state because the bent nitrosyl has a weaker Mn–N bond.

All of the observed excited-state frequencies are consistent with a decrease in the π-acceptor properties of the NO ligand when it changes from a linear to a bent structure. The back-bonding decrease is caused by both the decrease in the number of available π-acceptor orbitals and by a longer metal–nitrogen bond in the bent M–NO species. An opposing electronic effect is a formal increase in the metal oxidation state when the linear, formally NO$^+$ ligand changes to the bent, formally NO$^-$ ligand. On the basis of this study, the CN and metal–ligand vibrations in the excited electronic state are dominated by the decrease in the NO π-acceptor strength after bending and not by the expected formal oxidation state increase on the metal.

Acknowledgment. This work was made possible by a grant from the National Science Foundation (CHE85-09329) and an instrument grant from the Office of Naval Research.

Registry No. $K_3[Mn(CN)_5NO]$, 13821-02-8.

Contribution from the Department of Chemistry, Faculty of Science, Yamagata University, Koshirakawa Yamagata 990, Japan, and Electrotechnical Laboratory, Sakura-mura, Niihari-gun, Ibaragi 305, Japan

Anomalous Solution ESR Spectra Observed for Halogenocopper(II) Complexes with Tripodlike Ligands

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Halogenocopper(II) complexes with tripodlike ligands (L), [Cu(L)X]Y (X = Br$^-$ and I$^-$; Y = ClO$_4$ and PF$_6$), showed more than four hyperfine lines (5–9 lines) in the solution ESR spectra at room temperature. This was attributed to the interaction between the unpaired electron of the copper(II) ion and the nuclear spins of both the copper atom (^{63,65}Cu, $I = {}^3/_2$) and the halogen atom (^{79,81}Br, $I = {}^3/_2$; ^{127}I, $I = {}^5/_2$). The above discussion was confirmed by the crystal structure determination of three compounds, $[Cu(N_3S)N_3]ClO_4$ (**1**), $[Cu(N_3S)Br]ClO_4$ (**2**), and $[Cu(N_2S_2P)I]ClO_4$ (**3**), where N$_3$S and N$_2$S$_2$P represent bis(2-pyridylmethyl)(2-(methylthio)ethyl)amine and bis(2-(methylthio)ethyl)(2-pyridylmethyl)amine, respectively. Crystal data: **1**, space group $P2_1/a$, a = 16.316 (5) Å, b = 8.379 (1) Å, c = 14.409 (2) Å, β = 100.69 (2)°; **2**, space group $P2_1/a$, a = 14.600 (7) Å, b = 17.155 (8) Å, c = 7.686 (1) Å, β = 94.89 (2)°; **3**, space group $P2_1/n$, a = 17.292 (3) Å, b = 14.411 (2) Å, c = 7.8202 (7) Å, β = 100.29 (1)°. Complex **1** has a square-pyramidal structure; the sulfur atom of the thioether group is at the apical position of the square plane, and the azide ion is in the plane of the coordination sphere. The structural properties of **2** are essentially the same as those of **1** except that the N$_3$ ion in **1** is replaced by Br$^-$ ion in **2**. Complex **1** shows four hyperfine lines in the solution ESR spectrum, whereas five lines are observed for compound **2**, indicating that the presence of Br$^-$ ion at the corner of the square plane causes the unusual ESR spectrum. Complex **3** has a distorted-trigonal-bipyramidal structure where the unpaired electron in the d$_{z^2}$ orbital of the copper(II) ion can interact with the iodine atom through σ-bonding. In the series of X = I$^-$ complexes, hyperfine lines decrease from nine to seven with the variation of ligand from tris(2-(methylthio)ethyl)amine to tris(2-pyridylmethyl)amine. A similar situation was also found for the X = Br$^-$ complexes. These were successfully explained on the assumption that the interaction between the unpaired electron and the nuclear spin of the halogen atom is dependent on the character of the tripodlike ligand L.

