to that of the tetrahydrate. With decreasing temperature, the susceptibility of the blue form rises sharply between 30 and 40°K above values calculated from the Curie–Weiss law.

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Ultimately it reaches a constant value equal to 0.05 emu/mol. These behaviors are characteristic of parasitic ferromagnetism and indicative of the presence of weak ferromagnetic moments accompanying a transition to an antiferromagnetic state. The value of the constant susceptibility is larger than that of the tetrahydrate, suggesting that interaction between layers is stronger than in the tetrahydrate. This is reasonable because the layers are packed closer on dehydration.

The susceptibility of the royal blue modification obeys the Curie–Weiss law above 70°K. The Curie constant and the Weiss constant are evaluated as shown in Table I. The positive Weiss constant indicates the predominance of ferromagnetic interaction in the crystals. The observed susceptibility is accounted for on the basis of the coupled-pair model above about 35°K ($1/T \approx 0.03$), as shown in Figure 5. From the linear relation between log $[4k(\chi - N\alpha)T/N\beta^2]$ and $1/T$, the g factor and the exchange integral are determined as $g = 2.15$ and $J/k = 9.9$°K. The theoretical curve deviates from the observed susceptibility in a low-temperature region, as shown in Figure 6. The high-temperature expansion method usually gives a good approximation for ferromagnetism. However, the observed susceptibility cannot be explained adequately by the expansion method for the Heisenberg spin. Presumably these discrepancies are due to the presence of magnetic interaction between layers.

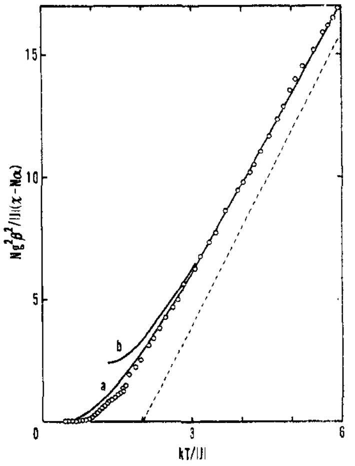

Figure 6.—$Ng^2\beta^2/|J|(\chi - N\alpha)$ of the royal blue form plotted against $kT/|J|$: circles, observed values; curve a, coupled-pair model; curve b, high-temperature expansion method; broken line, molecular field theory.

A single pmr absorption has been recorded for the blue form of copper(II) formate in conformity with the presumption that the layer structure of the tetrahydrate is practically unaffected by dehydration.

The isotropic contact hyperfine interaction field ΔH is given by[8,17]

$$\frac{\Delta H}{H} = -a_i\left(\frac{\gamma_e}{\gamma_N}\right)\frac{\chi - N\alpha}{g\beta N} \tag{3}$$

where H is the nuclear magnetic resonance field, a_i is the contact interaction constant, γ_e is the magnetogyric ratio of an electron, and γ_N is that of a nucleus. The contact interaction constnt a_i is calculated as 0.54 Oe from the observed shift $\Delta H/H$, the susceptibility observed at room temperature, and the g value calculated from the Curie constant. The foregoing theoretical derivation is based on Fermi contact interaction and disregards the pseudo-contact interaction[18] arising from the combined effect of electron spin–nuclear spin coupling, electron orbit–nuclear spin coupling, and electron spin–electron orbit interaction.

McConnell[17] has shown that for aromatic radical species, in which a spin density localized on a pπ orbital of a carbon atom interacts with a proton bonded to the carbon atom, the contact interaction constant a_i of a proton is related to the spin density ρ_i on the adjacent carbon atom by[19]

$$a_i = Q\rho_i \tag{4}$$

where Q is a proportionality constant characteristic of the particular mechanism giving rise to the $\mathbf{I}\cdot\mathbf{S}$ interaction between a nuclear spin $\mathbf{I}$ and an electron spin $\mathbf{S}$. For aromatic $\cdot$C–H fragments having an unpaired electron in their pπ orbitals, Q has been determined empirically as -22.5 Oe. By use of this empirical value, the spin density ρ_i on the carbon atom of a formate group in the blue modification of copper(II) formate was calculated as -0.024 from the observed contact interaction constant a_i. The conclusion that the carbon atom bears a negative spin density is plausible because the central carbon atom of an allyl radical, $CH_2{=}CHCH_2\cdot$, having a structure analogous to that of a formate ion, $O{=}CHO\cdot$, carries a negative spin density of $-^1/_3$ according to a simple theoretical calculation.[20] The observed spin delocalization lends evidence in support of a presumption that superexchange interaction takes place through formate groups in the blue modification.

The pmr spectrum of powder crystals of copper(II) formate tetrahydrate shows an asymmetric absorption curve attributable to three types of crystallographically nonequivalent protons.[4,21] Although the curve is difficult to resolve owing to almost complete overlap, it must be composed of two unshifted curves and a curve shifted to the low-field side. The latter is assigned to protons in formate groups. The value of the shift is estimated to be approximately equal to that of the blue modification. This is expected because the tetrahydrate yields the blue modification on dehydration and the anti–anti bonding arrangement of Cu–O–C–O–Cu links characteristic of the former compound is presumed to be retained in the latter compound.[1,5]

According to the result of X-ray crystal analysis on the royal blue form of anhydrous copper(II) formate, there are two types of nonequivalent formate groups provided that exact values for bond lengths and bond

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angles in formate groups are taken into account. However, the differences are trivial: all hydrogen atoms in fromate groups are presumed to have practically the same magnetic environment in agreement with the experimental observation of a single pmr absorption. The contact interaction constant a_i is evaluated as 3.9_0 Oe from eq 3. Normally, no suitable external standards are available for the determination of absolute values for contact shifts at liquid nitrogen temperature. However, for the royal blue form showing a large shift, a polyethylene film could be used as an external standard. The coupling constant a_i was determined as about 3.4 Oe at 77°K. The value agrees with that observed at room temperature.

