

be required since the overlap of the originating orbitals, d_{xz} and d_{yz} , is not as great as those for the solid-state A_{2u} transition, d_{z^2} , and limited overlap would not lead to identical ground state energies for the two complexes. Peak A, however, is notably energy stable throughout the range of concentrations for which it is observable, from 0 to 58% Pt. This energy stability demonstrates a clear independence from platinum, indicating that neither the originating nor terminal orbitals are participating in delocalization of any kind. This interpretation rules out the possibility of the $e_g(xz,yz) \rightarrow a_{2u}(\pi^*)$ transition. A different assignment thus appears to be needed. The assignment should account for three factors: (1) no involvement with the delocalized orbital associated with the out-of-plane solid-state band, (2) solid-state red-shifting, since this band is of lower energy than its corresponding transition in solution, and (3) a reasonable alternate location for the $e_g(xz,yz) \rightarrow a_{2u}(\pi^*)$ transition.

Possible candidates for peak A will be the several lowest energy ${}^1E_u \leftarrow {}^1A_{1g}$ transitions in $Ni(CN)_4^{2-}$. Since spin-orbit coupling is not a major effect in Ni ,⁹ only singlet-singlet transitions will be considered as bases for the state transitions. A widely accepted energy-level scheme is that of Gray and Ballhausen,¹² in which, for both $Ni(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$, the occupied metal d orbitals are distinct in energy from ligand orbitals. Although SCF-X α -SW calculations¹⁶ on $Pt(CN)_4^{2-}$ and $[Pt(CN)_4]_2$ show extensive mixing of both bonding and nonbonding ligand orbitals with metal d orbitals, which introduces many more choices for transitions, preliminary SCF-X α -SW calculations on $Ni(CN)_4^{2-}$ ²⁸ show a clear separation of metal d levels from bonding ligand orbitals. Thus, the most reasonable candidates for peak A will be the following transitions: (i) $a_{1g}(z^2) \rightarrow e_u(\pi^*)$; (ii) $b_{2g}(xy) \rightarrow e_u(\pi^*)$; (iii) $e_g(xz,yz) \rightarrow b_{2u}(\pi^*)$; (iv) $e_u(\pi^b) \rightarrow b_{1g}(x^2 - y^2)$.

The third consideration noted earlier, an alternate location for the $e_g(xz,yz) \rightarrow a_{2u}(\pi^*)$ transition, should now be discussed in preparation for considering the most likely assignment for peak A. Since we are ruling out this transition for peak A, it most likely will reside nearby in the low end of the remaining $Ni(CN)_4^{2-}$ charge-transfer transitions. The second-lowest prominent $E_u \leftarrow A_{1g}$ transition is at $\sim 50\,500\text{ cm}^{-1}$ and appears to be the most likely location of $e_g(xz,yz) \rightarrow a_{2u}(\pi^*)$.

Peak A should thus be due to a transition of lower energy than $e_g(xz,yz) \rightarrow a_{2u}(\pi^*)$. This requirement eliminates transition iv since the $b_{1g}(x^2 - y^2)$ orbital has been placed close to or above the $a_{2u}(\pi^*)$ orbital^{12,16,26} and $e_u(\pi^b)$ is $>1\text{ eV}$ below the occupied 3d levels.²⁶ Transition iii is also suspect since the $b_{2u}(\pi^*)$ orbital

is nonbonding in the complex and most certainly is above the $a_{2u}(\pi^*)$ orbital.

The remaining transitions, i and ii, are still plausible candidates on the basis of semiquantitative energy arguments. Transition i, however, is clearly associated with an orbital involved with the extensive out-of-plane delocalized transition, $a_{1g}(z^2) \rightarrow a_{2u}(\pi^*)$. Thus, the first consideration, noninvolvement with delocalized orbitals, rules out transition i. Transition ii thus passes the first and third considerations, and it also satisfies the second: a susceptibility to solid-state perturbation. While the mechanism of perturbations is not within the scope of this paper, it is reasonable to note that, though we have ruled out band formation for peak A in $Ni(CN)_4^{2-}$, both factor-group splitting²⁹ and crystal field interactions remain as other possible mechanisms. The latter could conceivably raise the energy levels of the $3d_{xy}$ levels more than π_h^* levels due to the 45° staggering of adjacent planes²¹ and the distance from Ni to the π_h^* orbitals, which would lead to red-shifting upon crystallization from solution. A solvent effect has been observed for this transition by Mason and Gray¹¹ in which they observed a 1100-cm^{-1} red-shift upon changing the solvent from H_2O to CH_3CN .