Introduction

In general, the mononuclear copper(II) complexes show four hyperfine lines in the solution ESR spectra at room temperature. This is due to (i) the averaging of the g values and (ii) the presence of interaction of the unpaired electron of the copper(II) ion with the nuclear spin of the copper atom (^{63,65}Cu; $I = {}^3/_2$).[2-4]

In 1980, Nishida et al.[5] observed that some halogenocopper(II) complexes containing the tripodlike ligand L, [Cu(L)X]Y (X = Br$^-$ and I$^-$; Y = ClO$_4$ and PF$_6$), show unusual solution ESR spectra at room temperature. As examples, the solution ESR spectra of $[Cu(NS_3)X]ClO_4$ (X = Cl$^-$, Br$^-$, and I$^-$) are illustrated in Figure 2, where NS$_3$ represents tris(2-(methylthio)ethyl)amine (cf. Figure 1). In the case of X = Cl$^-$, four hyperfine lines are observed. On the other hand, seven and nine peaks with almost the same interval are observed for X = Br$^-$ and X = I$^-$ complexes, respectively. The $|A_{\mathrm{iso}}|$ values are 66, 65, and 85 G for X = Cl$^-$, Br$^-$, and I$^-$ complexes, respectively. We inferred that the anomalous ESR spectra observed for $[Cu(NS_3)X]^+$ (X = Br$^-$ and I$^-$) should be attributed to the interaction of the unpaired electron of the copper(II) ion with the nuclear spins of both the copper atom and the halogen atoms (^{79,81}Br, $I = {}^3/_2$; ^{127}I, $I = {}^5/_2$). In the case of the chlorine atom, its nuclear magneton is much smaller (about one-fifth) than those of bromine and iodine atoms.[3] The covalency of the Cu–X interaction may depend on X, and more covalent bonds will form in the order Cl < Br < I. These will explain the fact that the complexes with X = Cl$^-$ show a usual ESR spectrum irrespective of the presence of interaction between the unpaired electron and the nuclear spin of the chlorine atom.

In the course of this study we also found[6] that six hyperfine lines are observed for the solution ESR spectrum of $[Cu(N_2S_2P)Br]ClO_4$ (cf. Figures 1 and 3), the spectrum being slightly different from that of $[Cu(NS_3)Br]^+$. The crystal structure determination[6] revealed that both $[Cu(NS_3)Br]ClO_4$ and $[Cu(N_2S_2P)Br]ClO_4$ have a trigonal-bipyramidal structure. The reason for the difference in ESR spectra of these two complexes is not clear at present.

In this article we have measured the solution ESR spectra of copper(II) complexes of the various tripodlike ligands illustrated in Figure 1 and determined the crystal structures of three compounds, $[Cu(N_3S)N_3]ClO_4$ (**1**), $[Cu(N_3S)Br]ClO_4$ (**2**), and $[Cu(N_2S_2P)I]ClO_4$ (**3**), in order to elucidate the origin for the unusual solution ESR spectra observed for these copper(II) complexes.

Experimental Section

Copper(II) Complexes. Copper(II) complexes with NS$_3$,[7] N$_2$S$_2$P,[8] N$_3$S,[9] and N$_4$P[9] (for an explanation of the abbreviations of ligands, see

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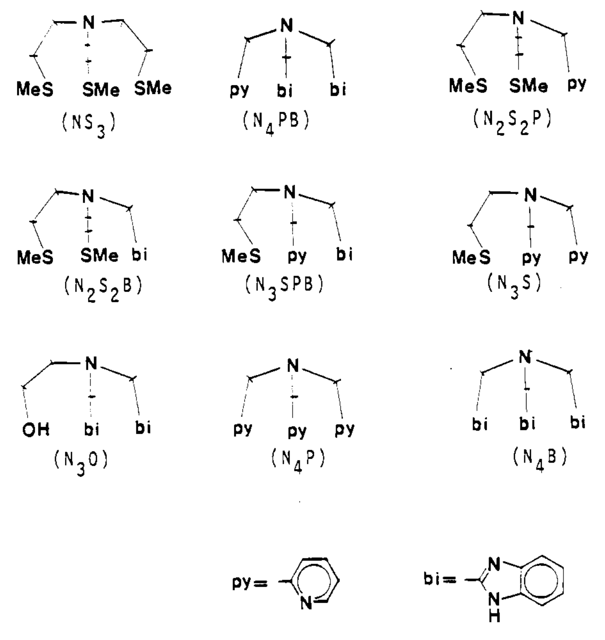

Figure 1. Chemical structures of ligands cited in this paper and their abbreviations.

