compared to **3** illustrates the extra stabilization of the +2 oxidation state of iron while coordinated to ring nitrogen of pyrimidine instead of pyridine. Additional studies are in progress to discern the nature of the charge-transfer transitions in these iron complexes.

Summary. The following are the principal results and conclusions of this investigation.

(i) Fe(II) and Fe(III) "bis" complexes of a designed ligand PrpepH (**4**) that resembles a portion of the metal-chelating locus of the antitumor antibiotic bleomycin (BLM, **1**) have been isolated and structurally characterized. The Fe(II) chelate **5** is the first example of a Fe(II) complex in which deprotonated amido nitrogen is coordinated to a Fe(II) center. The Fe(II)–N_{pep} bond is 1.984 (6) Å long. The Fe(III) complex **6** is only the second example of a Fe(III) chelate containing a Fe(III)–N_{pep} bond.

(ii) Successful isolation and characterization of **5** and **6** suggests that the β-hydroxyhistidine moiety of BLM could provide two N donors (deprotonated peptido N and imidazole ring N) to iron in both +2 and +3 oxidation states.

(iii) Comparison of metric parameters of the iron complexes of two tailored ligands PypepH (**2**) and PrpepH (**4**) establishes the fact that the pyrimidine ring nitrogen is a better donor for Fe(II) while the amido nitrogen prefers Fe(III) center. Spectral and electrochemical parameters of these complexes also indicate that the pyrimidine ring nitrogen confers extra stabilization to the Fe(III) center.

(iv) Taken together, results from this work suggest that the pyrimidine ring and the β-hydroxyhistidine portion of BLM could remain coordinated to iron in both +2 and +3 oxidation states. Also, presence of the pyrimidine ring nitrogen in the first coordination sphere of iron is expected to lower the reduction potential of Fe(III)–BLM and allow facile reduction to Fe(II)–BLM by the physiological reductants.

Acknowledgment. This research was sponsored by a grant from the Cancer Research Coordinating Committee of the University of California.

Supplementary Material Available: Crystal structure data for $[Fe(Prpep)_2]\cdot 2CH_3OH$ (**5**) and $[Fe(Prpep)_2]ClO_4\cdot 2CH_3OH\cdot CH_3CN$ (**6**), including atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms in **5** (Table S1) and **6** (Table S2), complete lists of bond lengths and angles for **5** (Tables S3 and S4) and **6** (Tables S7 and S8), anisotropic thermal parameters for **5** (Table S5) and **6** (Table S9), and H atom coordinates and isotropic thermal parameters for **5** (Table S6) and **6** (Table S10) (9 pages); the values of $10|F_o|$ and $10|F_c|$ for **5** (Table S11) and **6** (Table S12) (45 pages). Ordering information is given on any current masthead page.

Contribution from the Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Katahira, Sendai, Japan 980

Hyperfine Interactions of Coordinating Nitrogens in the Copper(II) Complexes Having a N_2S_2 Donor Set and Blue Copper Proteins

Ryo Miyamoto, Yasunori Ohba, and Masamoto Iwaizumi*

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Hyperfine coupling (hfc) parameters for coordinating nitrogens in some copper(II) complexes with planar and tetrahedrally distorted N_2S_2 coordination structures were obtained from their single-crystal-like ENDOR spectra. They are compared with those obtained for the N_4-, *cis*- and *trans*-N_2O_2-, and NO_3-type copper(II) complexes reported in a previous paper. The hfc parameters of coordinating nitrogens in the nitrogen and oxygen donor systems are mainly determined by deformation of the copper orbital containing the unpaired electron caused by the ligand field of the coordinating atoms, but in the N_2S_2 systems, spin distribution onto the sulfurs also makes an appreciable contribution to the ^{14}N hfc's, in addition to the effect of deformation of the copper orbital. Little difference was observed in the nitrogen hfc parameters between the systems containing thioether and thiol sulfurs, between *cis*-N_2S_2 and *trans*-N_2S_2 donor configurations, and between the planar and tetrahedrally distorted structures, but appreciable differences were observed between the sp^2-type nitrogens and the sp^3-type ones. The nitrogen hfc's in some blue copper proteins reported in literature are discussed in connection with the above results, and the largely different two ^{14}N hfc's observed for the proteins are shown to be explained qualitatively by the large deformation of the copper orbital containing the unpaired electron due to the existence of a trigonal-pyramidal or trigonal-bipyramidal coordination structure.