The conclusions from our observations are that the in-plane $35\,400\text{ cm}^{-1}$ transition in $Ni(CN)_4^{2-}$ ($37\,200\text{ cm}^{-1}$ in solution) is likely due to a $b_{2g}(xy) \rightarrow e_u(\pi^*)$ orbital transition and the $50\,500\text{ cm}^{-1}$ transition (C) is possibly the $e_g(xz,yz) \rightarrow a_{2u}(\pi^*)$ transition. This essentially is a complete switch from two previous assignments^{11,13} of the corresponding transitions in $Pt(CN)_4^{2-}$. Such a switch is not without some precedent: Peipho, Schatz, and McCaffery⁹ have proposed that their assignment for the $46\,100\text{-cm}^{-1}$ $Pt(CN)_4^{2-}$ E_u transition (D) be applied to the $37\,200\text{-cm}^{-1}$ transition in $Ni(CN)_4^{2-}$ (A).

We are currently studying series of various salts of $Ni(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$ and continuing SCF-X α -SW calculations on $Ni(CN)_4^{2-}$ transitions to further elucidate the several effects apparently present in these compounds.

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Excited-State Raman Spectroscopic Study of Bonding Changes in $K_3[Mn(CN)_5NO]$ Induced by Nitrosyl Bending

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The Raman spectrum of $K_3[Mn(CN)_5NO]$ in the manganese to nitrosyl charge-transfer excited electronic state is reported. The CN stretching frequencies in the excited electronic state decrease by about 100 cm^{-1} from those in the ground electronic state. The dependence of the Raman intensity on the laser pulse energy shows that the observed band arises from a two-photon process. Two excited-state Raman peaks are found in the metal-ligand region of the spectrum at 533 and 565 cm^{-1} and are assigned to the excited-state MnCN bending mode and the Mn-N stretching mode, respectively. These peaks also exhibit a two-photon dependence on the laser pulse energy. The changes in the vibrational frequencies between the ground and excited electronic states are interpreted in terms of the loss of the highly covalent linear $\{MNO\}^6$ unit caused by bending of the MNO bond in the excited electronic state.

Transition-metal nitrosyl complexes that contain a linear MNO unit can undergo a geometry change to a bent MNO unit in metal

to ligand charge-transfer excited states.¹⁻³ The photochemical consequences of this geometry change were first pointed out in

a study of the d^6 , $\{MNO\}^6$ complex $[Fe(das)_2(X)(NO)]^{2+1}$ and more completely documented in the d^{10} , $\{MNO\}^{10}$ complex $Co(CO)_3NO$.^{2,4}

Direct spectroscopic evidence for the MNO bend in the nitroprusside ion $Fe(CN)_5NO^{2-}$ was recently obtained by using excited-state Raman spectroscopy.³ In this two-photon experiment, one photon was used to excite the complex and the second photon was used to probe the molecule in its relaxed excited state. The most common experiment has been the "one-color" experiment in which the leading edge of a laser pulse pumps the system and the trailing edge probes the excited state.⁵ In nitroprusside, the 1939-cm^{-1} stretching frequency of the linear NO in the ground electronic state decreased to 1821 cm^{-1} in the electronic excited state.³ The 120-cm^{-1} decrease is caused by the change from a linear sp -hybridized NO containing a triple bond to the bent sp^2 -hybridized NO containing a double bond. Bands corresponding to excited-state metal-ligand vibrations were also found, but the CN stretching vibrations in the excited electronic state were too weak to be observed.