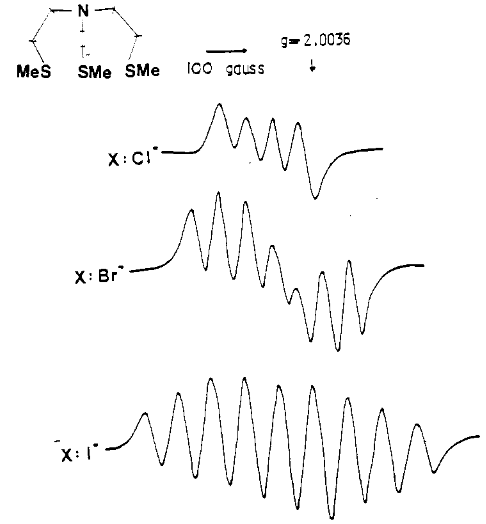

Figure 2. ESR spectra of $[Cu(NS_3)X]ClO_4$ complexes (in nitromethane at 295 K).

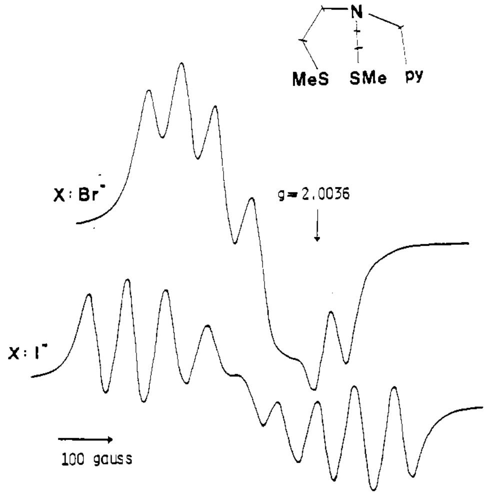

Figure 3. ESR spectra of $[Cu(N_2S_2P)X]ClO_4$ (in nitromethane at 295 K).

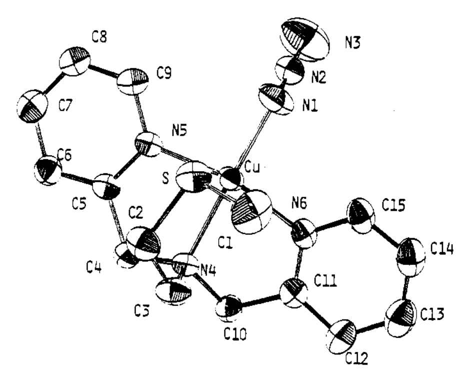

Figure 4. ORTEP drawing of $[Cu(N_3S)N_3]^+$.

Table I. Selected Bond Distances (Å) and Angles (deg) for **1**

Cu–S	2.665 (2)	Cu–N1	1.945 (5)
Cu–N4	2.075 (4)	Cu–N5	1.975 (5)
Cu–N6	1.979 (4)		
S–Cu–N1	96.9 (2)	S–Cu–N4	85.5 (6)
S–Cu–N5	104.3 (1)	S–Cu–N6	86.6 (1)
N1–Cu–N4	177.4 (2)	N1–Cu–N5	96.1 (2)
N1–Cu–N6	97.6 (2)	N4–Cu–N5	82.4 (2)
N4–Cu–N6	83.4 (2)	N5–Cu–N6	161.3 (2)

Figure 1) were a gift from Dr. M. Suzuki at Kanazawa University. Complexes with N_2S_2B,[10] N_4B,[11] and NS_2[12] (NS_2 = bis(2-(methylthio)ethyl)amine) were prepared according to the literature methods.

Physical Measurements. ESR spectra were obtained with a JEOL ESR apparatus, Model JES-FE-3X, in nitromethane or *N*,*N*-dimethylformamide (dmf) at 291 K by using the X-band, DPPH and MnO (in MgO) being used as a standard marker.

X-ray Data Collection. The crystals were mounted on a Rigaku AFC-5 automatic diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 294 ± 1 K. Automatic centering and the least-squares routines were carried out on 25 reflections for each complex to obtain the cell constants. Crystal data: **1**, $[Cu(N_3S)N_3]ClO_4$, M_r = 478.4, monoclinic, space group $P2_1/a$, a = 16.316 (5) Å, b = 8.379 (1) Å, c = 14.409 (2) Å, β = 100.69 (2)°; **2**, $[Cu(N_3S)Br]ClO_4$, M_r = 516.3, monoclinic, space group $P2_1/a$, a = 14.600 (7) Å, b = 17.155 (8) Å, c = 7.686 (1) Å, β = 94.89 (2)°; **3**, $[Cu(N_2S_2P)I]ClO_4$, M_r = 546.3, monoclinic, space group $P2_1/n$, a = 17.292 (3) Å, b = 14.411 (2) Å, c = 7.8202 (7) Å, β = 100.29 (1)°.