Introduction

In the previous paper,[1] we reported that the hyperfine coupling (hfc) constants of the donor nitrogens in nitrogen-coordinated copper(II) complexes show a good correlation with the donor sets and with the hybridized state of the nitrogens. In that paper we treated only the complexes having the donor sets N_4, *cis*-N_2O_2, *trans*-N_2O_2, and NO_3.

In this paper, we discuss ^{14}N hfc's in copper(II) complexes with the N_2S_2 donor set. The ^{14}N hfc's were obtained from ENDOR spectra. Few data have been reported for ^{14}N ENDOR spectra of copper(II) complexes with the N_2S_2 donor set, probably because of the low stability of the complexes in solution. However, ^{14}N hfc's in this system seem particularly interesting because the ^{14}N hfc's reported for some blue copper proteins,[2] in which copper is considered to be coordinated by nitrogens and sulfurs, seem to be very abnormal compared to the ones for the complexes treated in our previous paper.[1] It may therefore be valuable to know the general features of ^{14}N hf interactions in copper complexes in which copper is coordinated by nitrogens and sulfurs. In this paper we present the general features of hfc's of the donor nitrogens in some copper(II) complexes with planar and tetrahedrally distorted N_2S_2 coordination structures, and on the basis of these results, we discuss the ^{14}N hfc's reported for the blue copper proteins.

Experimental Section

The ligands used in this work (Figure 1) were obtained commercially and used without further purification except for 2-((methylthio)methyl)pyridine (mtmpy) and *N,N'*-ethylenebis(thioacetylacetone imine) (H_2sacen) which were synthesized according to the literature.[3,4] The copper(II) complexes were prepared by mixing a solution of $CuCl_2$ or $Cu(NO_3)_2$ and a solution of the ligand under proper pH conditions. The complexes of thiols are, in general, so unstable that complex solutions for EPR and ENDOR measurements were prepared by a rapid mixing and freezing method. Formation of the complexes with the N_2S_2 donor set

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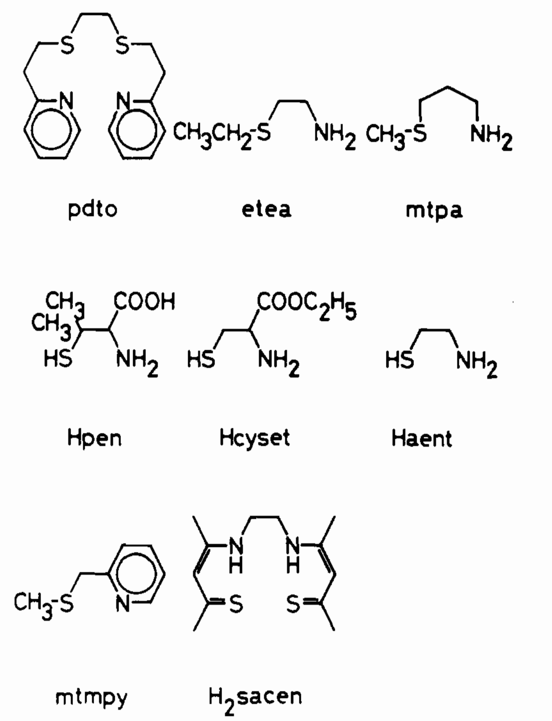

Figure 1. Ligands: pdto, 1,8-bis(2-pyridyl)-3,6-dithiaoctane; etea, (2-(ethylthio)ethyl)amine; mtpa, (3-(methylthio)propyl)amine; Hpen, DL-penicillamine; Hcyset, L-cysteine ethyl ester; Haent, 2-aminoethanethiol; mtmpy, 2-((methylthio)methyl)pyridine; H_2sacen, *N,N'*-ethylenebis-(thioacetylacetone imine).

Table I. EPR and ENDOR Parameters

no.	complex	medium[a]	$g_\parallel$	$^{Cu}A_\parallel$/MHz	^{N}A/MHz[b]
1	Cu(pdto)	MeOH	2.177	507.2	37
2	$Cu(etea)_2$	H_2O–MeOH	2.198	536.4	30
3	$Cu(mtpa)_2$	H_2O–MeOH	2.226	547.8	30
4	$Cu(pen)_2$	H_2O	2.131	565.3	29
5	$Cu(cyset)_2$	H_2O	2.135	566.2	28
6	$Cu(aent)_2$	H_2O	2.129	577.1	27
7	Cu(mtmpy)	H_2O–triol	2.192	475.9	34
8	Cu(sacen)	Ni(sacen)	2.108	555.1	38.4
9	Cu(sacen)	Zn(sacen)	2.126	493.5	37.0

[a] Key: MeOH; methanol, triol; glycerol. [b] ^{14}N hfc constants in the $g_\parallel$ direction obtained from ENDOR.