In an effort to obtain more information about the effect of the MNO bend on the vibrations of the other ligands, we studied the excited state Raman spectra of the isoelectronic $Mn(CN)_5NO^{3-}$ ion. The most significant result of this study is the measurement of the cyanide stretching modes in the excited electronic state. We report here the Raman spectrum of this ion in the manganese to nitrosyl charge-transfer excited electronic state. In addition, we report new results for the nitroprusside ion. The observed changes in the cyanide ligand stretching frequencies and of those in the metal-ligand region of the spectrum are interpreted in terms of the change from a highly covalent $\{MNO\}^6$ unit to a more classical metal-ligand unit in the bent configuration in the excited electronic state.

Experimental Section

$K_3[Mn(CN)_5NO]$ was synthesized by using literature methods.⁶ Aqueous solutions ($\sim 1\text{ M}$) of $Mn(CN)_5NO^{3-}$ were prepared by dissolving $K_3[Mn(CN)_5NO]$ in H_2O or D_2O . The room-temperature solution was circulated by a peristaltic pump through a 20-gauge hypodermic needle to produce a jet stream. The flow rate was about 0.3 mL/s .

The excited-state Raman spectra were obtained by exciting and probing with 406 nm , 10 ns pulses ($0.8\text{--}3\text{ mJ/pulse}$) at a 60-Hz repetition rate from an excimer-pumped dye laser (Lambda Physik EMG 201 MSC and FL2001). The laser output was focused by using a plano-convex lens with 150-mm focal length. The focus was adjusted to lie about 0.8 cm behind the jet stream in order to minimize dielectric breakdown. Each laser shot irradiates a fresh solution. The absorption band at 405 nm has been assigned by Gray et al. to the $6e(d_{xz,yz})$ to $7e(\pi^*NO)$ MLCT transition.⁷ The Raman-scattered light was passed through a triple monochromator (Instruments SA, Inc., Models DHR320 and HR640) and detected by an intensified diode array optical multichannel analyzer (EG&G, PARC Model 1460). All of the signals were digitized and stored in the computer for the later manipulations.

Results

1. CN Stretching Region. A broad excited-state Raman band in the CN stretching region of the spectrum is centered at 2010 cm^{-1} as shown in Figure 1. Three other bands that are observed in this region, the cluster of three sharp peaks at about 2111 cm^{-1} , the sharp peak at 1774 cm^{-1} , and the broad peak at 1644 cm^{-1} , are the ground-state cyanide stretches, the nitrosyl stretch and

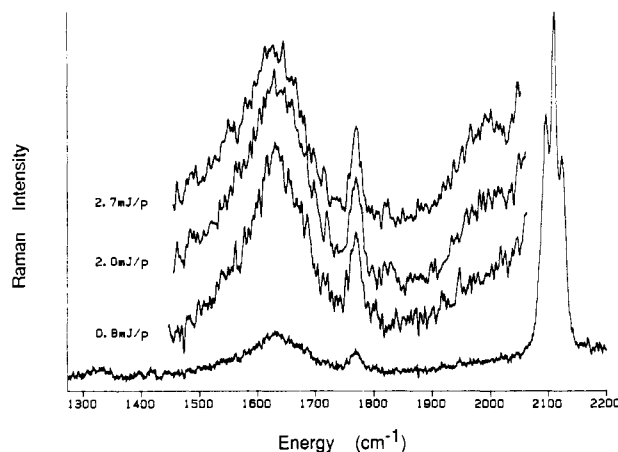


Figure 1. Power dependence of the excited-state Raman spectra of $K_3[Mn(CN)_5NO]$ in H_2O . The bottom trace shows the spectrum of the $1300\text{--}2200\text{-cm}^{-1}$ region obtained at 0.8 mJ/pulse . The three upper traces show the spectra obtained by using different laser pulse energies normalized to the 1644-cm^{-1} water peak.

the ground-state solvent water OH bend, respectively.^{8,9} These peaks do not show a dependence on the laser power (vide infra) and occur at exactly the positions of the known ground-state vibrations. No new peaks are observed at higher frequencies. The only bona fide excited state Raman band in this region is the band at 2010 cm^{-1} . The three most important features of this band, its dependence on the laser pulse energy, its shift to lower frequency from that in the ground state, and its breadth, are discussed individually below.