The θ–2θ scan technique was employed to record the intensities of a unique set of reflections for which $3° < 2\theta < 55°$. Three check reflections were measured every 100 reflections; they exhibited no significant decay during the data collection. Intensities were corrected for Lorentz and polarization effects but not for absorption. The intensities of 3984 (**1**), 4257 (**2**), and 4289 (**3**) independent reflections were measured, and 2920, 3018, and 3097 of them with $F_o > 3\sigma(F_o)$ were used for the determination of crystal structure for compounds **1**, **2**, and **3**, respectively.

Structure Solution and Refinement. In each case the positional parameters of the copper atom were determined by direct methods.[13] The remaining non-hydrogen atoms were located by subsequent Fourier maps and least-squares refinement. The refinement was effected by the block-diagonal least-squares technique by using the anisotropic temperature factors. In the last stage of refinement, the difference Fourier map showed no significant peak and all the parameter shifts were less than 0.4σ. The structures were refined to R $(=\sum||F_o| - |F_c||/\sum|F_o|)$ = 0.052, 0.070, and 0.071 and R' $(=\sum||F_o| - |F_c||^2/\sum|F_o|^2]^{1/2})$ = 0.059, 0.082, and 0.081 for compounds **1**, **2**, and **3**, respectively. Programs used for the structure solution and anisotropic refinement were supplied by the UNICS system,[14] and the atomic scattering factors were taken from ref 15.

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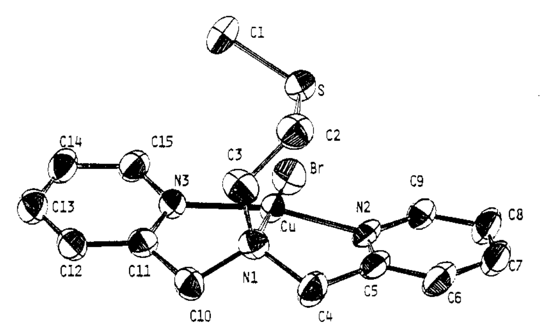

Figure 5. ORTEP drawing of $[Cu(N_3S)Br]^+$.

Table II. Selected Bond Distances (Å) and Angles (deg) for **2**

Cu-Br	2.375 (2)	Cu-S	2.762 (3)
Cu-N1	2.051 (8)	Cu-N2	1.987 (7)
Cu-N3	1.992 (7)		
Br-Cu-N1	174.2 (2)	Br-Cu-S	101.3 (1)
Br-Cu-N2	96.7 (2)	Br-Cu-N3	88.3 (2)
S-Cu-N1	84.5 (2)	S-Cu-N2	100.7 (2)
S-Cu-N3	84.7 (2)	N1-Cu-N2	81.2 (3)
N1-Cu-N3	83.1 (3)	N2-Cu-N3	162.8 (3)

Table III. Selected Bond Distances (Å) and Angles (deg) for **3**

Cu-I	2.604 (1)	Cu-S1	2.452 (4)
Cu-S2	2.340 (4)	Cu-N1	2.053 (8)
Cu-N2	2.052 (9)		
I-Cu-N2	99.9 (2)	I-Cu-N1	177.1 (3)
I-Cu-S1	91.2 (1)	I-Cu-S2	92.70 (9)
S1-Cu-S2	110.4 (1)	S1-Cu-N1	85.9 (3)
S1-Cu-N2	115.1 (3)	S2-Cu-N1	88.2 (3)
S2-Cu-N2	132.2 (3)	N1-Cu-N2	81.4 (3)

Complete F_o and F_c tables, listings of details of the experimental conditions in the X-ray data collection, atomic coordinates, and anisotropic temperature factors, and full listings of bond distances and angles have been deposited as supplementary material.

Results and Discussion

Molecular Structures of Compounds 1 and 2. An ORTEP drawing of the structure of **1**, including the atomic numbering scheme, is given in Figure 4. Intramolecular distances and selected bond angles are listed in Table I. The complex consists of a molecular $[Cu(N_3S)N_3]^+$ cation and a perchlorate anion. The copper atom is coordinated by four nitrogen atoms (three from the N_3S ligand and one from the N_3^- ion) and the thioether sulfur atom. The length (2.67 Å) of the Cu-S(thioether) bond is very large, and thus we can consider that complex **1** has a square-pyramidal structure, the plane consisting of N1, N4, N5, and N6.