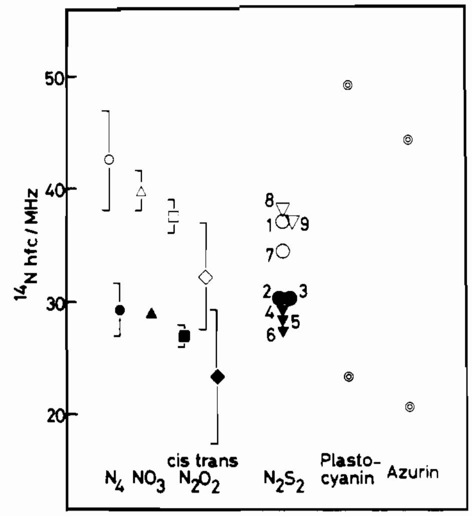

Figure 2. ^{14}N hfc parameters of the coordinating nitrogens in copper complexes having the N_4, NO_3, *cis*- and *trans*-N_2O_2, and N_2S_2 donor sets and in some blue copper proteins. For the copper complexes having the N_4, NO_3, and *cis*- and *trans*-N_2O_2 donor sets, only ranges of the parameters are shown. Open symbols are for sp^2-type nitrogens and solid symbols are for sp^3-type nitrogens. For the N_2S_2 type complexes the symbols ▽ and ▼ are for complexes coordinated by thiol sulfur and the symbols ○ and ● are for complexes coordinated by thioether sulfur.

was confirmed by comparison of their EPR spectra with those in the literature[5] or based on the Peisach's correlation diagram of EPR parameters ($g_\parallel$ and $^{Cu}A_\parallel$) and donor sets.[6] The preparation method used for each complex is as follows.

Cu(pdto). The complex solution for EPR and ENDOR measurements was obtained by mixing methanol solutions containing 0.01 g of $CuCl_2 \cdot 2H_2O$ and 0.04 g of the ligand in 2 mL each of solvent.

$Cu(etea)_2$. A 0.13 M aqueous solution of the ligand and a 13.0 mM aqueous solution of $Cu(NO_3)_2$, both of which were adjusted to have an ionic strength of 1.5 with $NaNO_3$, were mixed, and then the pH was adjusted to 9.5 with NaOH. For EPR and ENDOR measurements, methanol in an amount of half the volume of the aqueous complex solution was added.

$Cu(mtpa)_2$. To a 50 mM aqueous solution of the ligand was added the same volume of a 12.5 mM aqueous solution of $Cu(NO_3)_2$, after the solutions were adjusted to have an ionic strength of 1.5 with $NaNO_3$. The pH of the solution became 11.5 by mixing the solutions. For EPR and ENDOR measurements, an equivalent volume of methanol was added to the aqueous complex solution.

$Cu(pen)_2$. The complex solution for EPR and ENDOR measurements was obtained by the method of rapid mixing and freezing of a 25 mM aqueous solution of $Cu(NO_3)_2$ and a 100 mM aqueous solution of the ligand, which was adjusted to have a pH of 10.2.

$Cu(cyset)_2$. The complex solution was obtained by the rapid mixing and freezing of a 25 mM $Cu(NH_3)_4$ aqueous solution and a 100 mM ligand aqueous solution whose ionic strength and pH were adjusted to be 1.5 and 11.5 with $NaNO_3$ and NaOH, respectively.

$Cu(aent)_2$. The complex solution was obtained by the rapid mixing and freezing of a 12.5 mM $Cu(NH_3)_4$ aqueous solution and a 50 mM ligand aqueous solution whose ionic strength and pH were adjusted to be 1.5 and 10.0 by $NaNO_3$ and NaOH, respectively.

$Cu(mtmpy)_2$. The oily ligand was converted without isolation to the stable nickel(II) complex after the synthesis of the ligand. The resulting nickel(II) complex was dissolved together with 10% equimolar $CuCl_2$ in a water–glycerol (1:1) mixture. The resulting solution containing $Cu(mtmpy)_2$ was used for EPR and ENDOR measurements.