The intensity of the 2010-cm^{-1} peak increased nonlinearly with the pulse energy. A plot of the log of the peak intensity versus the log of the laser power was linear with a slope of 1.6 ± 0.2 . This result clearly demonstrates that the 2010-cm^{-1} peak does not arise from a one-photon process. The observed slope is smaller than the slope of 2 that would be expected for a two-photon process. The slightly smaller value indicates that relaxation of the excited state takes place within the duration of the laser pulse. From this observation, an order of magnitude lifetime of the excited state can be inferred to be on the order of 10 ns . The nonlinear power dependence offers definite evidence that the observed peak is not a weak peak from the ground electronic state of the complex.

In conjunction with this study, the excited-state Raman spectrum of the nitroprusside ion was reinvestigated. By use of the multichannel detection system, the excited-state CN stretches could also be detected in the spectrum of this ion. A broad band centered at 2000 cm^{-1} with a slope of 1.6 ± 0.2 in the log I vs log laser power plot is observed.

The excited-state NO stretch in $Mn(CN)_5NO^{3-}$ is too weak to be detected. It is expected in the $1650\text{--}1700\text{-cm}^{-1}$ region of the spectrum by analogy to spectrum of the $Fe(CN)_5NO^{2-}$ complex in which the excited-state NO stretch is clearly observed.³ This region is partially obscured by the broad solvent H_2O peak. The excited-state Raman spectrum was obtained in D_2O . No solvent peak is present in the desired region, but no excited-state NO stretch was found. All of the other excited state peaks are unaffected by the change in solvent. The 406-nm excitation line is in resonance with the metal-nitrosyl charge-transfer band. It is not known if 406 nm is in resonance with any of the excited states after the molecule is excited. The absence of the NO peak is probably caused by poor resonance enhancement in the excited electronic state.

2. Metal-Ligand Region. Two excited-state Raman peaks are found in the metal-ligand region of the spectrum at 533 and 565 cm^{-1} as shown in Figure 2. The remaining peaks in this region

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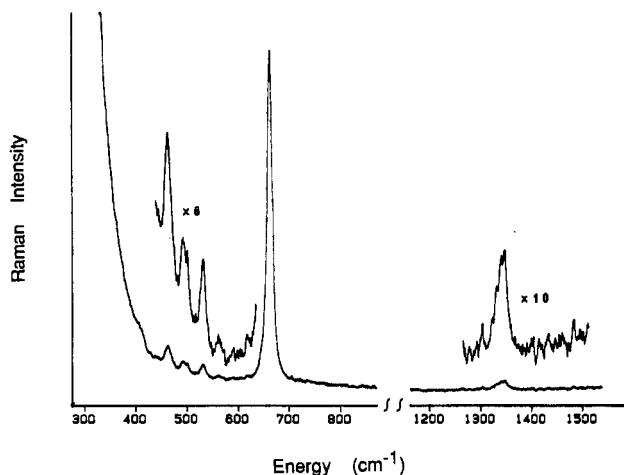


Figure 2. Excited-state Raman spectra of an aqueous solution of $K_3[Mn(CN)_5NO]$ in the metal-ligand and metal-ligand overtone regions.

at 662, 494, 461, and 413 cm^{-1} are all ground-state metal-ligand bands.^{8,9} These ground-state peaks all correspond to known ground-state vibrations, and all show linear dependences on the laser pulse energy.

The intensities of both the 553- and the 565- cm^{-1} peaks increase nonlinearly with increasing laser pulse energy. The quantitative dependence of their intensities on the laser pulse energy could not be determined as accurately as that of the CN stretch because they overlap the ASE background of the laser. The most accurate measurement was made on the most intense of the two. The log-log plot had a slope of 1.6 ± 0.3 identical within experimental error with that of the cyanide peak. The nonlinear dependence is strong evidence for the excited-state origin of these peaks.