An ORTEP drawing of compound **2** is illustrated in Figure 5, and the structural parameters are summarized in Table II. The structure of **2** is essentially the same as that of **1**; the geometry around the copper(II) ion is best described as a square pyramid (the plane consists of N1, N2, N3, and Br^-), and the sulfur atom of the thioether group is at the apical position. Since the unpaired electron of the square-pyramidal copper(II) complexes resides in the $d_{x^2-y^2}$ orbital,[16] the unpaired electron interacts with the bromine atom through σ-bonding in compound **2**.

Molecular Structure of Compound 3. An ORTEP drawing of compound **3** is shown in Figure 6, and the selected bond lengths and angles are given in Table III. The copper atom is coordinated by two thioether sulfur atoms, the two nitrogen atoms of the N_2S_2P ligand, and the I^- ion. The almost linear I–Cu–N1 moiety (177°) has the appearance of the axis in a rough trigonal bipyramid, in which the equatorial positions are occupied by S1, S2, and N2 atoms. This is essentially the same structure as that observed for $[Cu(N_2S_2P)Br]ClO_4$.[6] In this case the one unpaired electron is housed in the d_{z^2} orbital,[17-22] and thus the interaction between the unpaired electron and iodine atom can occur through σ-bonding.

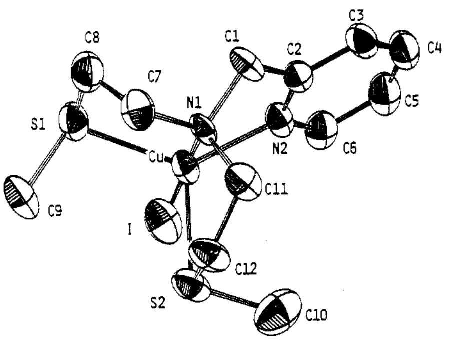

Figure 6. ORTEP drawing of $[Cu(N_2S_2P)I]^+$.

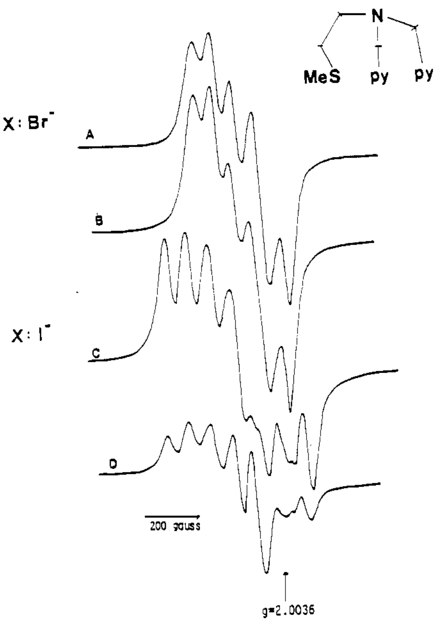

Figure 7. ESR spectra of $[Cu(N_3S)X]ClO_4$ at 295 K: (A) X = Br^- in dmf; (B) X = Br^- in nitromethane; (C) X = I^- in nitromethane; (D) X = I^- in dmf.

Structure in Solution and in the Solid State. It is generally known that the tripodlike ligands form five-coordinate metal complexes.[17-22] In the case of copper(II) complexes, two possible structures, the trigonal bipyramid and the square pyramid, can be distinguished in terms of the absorption (room-temperature) and ESR (frozen-state) spectral data.[17-22] For example, the X-ray diffraction method revealed that $[Cu(NS_3)Br]ClO_4$ has a trigonal-bipyramidal structure,[6] and this result is consistent with those of absorption (room temperature)[7,10] and frozen-state ESR data.[9,23] The same results have been obtained for $[Cu(N_2S_2P)Br]ClO_4$ (trigonal bipyramid)[6,10] and $[Cu(N_3O)X]ClO_4$ (X = Cl^- and Br^-; square-pyramid).[10,24] In the present work, the structure of $[Cu(N_3S)X]ClO_4$ (X = N_3^- and Br^-) has been determined to be a square pyramid, which is consistent with the absorption and ESR spectral data.[9] These facts suggest that the structure of [Cu(L)X]Y depends on the ligand (L) and halogen (X), but the structure in the solution is essentially the same as that in the solid state, and also the solution coordination is not significantly tem-