Cu(sacen). An ethanol solution of nickel(II) or zinc(II) acetate contaning copper(II) acetate in the amount of 2–3% of the nickel or zinc salt was added to an ethanol solution of the ligand. The precipitates were recrystallized from acetone to obtain copper-doped nickel or zinc complex crystals, and the crystal powders were used for EPR and ENDOR measurements.

EPR spectra were recorded on a Varian E112 X-band EPR spectrometer equipped with a Oxford ESR 9 cryostat at temperatures ~ 20–30 K. The magnetic fields and microwave frequencies were measured by an Echo Electronic EFM 2000 NMR field meter and a Takedariken TR 5204 frequency counter, respectively.

ENDOR spectra were measured by the EPR spectrometer equipped with a Varian E1700 ENDOR unit and an ENI 550L RF power amplifier by use of RF amplitude modulation. Magnetic field modulation was not used. The temperature was controlled at ~10 K by the Oxford ESR 9 cryostat.

^{14}N hfc parameters were obtained from the single-crystal-like ENDOR spectra, which were recorded by setting the magnetic field at the lowest field extreme of the EPR spectra. The obtained ^{14}N hfc parameters corresond to the hfc constants in the $g_\parallel$ direction. In some cases, ^{14}N ENDOR signals overlapped the ^1H ENDOR signals. However, the measurements under different conditions of temperature, microwave power, and concentration or the application of the angle-selected ENDOR method was effective enough to distinguish ^{14}N ENDOR signals

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(5) (a) Sakaguchi, U.; Addison, A. W. *J. Chem. Soc., Dalton Trans.* **1979**, 600. (b) Ainscough, E. W.; Brodie, A. M.; Larsen, N. G. *Inorg. Chim. Acta* **1982**, *60*, 25. (c) Davis, F. J.; Gilbert, B. C.; Norman, R. O. C.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1763.

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from the ^1H signals in the present case. It may be also notable that the use of adiabatic rapid passage of the microwave power is also sometimes effective to distinguish the ^{14}N and ^1H ENDOR signals,[12] though this method was not applied in the present case.

Results

The $g_{\parallel}$, $^{Cu}A_{\parallel}$, and ^{14}N hfc parameters obtained are listed in Table I. The $g_{\parallel}$ and $^{Cu}A_{\parallel}$ values are in the range for the N_2S_2 donor set in the Peisach's diagram of the correlation between the EPR parameters and the donor sets.[6] Ni(sacen) has a planar coordination structure, while Zn(sacen) has a tetrahedral one.[7] The increase of $g_{\parallel}$ and the decrease of $^{Cu}A_{\parallel}$ of Cu(sacen) by the change of the nickel complex matrix to the zinc complex matrix apparently indicates that the copper complex doped in the zinc complex system has a tetrahedrally distorted structure, reflecting the coordination structure of the matrix molecule. The ^{14}N hfc parameters are plotted in Figure 2 together with the data for the complexes having the other types of donor sets obtained in the previous paper[1] and the data for *Populus nigra* plastocyanin and *Pseudomonus aeruginosa* azurin reported by Roberts et al.[2] for comparison.

As Figure 2 shows, the ^{14}N hfc parameters appreciably differ by the hybridized state of nitrogens; the nitrogens with sp^2-type hybridization have larger hfc parameters than those with sp^3-type hybridization. Such an effect of the hybridization on the hfc's has been pointed out and discussed for the complexes with N_4, *cis*- and *trans*-N_2O_2, and NO_3 donor sets in the previous paper.[1] The results indicate that ^{14}N hfc's are valuable in estimating the type of nitrogen, i.e., aromatic aza or deprotonated amide nitrogens or aliphatic amine nitrogens.

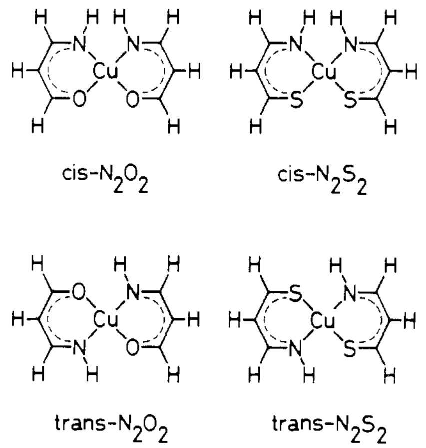
Excluding such differences by hybridized states, no appreciable differences were observed for the ^{14}N hfc parameters among complexes; i.e., there are no appreciable differences between the hfc parameters for systems having thiol sulfurs and thioether sulfurs and those in the planar coordination system and the tetrahedrally distorted one. It is notable also that the observed hfc parameters are in the range for the N_4 and N_2O_2 donor sets.