A weak peak with a linear power dependence is observed at 1330 cm^{-1} . This peak is assigned to the first overtone of the ground-electronic-state 662- cm^{-1} Mn-N stretch. The observation of significant overtone intensity in this mode is evidence for a large manganese-nitrogen distortion in the excited electronic state.^{10,11}

The metal-ligand region of the excited-state Raman spectrum of $Fe(CN)_5NO^{2-}$ contained one peak at 548 cm^{-1} . In a previous study using a scanning double monochromator, three peaks at 501, 548, and 716 cm^{-1} were found. Only the 548- cm^{-1} peak is observed by using a triple monochromator. Two peaks that were previously reported could not be observed. The 548- cm^{-1} peak has a nonlinear power dependence.

Discussion

1. CN Stretching Region. The CN stretching frequency in the charge-transfer excited electronic state of $Mn(CN)_5NO^{2-}$ is shifted by 102 cm^{-1} toward lower energy relative to the ground-electronic-state CN frequencies. In the ground electronic state, three relatively sharp CN stretching peaks are observed at 2096, 2111, and 2125 cm^{-1} . These values are in good agreement with the reported values of the ground-electronic-state CN stretches.^{8,9} In the excited state spectrum, the peaks are not resolved but instead appear as one broad peak centered at 2010 cm^{-1} (Figure 1). The CN stretching frequencies in the excited state of the isoelectronic nitroprusside ion also decreased by 158 cm^{-1} from those in the ground state. The changes in the CN stretching region are thus similar for both the manganese and the iron complexes.

The 100- cm^{-1} magnitude of the decrease in the CN stretching frequencies is consistent with known decreases in $M(CN)_5L^{n-}$ complexes as L is changed from the nitrosyl ligand to classical ligands such as water or ammonia. The largest and most carefully studied series of complexes has been the $Fe(CN)_5L^{n-}$ series.¹³ When L is the linear nitrosyl ligand forming the $\{FeNO\}^6$ unit,

the totally symmetric CN stretching frequency is 2158 cm^{-1} .¹² In contrast, when L is a classical ligand, the frequencies decrease by about 100 cm^{-1} . As examples, when L = CN^- , the frequency decreases to 2040 cm^{-1} , when L = NH_3 , the frequency is 2055 cm^{-1} , and when L = H_2O , the frequency is 2045 cm^{-1} . Thus, changing the complex from one containing the $\{FeNO\}^6$ unit to one containing a classical $Fe(II)-L$ unit causes a decrease in the CN stretching frequency of 110–160 cm^{-1} . These comparison examples by necessity are all ground-state complexes. However, these examples show that the 100- cm^{-1} decrease in the CN stretching frequency is reasonably attributed to loss of the highly covalent $\{MNO\}^6$ unit as the nitrosyl ligand is changed from linear to bent in the excited electronic state.

The breadth of the observed band in the excited-state Raman spectrum is also a result of the linear to bent geometry change. When the point group changes from C_{4v} in the linear ground state to C_2 in the bent excited state, more bands become Raman active. In addition, the in-plane cyanide ligands become inequivalent and the differences in the stretching frequencies become larger. The observed broad band in Figure 1 is thus interpreted as the superposition of unresolved CN normal modes.

2. Metal-Ligand Stretching Region. The assignment of the peaks in the metal-ligand region of the excited-state Raman spectrum is not as unambiguous as that of the CN stretch. Two peaks are observed in the excited-state spectrum of $Mn(CN)_5NO^{2-}$ that can logically be associated with any of three normal modes whose ground-state frequencies are in the same region.¹² In the case of the isoelectronic $Fe(CN)_5NO^{2-}$ complex, one excited-state peak can logically be associated with any of three normal modes whose ground state frequencies are in the same region. The tentative identification of the excited-state peaks proposed below relies heavily on comparison with ground-state complexes that do not contain the $\{MNO\}^6$ group.