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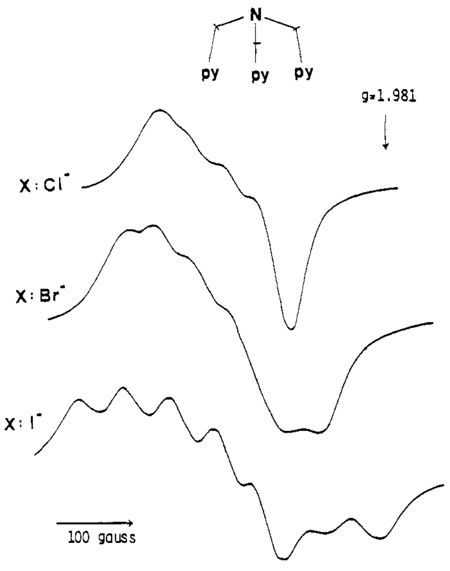

Figure 8. ESR spectra of $[Cu(N_4P)X]ClO_4$ in dmf at 295 K.

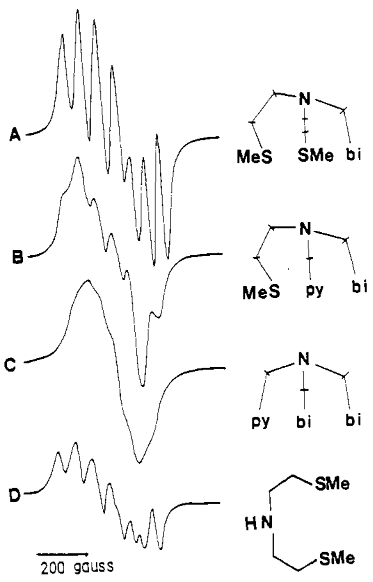

Figure 9. ESR spectra at 295 K: (A) $[Cu(N_2S_2B)Br]PF_6$ in acetonitrile; (B) $[Cu(N_3SBP)Br]PF_6$ in acetonitrile; (C) $[Cu(N_4BP)Br]PF_6$ in acetonitrile; (D) $[Cu(NS_2)Br]ClO_4$ in dmf.

perature-dependent[25-29] except for some rare examples reported by Addison et al.[11]

The solvent effect on the coordination structure of these complexes in solution has been studied by Addison et al.[28] According to their results, it seems best to use nitromethane for studying these complexes. In our cases, similar ESR spectra are observed at room temperature in both nitromethane and *N,N*-dimethylformamide (dmf), except for some examples that will be shown later.

Elucidation of ESR Spectra. The solution ESR spectra of the complexes with NS_3 and N_2S_2P are shown in Figures 2 and 3, respectively. Spectra of complexes with N_2S_2B, N_3S, N_4P, and N_2S are illustrated in Figures 7–9. All the X = Cl^- and N_3^- complexes exhibit four hyperfine lines. In the case of X = Br^- complexes, seven (NS_3, Figure 2; N_2S_2B, trace A in Figure 9), six (N_2S_2P, Figure 3; N_3SPB, trace B in Figure 9), five (N_3S, traces A and B in Figure 7; N_4P, Figure 8; N_4PB, trace C in Figure 9), and eight (N_2S, trace D in Figure 9) lines are observed. The present crystal structure determination clearly indicates that the presence of Br^- ion at the corner of the square plane causes the unusual ESR spectrum of $[Cu(N_3S)Br]^+$. It is noteworthy that the intervals between lines are not regular for $[Cu(N_3S)Br]^+$ and $[Cu(N_2S_2P)Br]^+$ complexes, which is different from the spectra of $[Cu(NS_3)Br]^+$ and $[Cu(N_2S_2B)Br]^+$.

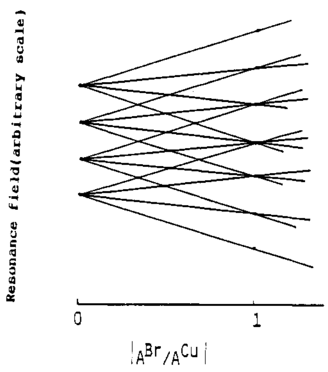

Figure 10. Schematic representation of the resonance field in copper–bromine complexes.