As with the complexes having bidentate ligands, there is no experimental information on whether the complexes have the cis form or the trans form. However, it seems reasonable to assume that the bidentate ligands with nitrogen and sulfur donor atoms take the trans form as in complexes having the N_2O_2 donor set where most of bidentate ligands take the trans form. Hence, it may be said from Figure 2 that there is no marked differences between the ^{14}N hfc parameters of the *cis*-N_2S_2 complexes and *trans*-N_2S_2, in contrast with the cases of the *cis*- and *trans*-N_2O_2 complexes showing appreciable differences.

Discussion

Effects of Sulfur Coordination on the ^{14}N Hfc Parameters. The contribution of the dipolar couplings of the unpaired electron on copper to the observed ^{14}N hfc parameters is nearly 1–2 MHz,[1] and the observed ^{14}N hfc parameters arise mainly from spin densities populated on the nitrogen. In the previous paper,[1] we pointed out that such a distribution strongly depends on deformation of the copper orbital containing the unpaired electron, which is mainly caused by crystalline fields of the donor atoms. In the complexes having NO_3, *cis*-N_2O_2, and *trans*-N_2O_2 donor sets, the copper unpaired electron orbital hybridizes so that the electron cloud expands towards the oxygen atoms and shrinks in the direction of the nitrogens, which have a stronger crystal field than oxygens. Such a deformation of the orbital affects overlaps with the orbitals of the donor atoms and hence ^{14}N hfc parameters.

In the case of the complexes having the N_2S_2 donor set, the copper orbital containing the unpaired electron is expected to expand toward the nitrogen atoms and to shrink in the direction of the sulfurs, because the sulfur atom gives a stronger crystal field than the nitrogen. The unpaired electron is, therefore, expected to have more density on the donor nitrogens than the sulfurs and to give a larger ^{14}N hfc parameters than those in the N_4 and *cis*- and *trans*-N_2O_2 complexes.


cis-N_2O_2 cis-N_2S_2

trans-N_2O_2 trans-N_2S_2

Figure 3. Model complexes for extended Hückel MO calculations.

Table II. Spin Distribution in the Model Complexes Obtained by the Extended Hückel MO Method[a]

donor set	Cu	N	O	S
cis-N_2O_2	0.423	0.199	0.090	
cis-N_2S_2	0.362	0.141		0.178
trans-N_2O_2	0.464	0.113	0.155	
trans-N_2S_2	0.385	0.167		0.141
tthd-*cis*-N_2S_2[b]	0.378	0.131		0.180
tthd-*trans*-N_2S_2[b]	0.392	0.163		0.141

[a] The values obtained by normalizing the coefficients of atomic orbitals in the unpaired electron MO's. [b] Tetrahedral distortion (tthd) is made by twisting ligands along the x axis,[9] and the dihedral angle between the ligands is 20°.

However, the observed ^{14}N hfc parameters in the N_2S_2 type complexes are not larger than those in the N_4 and *cis*- and *trans*-N_2O_2 complexes; they are, instead, comparable to those for complexes of these types. This result may be attributed to the fact that the orbitals of the coordinating sulfurs tend to overlap more with copper than do those of the nitrogens or oxygens, because of their larger orbital radial functions, which reduce the unpaired electron density on copper by distribution onto the sulfurs. Such an effect operates opposite to the effect of the deformation of the orbital containing the unpaired electron by crystal fields. In the following section, these effects are clarified by extended Hückel MO calculations.

Extended Hückel MO Calculations on the Copper Unpaired Electron Distribution. The effect of donor atoms on the copper orbital containing the unpaired electron and on the spin distribution at the copper binding sites has been examined by the extended Hückel MO calculations. The calculations were carried out by using the model complexes shown in Figure 3. The geometries of the model complexes were determined by modifying the known structure of $Cu(acac)_2$ using the bond lengths of Cu–N (1.95 Å), Cu–O (1.96 Å), Cu–S (2.25 Å), and C–C (1.41 Å). The MO parameters needed for the calculations were taken from literature.[8] The unpaired electron densities on the copper and the donor atoms obtained by the calculations are shown in Table II. Figure 4 shows the calculated copper orbitals containing the unpaired electron drawn as a function of spin densities. Figure 4 apparently indicates that the elctron cloud expands toward the donor atoms giving weaker crystal fields; in the N_2O_2 system it expands toward the oxygens, while it expands toward the nitrogens in the N_2S_2 system.