The largest and best-studied series of compounds that can be used as comparative examples is the $Fe(CN)_5L^{n-}$ series.¹³ A second series that will prove informative is the series of first-row transition-metal hexacyanides $M(CN)_6^{n-}$.¹⁴

The peak in the excited-state Raman spectrum of $Mn(CN)_5NO^{2-}$ at 533 cm^{-1} is tentatively assigned to the Mn-CN bending mode in the excited electronic state. The ground-state bend occurs at 494 cm^{-1} . This assignment is based on two lines of reasoning. First, the observed 533- cm^{-1} frequency is in the region of M-CN bending modes in first-row transition-metal cyanides that do not contain the FeNO group. In the iron(II) complexes, the Fe-CN bend is found between 500 and 580 cm^{-1} . (The bending mode occurs at 584 cm^{-1} when L = CN^- , at 572 cm^{-1} when L = H_2O , and at 566 cm^{-1} when L = NH_3 .) Second, the 533- cm^{-1} excited-state peak is too high in frequency to be a Mn-C stretch. All of the M-C stretching modes in the comparison compounds are found between 389 and 435 cm^{-1} . We thus assign the 533- cm^{-1} band to the Mn-CN bending mode, which increases in energy by 39 cm^{-1} in the excited electronic state because of the change from the highly covalent linear $\{MnNO\}^6$ unit in the ground state to a more classical metal-ligand interaction in the excited state.

The peak at 565 cm^{-1} is tentatively assigned to the Mn-N stretching mode in the excited electronic state. As discussed above, a frequency of 565 cm^{-1} is too high to be consistent with the known metal-carbon stretching modes. Quinby-Hunt and Feltham have observed that the metal-nitrosyl stretching frequency is lower in the bent geometry than in the linear geometry.¹⁵ In the interesting comparison compound $[Ru(Cl)(NO)_2(PPh_3)_2]^+$, which contains both a bent and a linear nitrosyl, the bent nitrosyl has a metal-nitrogen bond length 0.12 Å longer than that of the linear nitrosyl and presumably a lower metal-nitrogen stretching frequency.¹⁶ We thus assign the 565- cm^{-1} band to the Mn-N stretching mode, which decreases in energy by 97 cm^{-1} in the excited electronic

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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.

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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 = ClO₄ and PF₆), 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, $I = 3/2$; ¹²⁷I, $I = 5/2$). The above discussion was confirmed by the crystal structure determination of three compounds, [Cu(N₃S)N₃]ClO₄ (1), [Cu(N₃S)Br]ClO₄ (2), and [Cu(N₂S₂P)I]ClO₄ (3), where N₃S and N₂S₂P 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, $\beta = 100.69$ (2)°; 2, space group $P2_1/a$, $a = 14.600$ (7) Å, $b = 17.155$ (8) Å, $c = 7.686$ (1) Å, $\beta = 94.89$ (2)°; 3, space group $P2_1/n$, $a = 17.292$ (3) Å, $b = 14.411$ (2) Å, $c = 7.8202$ (7) Å, $\beta = 100.29$ (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 N₃ 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_{z²} 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 = ClO₄ and PF₆), show unusual solution ESR spectra at room temperature. As examples, the solution ESR spectra of [Cu(NS₃)X]ClO₄ (X = Cl⁻, Br⁻, and I⁻) are illustrated in Figure 2, where NS₃ 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 $|A_{\text{iso}}|$ 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(NS₃)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, $I = 3/2$; ¹²⁷I, $I = 5/2$). 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 found⁶ that six hyperfine lines are observed for the solution ESR spectrum of [Cu(N₂S₂P)Br]ClO₄ (cf. Figures 1 and 3), the spectrum being slightly different from that of [Cu(NS₃)Br]⁺. The crystal structure determination⁶ revealed that both [Cu(NS₃)Br]ClO₄ and [Cu(N₂S₂P)Br]ClO₄ 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(N₃S)N₃]ClO₄ (1), [Cu(N₃S)Br]ClO₄ (2), and [Cu(N₂S₂P)I]ClO₄ (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 NS₃,⁷ N₂S₂P,⁸ N₃S,⁹ and N₄P⁹ (for an explanation of the abbreviations of ligands, see

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