Similar behaviors were also found for X = I^- complexes; nine hyperfine lines are observed for complexes with NS_3 (Figure 2) and N_2S_2P (Figure 3), but seven lines are found for N_4P (cf. Figure 8), and a very complicated spectrum was observed for N_3S (trace C in Figure 7). The spectral features in dmf are generally similar to those in nitromethane, but some differences were observed for $[Cu(N_3S)I]^+$ (cf. ESR spectra in Figure 7).

In some cases, there may be two species in solution for these copper(II) complexes. In 1977, Barbucci et al.[21] reported that the frozen ESR spectrum (77 K) of $[Cu(Me_6tren)I]I$ (Me_6tren = tris(2-(dimethylamino)ethyl)amine) was unusual, appearing to be a superposition of the spectra of two slightly different trigonal-bipyramidal species. Also, there may be an equilibrium between the two structures trigonal bipyramid and square pyramid. However, even if there are two species in the solution, this model cannot explain the nine hyperfine lines with almost the same interval observed for $[Cu(NS_3)I]^+$ and $[Cu(N_2S_2P)I]^+$ complexes. In our compounds, the interaction between the unpaired electron and the nuclear spin of the nitrogen atom ($I = 1$) is possible, but its magnitude is small (<15 G),[3,4] and thus this cannot be a main reason for the unusual spectra studied here. This is supported by the fact that all the X = Cl^- and N_3^- complexes show a usual solution ESR spectrum. All these facts support our proposal to elucidate the anomalous solution ESR spectra.

In the present systems, the spin Hamiltonian is written as

$$\mathcal{H} = g\beta H_0 \cdot S + A^{Cu} \cdot I_i^{Cu} \cdot S + A^X \cdot I_i^X \cdot S \qquad (1)$$

where I^{Cu} and I^X represent the nuclear spin momentum values of the copper and halogen atom, respectively. A^{Cu} and A^X denote the hyperfine coupling constants due to the interaction of the unpaired electron with the nuclear spins of copper and halogen atoms, respectively. The solution for eq 1 has already been obtained by several authors,[30] and the result based on the first-order approximation is roughly shown in Figure 10 (for X = Br^- complexes).

In the case where interaction between the unpaired electron and the nuclear spin of the halogen atom is absent ($A^X = 0$), four hyperfine lines are expected, and this corresponds to the cases of X = Cl^- and X = N_3^- complexes. According to the scheme in Figure 10, seven hyperfine lines are anticipated for X = Br^-

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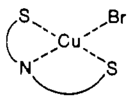
complexes when $|A^{Cu}|$ is nearly equal to $|A^{Br}|$ ($|A^{Br}/A^{Cu}| \approx 1$), which corresponds to the cases of $[Cu(NS_3)Br]^+$ and $[Cu(N_2S_2B)Br]^+$.

When $|A^{Br}/A^{Cu}|$ is not equal to 1, the observable spectrum will depend on the ratio $|A^{Br}/A^{Cu}|$ and the line width of the peak. On the basis of the frozen ESR spectrum (77 K), it is clear that $[Cu(NS_2)Br]^+$ has a square-planar structure



and it is less likely that there is an equilibrium of the trigonal bipyramid and the square pyramid in solution, because NS_2 is not a tripodlike ligand. Thus, it seems most reasonable to assume that the $|A^{Br}/A^{Cu}|$ value in this complex is not equal to 1, although the exact $|A^{Br}/A^{Cu}|$ value cannot be evaluated at present. If two or three peaks in the higher field of $[Cu(NS_2)Br]^+$ collapse to one broad band, such a spectrum should resemble those of $[Cu(N_2S_2P)Br]^+$, $[Cu(N_3S)Br]^+$, etc. Thus, we can elucidate the solution ESR spectra of $X = Br^-$ complexes in terms of the scheme in Figure 10 on the assumption that the ratio $|A^{Br}/A^{Cu}|$ is variable due to the change of the ligand character.

The same discussion as described above is also applicable to the $X = I^-$ complexes: If $|A^I| = |A^{Cu}|$, nine hyperfine lines are expected, which is verified by the $[Cu(NS_3)I]^+$ and $[Cu(N_2S_2P)I]^+$ complexes. If $|A^I/A^{Cu}| \neq 1$, the observable hyperfine lines should change, and this is confirmed by several examples; seven lines are observed for $[Cu(N_4P)I]^+$, and a very complicated spectrum was observed for $[Cu(N_3S)I]^+$ in nitromethane. Thus, we can successfully elucidate the unusual solution ESR spectra observed in this study on the assumption that the unpaired electron of the copper(II) ion interacts with the nuclear spins of both copper and halogen atoms, and its ratio $|A^X/A^{Cu}|$ is variable, depending on the ligand used.