The decrease of the unpaired electron density on copper in the N_2S_2-type complexes can be seen from Table II. It is also apparent from the table that the spin distribution onto the sulfur affects extensively the decrease in the spin density on copper. On the other hand, the spin densities on the nitrogens in the *cis*-N_2O_2 complex are larger than those in the *trans*-N_2O_2 complex. This calculation is well reflected in the observed ^{14}N hfc parameters for the cis- and trans-type complexes, and it is explained by the

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[12] Iwaizumi, M. In *Electronic Magnetic Resonance of the Solid State*; Weil, J. A., Ed.; Canadian Society for Chemistry: Ottawa, 1987; p 535.

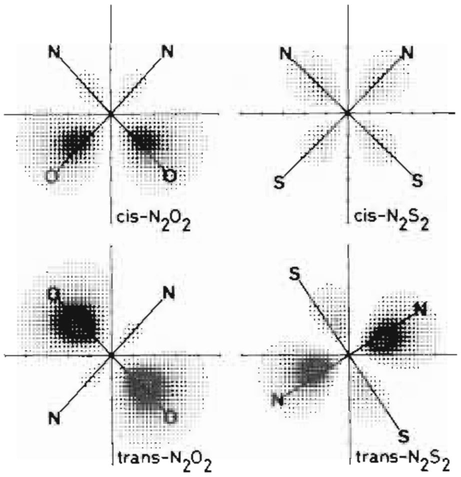

Figure 4. Copper unpaired electron orbitals of the model complexes represented as a function of spin densities.

fact that hybridization of the copper orbital containing the unpaired electron would occur more in the trans-type complexes than in the cis-type complexes, since the hybridization of the copper orbital containing the unpaired electron in the trans form occurs among the lower lying $3d_{xy}$, $3d_{z^2}$, and 4s orbitals,[9] and it is advantageous in the case of the cis form where it requires mixing with the energetically higher $4p_x$ orbital.

Table II shows, however, that there are no large differences between the spin densities on the nitrogens of the *cis*- and *trans*-N_2S_2 complexes, consistent with the observation that there may be no large differences between the ^{14}N hfc parameters of the *cis*- and *trans*-N_2S_2 complexes. This result may be due to the absence of a large difference between the ligand fields of sulfur and nitrogen. Table II also shows that the spin density on copper in the *cis*-N_2S_2 complexes is smaller than that in the *trans*-N_2S_2 complexes. This result may be related to the fact that the orbital deformation is smaller in the cis-type complexes than in the trans-type complexes (Figure 4). The smaller orbital deformation in the cis-type complexes will lead to larger orbital overlap between the copper and sulfurs, resulting in a smaller spin density on copper in the cis-type complexes. On the other hand, the smaller orbital deformation in the *cis*-N_2S_2 complexes will lead to stronger ligand fields from the donor atoms. The smaller $g_\parallel$ shifts from g_e in Cu(pdto) and Cu(sacen) of the cis-type complexes (Table I) may be due to such an effect.

Table II also contains data on the effect of the tetrahedral distortion. It shows that the spin densities on nitrogen decrease by distortion, but the effect is not necessarily large.

^{14}N Hfc's in Blue Copper Proteins. The blue copper proteins have drawn much attention because of their specific physicochemical characters. Recently, ^{14}N ENDOR data for a series of blue copper proteins have been reported by Roberts et al.[2] The data for *P. nigra* plastocyanin and *P. aeruginosa* azurin shown in Figure 2 are taken from their data. Each copper protein shows two ^{14}N ENDOR signals, and their hfc constants are largely different from each other. The X-ray structural data have been reported for *P. nigra* plastocyanin and *Alcaligenes denitrficans* azurin.[10] According to these reports, the observed ^{14}N ENDOR signals are attributed to the imidazole nitrogens. In view of the result of Figure 1, the fact that the imidazole nitrogens show such different hfc constants seems very abnormal.