The contact interaction constant of the royal blue form is much larger than that of the blue form, although the absolute value of the exchange integral of the former is smaller than that of the latter. This suggests that two types of exchange mechanism are involved in the superexchange interaction through formate groups.

Two paths are conceivable for the migration of a positive hole through a formate ion, one *via* π-electron clouds and the other *via* σ-bonding electron orbitals of O–C–O bonds as shown in Figure 7. The σ path relates to the correlation of the $3d_{x^2-y^2}$ orbital of a copper ion to the sp^2 orbital of an oxygen atom bonded to the copper ion. The polarization in the sp^2 orbital of the oxygen atom creates a negative spin density in the sp^2 orbital of the carbon atom and gives rise to ferromagnetic interaction between copper ions. The π path involves promotion, $3d_{x^2-y^2} \rightarrow 3d_{xz}$, in a copper ion as well as the overlap of the $3d_{xz}$ orbital with the $2p_z$ orbital of an oxygen atom bonded to the copper ion. In this case, unpaired electrons of copper ions are coupled antiferromagnetically.

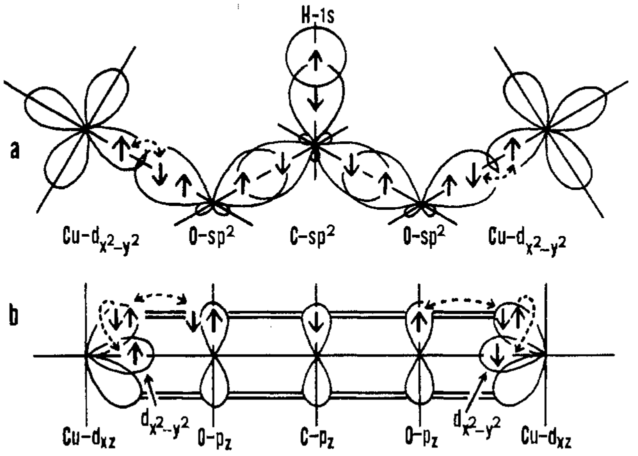

Figure 7.—Alternative paths for the migration of a positive hole through a formate group: (a) σ path and (b) π path resulting in ferromagnetic and antiferromagnetic interaction, respectively, between two copper ions.

The contact interaction constant a_i observed for the royal blue form is too large to attribute to a spin density in the pπ orbital of the carbon atom. In the case of the σ path, a fraction of an unpaired electron is distributed in the sp^2 orbitals of the carbon atom of a formate group as discussed above. If one unpaired electron is populated in three sp^2 orbitals of the carbon atom in equal weights, each σ bond has a spin density of $^1/_3$, and consequently a negative spin nearly equal to $- ^1/_3$ is distributed on a hydrogen atom bonded to the carbon atom as shown in Figure 7. Since the contact coupling constant of a hydrogen atom is equal to 508 Oe,[17] the Q value is roughly estimated at about −170 Oe for a ·C–H fragment having an unpaired electron in the sp^2 orbital. This value gives a reasonable spin density, -0.02_3, on the carbon atom. Therefore, the large coupling constant is presumed to be due mainly to unpaired electrons present in the σ system. The esr of copper(II) ions in dibarium(II) zinc(II) formate tetrahydrate has shown that an appreciable diffusion of σ electrons takes place from the ligand to the $3d_{x^2-y^2}$ orbital of the copper ion while there is no appreciable extent of bonding in the π system.[22] In addition, the population of 0.016 unpaired electron has been estimated in the sp^2 orbital of the carbon atom. This value of the spin density agrees well with that of the royal blue form in support of our deduction. These facts lead to a conclusion that the large σ contribution masks the antiferromagnetic interaction associated with the π path and results in ferromagnetism in the royal blue form.

For the blue form, a spin density on the carbon atom is estimated as −0.003 (= −0.54/170) provided that the coupling constant is attributed to a spin density in the pσ orbital of the carbon atom. Evidently the value is too small to induce superexchange interaction much stronger than in the royal blue form (see J values in Table I). On the other hand, the Q value related to a spin in the pπ orbital gives rise to a reasonable spin density, -0.02_4, on the carbon atom as mentioned above. This value is almost equal to the spin density in the pσ orbital of the carbon atom in the royal blue form. However, the π path involves an exchange interaction much stronger than does the σ path, because the polarized spin in the π system can migrate to a distance with little attenuation whereas the spin polarization in the σ system is rapidly attenuated. These suggest the predominance of the π path in the blue form in accordance with the sign of the exchange integral.

Our conclusion of a predominant π character of superexchange interaction in the blue modification as well as the tetrahydrate apparently contradicts the results of an esr study of copper(II) ions in dibarium(II) zinc(II) formate tetrahydrate.[22] However, the two compounds differ from each other in their structures. For instance, the two C–O bonds of a formate group in the tetrahydrate have practically the same distance (1.25–1.26 Å), whereas in dibarium(II) copper(II) formate tetrahydrate, which is isomorphous with dibarium(II) zinc(II) formate tetrahydrate, a C–O bond closer to copper (1.35–1.43 Å) is considerably longer than the other C–O bond in the same formate group (1.23–1.26 Å).[23] The unequal C–O distances do not favor the migration of π electrons.

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