In the case where the metal ion has a single open-shell orbital, φ, occupied with, e.g., spin α (denoted by φ^+) and the neighboring closed-shell ion (halogen ion in the present case) has an occupied pair of orbitals, χ^+ and χ^-, with the same spatial symmetry as φ, these orbitals will in general not be orthogonal but will have an overlap integral $S \neq 0$ between them. Thus the total wave function for a three-electron system is, to zero order, given by $|\chi^+{}_b\chi^-{}_b\varphi^+{}_b|$, where

$$\chi_b = 1/N_a{}^{1/2}(\chi + \gamma\varphi)$$

$$\varphi_b = 1/N_b{}^{1/2}(\varphi - \lambda\chi)$$

and γ is called a "covalent" mixing factor.[31,32] If we assume $N_a \approx N_b \approx 1$, we get[33] $\lambda = (\gamma + S)/(1 + \gamma S) \approx \gamma + S$. These "overlap" and "covalent" effects convey a spin density onto ligand sites whose spin direction is parallel to that of the local metal moment. This is the main origin for the nonzero value of A^X.[31,32] The unpaired spin density on the halogen atom is roughly calculated to be $\lambda^2/2N_a$;[33] this indicates that the A^X increases when the energy gap between φ(d orbital) and χ(halogen atom) decreases.[34] Thus, we can estimate that γ is variable due to the change of ligand atoms, because the energy of the d orbital is dependent on the ligand atoms surrounding the metal ion as exemplified by the fact that the reduction potential of [Cu(L)X]Y is highly dependent on the ligand character.[12] The above discussion supports our assumption that the ratio $|A^X/A^{Cu}|$ is variable due to the change of the ligand.

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Supplementary Material Available: Listings of details of the experimental conditions in the X-ray data collection, atomic coordinates, anisotropic temperature factors, and all bond distances and angles (10 pages); complete listings of F_o and F_c values (43 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry, Inductive Metal-Metal Bond Transfer, and Magnetic Susceptibility of Adducts of Tetrakis(trifluoroacetato)dichromium

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Bonding of donors (B) to chromium(II) trifluoromethanecarboxylates, $Cr_2(O_2CCF_3)_4$, has been explored with respect to the influence one Cr-L bond has on the other. In order to obtain enthalpies for the free acid, a displacement reaction had to be studied, and a novel extension of the *E*, *C*, and W equation was derived to provide this information. Despite the weak chromium-chromium bond, adduct formation at one axial site is found to significantly lower the enthalpy of adduct formation at the second. Enthalpies and equilibrium constants for first and second adduct formation with a range of donors were measured and the data used to calculate transmittance parameters by using a previously proposed inductive-transfer model in these weakly bonded metal-metal carboxylates. The $Cr_2(O_2CCF_3)_4$ core interacts with Lewis bases in primarily an electrostatic fashion, and the weak metal-metal bond was found less capable of transmitting both covalent and electrostatic effects than the metal-metal bonds in either $Mo_2(O_2CCF_2CF_2CF_3)_4$ or $Rh_2(O_2CCH_2CH_2CH_3)_4$. This is consistent with a weak covalent bond and a large Cr-Cr distance for the *C* and *E* perturbation, respectively. Magnetic susceptibility measurements of $Cr_2(O_2CCF_3)_4B_2$ adducts demonstrate a dramatic rise in the magnetic susceptibility of the adducts as the donor strength of B increases. Arguments are presented that interpret these findings as resulting from partial breaking of the metal-metal bond in proportion to donor bond strength. Consistent with this interpretation, which assumes some degree of d-orbital overlap in the $Cr_2(O_2CCF_3)_4$ core, we find singlet-triplet splittings ($-2J$ from 611 to 688 cm^{-1}) that are larger than the range observed for the extensively studied dinuclear Cu(II) carboxylates.

Introduction

The dimeric metal carboxylates, $M_2(O_2CR)_4$, are convenient systems for studying the transmission of inductive effects through the metal-metal bond of clusters. Charge neutrality allows study in noncoordinating or weakly coordinating solvents, and the metal centers display open axial (trans to the metal-metal bond) coordination sites to which Lewis bases readily bind. Earlier work from this laboratory[1-5] has focused upon spectroscopic and

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