Roberts et al. assigned the observed ^{14}N ENDOR signals with larger ^{14}N hfc constants to the nitrogens with shorter Cu–N bond lengths.[2] The results obtained in the present work, however, indicate that the hf interactions of the donor nitrogens are determined by the effect of orbital deformation by ligand fields. In early experimental studies before the single-crystal EPR study on plastocyanin was published,[11] the copper binding sites had been considered to have distorted tetrahedral N_2S_2 structures. In the previous paper, however, we showed that tetrahedral distortion does not cause such large changes in the ^{14}N hfc parameters.[1] The ^{14}N hfc data for Cu(sacen) doped in nickel and zinc complexes also indicate that the effect of tetrahedral distortion is not large, and the extended Hückel MO calculation (Table II) supports such experimental data. It is clear, therefore, that the assumption of the tetrahedral distortion does not explain the observed abnormality in the ^{14}N hfc constants of the blue copper proteins.

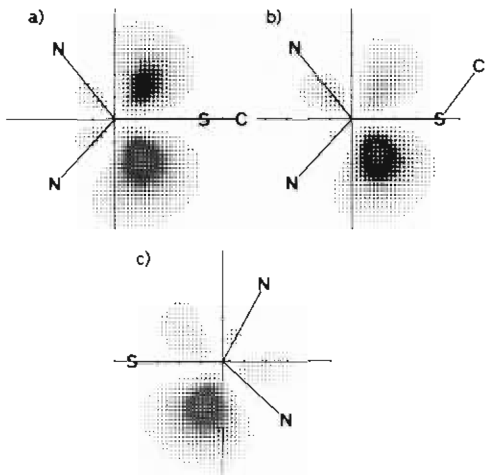

Figure 5. Copper unpaired electron orbitals of plastocyanin (a and b) and azurin (c) represented as a function of spin densities. In parts a and c the S–C bond is in the plane perpendicular to the trigonal plane, while in part b the S–C bond is rotated about the Cu–S bond by 45° from the position in part a.

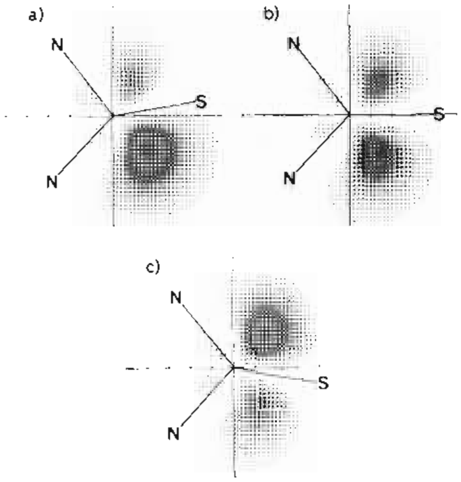

Figure 6. Modification of the copper unpaired electron orbital by displacement of coordinating sulfur. In parts a and c the Cu–S bond is rotated by ±10° in the trigonal plane from the normal position of the plastocyanin structure (b).

The copper binding sites shown by the X-ray analyses for *P. nigra* plastocyanin and *A. denitrificans* azurin can be regarded as having a N_2S–S trigonal-pyramidal structure and a O–N_2S–S trigonal-bipyramidal structure, respectively.[10] We examined the copper binding sites in blue copper proteins by means of extended Hückel MO calculations. In the MO calculations, the donor atoms were placed according to the X-ray data,[10] but only the donor atoms in the trigonal plane were taken into account and the imidazole and cystein were replaced by H_2CNCH_2 and CH_3S^- for simplification. The effect of the axial ligation on the copper unpaired electron orbital is minor, and it is not shown here. The copper orbitals containing the unpaired electron obtained by the calculation situated in the *xy* plane, as has been shown in the single-crystal EPR study,[11] are shown in Figure 5 as a function of spin densities.

Figure 5 indicates that the in-plane pπ orbital of sulfur makes a significant contribution to the form of the copper orbital containing the unpaired electron; the lobes of the copper orbital containing the unpaired electron are situated in the direction of the lobes of the sulfur in-plane pπ orbital. In plastocyanin, two coordinating nitrogens are situated nearly symmetrically with respect to the Cu–S bond.

As is shown in Figure 5a,b, when the S–C bond in CH_3S^- is perpendicular to the trigonal plane, the copper orbital containing the unpaired electron becomes nearly symmetrical to the Cu–S bond direction, but when the S–C bond is removed from the perpendicular plane, the copper orbital containing the unpaired electron becomes extensively unsymmetrical about the two nitrogens, causing a large difference between overlaps of the orbitals of the two nitrogens.

A marked difference between the overlaps of the copper orbital containing the unpaired electron with the two different nitrogens can be seen also for azurin, in which two nitrogens are situated unsymmetrically with respect to the Cu–S bond (Figure 5c). These unsymmetrical spin distributions about the two nitrogens are consistent with the observed results showing the very different two ^{14}N hfc's, although quantitative agreement with the experimental hfc values is not satisfactory.

It should be noted that the unpaired electron distribution on copper in the copper complexes with the N_2S trigonal structure is very sensitive to changes in the positions of the donor atoms as is shown in Figure 6. Such changes strongly affect the spin distribution onto the donor atoms. Interestingly, the copper orbital energies are not as sensitive to movement of the donor atoms in the trigonal plane, although movement of the copper ion in the direction perpendicular to the trigonal plane greatly affects the orbital energy. On the other hand, in the system having the tetragonal structure, the copper orbital energies are sensitive to deformation of the coordination structure, even when the coordinating atoms move in the tetragonal plane. The observation that the unpaired electron distribution in the trigonal system is very sensitive to changes that result from only small perturbations in energy may be related to the enzymatic function of the blue copper proteins.

Contribution from UA 403-CNRS ENSCP, 11 Rue Pierre et Marie Curie, 75005 Paris, France,
and Laboratoire de Chimie des Métaux de Transition, UA-CNRS 419,
Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

Synthesis, Structure, and Reactivity of a Novel Series of Propargylic Cationic Derivatives: $[Co_2(CO)_6(CH{\equiv}CCH_2SR_1R_2)]BF_4$, $[Co_2(CO)_6(CH{\equiv}CCH_2PR_3)]BF_4$, and $[Co_2(CO)_6(CH{\equiv}CCH_2Py)]BF_4$

Hani El-Amouri,[†] Michel Gruselle,[†] Gerard Jaouen,*[,†] Jean Claude Daran,[‡] and Jacqueline Vaissermann[‡]

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Treatment of the propargylic cation complex $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$ with sulfides SR_1R_2 [$R_1 = R_2 =$ Me (**1a**); $R_1 = R_2 =$ Et (**1b**); $R_1 = R_2 = Pr^i$ (**1c**); $R_1 =$ Me, $R_2 =$ Et (**1d**)], phosphines PR_3 [R = Et (**2a**); R = Ph(**2b**)], and pyridine = Py (**3**) yields the corresponding complexes of the general formulas $[(Co_2(CO)_6(CH{\equiv}CCH_2SR_1R_2)]BF_4$, $[(Co_2(CO)_6(CH{\equiv}CCH_2PR_3)]BF_4$, and $[(Co_2(CO)_6(CH{\equiv}CCH_2Py)]BF_4$. The complexation of the carbenium ion complex by heteroatoms modifies both the structure and the reactivity of the starting material. The X-ray crystal structure of the phosphonium derivative $[(Co_2(CO)_6(CH{\equiv}CCH_2PEt_3)]BF_4$ (**2a**) has been determined. **2a** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and the cell dimensions $a = 10.212$ (1) Å, $b = 15.007$ (3) Å, $c = 14.941$ (3) Å; and $\beta = 104.94$ (1)°. In addition, the reactivity of the sulfide derivatives with respect to different nucleophiles such as MeOPh, MeOH, Py, and PR_3 is also discussed.

Introduction

The propargylic cation of $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$ has proved to be an alkylating agent toward a wide range of nucleophiles and hence a useful species for organic synthesis.[1-6] However, this very reactive carbenium ion suffers from a lack of selectivity while its general instability has precluded X-ray structural determination. It should be pointed out however that a reasonable structural hypothesis for this cation has been deduced from NMR studies.[7,8] In order to overcome these limitations, we sought to introduce and examine the effects of a sulfide, pyridine, or phosphine group at the carbenium ion center ($-C^+H_2-$). This temporary complexation might be turned to an advantage in terms of reactivity and stability. In this paper we describe the synthesis of propargylic cationic derivatives of the type $[(Co_2(CO)_6(CH{\equiv}CCH_2SR_1R_2)]BF_4$ [$R_1 = R_2 =$ Me (**1a**); $R_1 = R_2 =$ Et (**1b**); $R_1 = R_2 = Pr^i$ (**1c**); $R_1 =$ Me, $R_2 =$ Et (**1d**)] and $[(Co_2(CO)_6(CH{\equiv}CCH_2PR_3)]BF_4$ [R = Et (**2a**); R = Ph (**2b**)] where the presence of the heteroatom indeed modifies the stability and electrophilicity of these species relative to the dicobalt propargylic carbenium ion while suppressing the direct interaction of the adjacent ($-C^+$) atom with one of the cobalt metals in the cluster.

Experimental Section

Manipulations were carried out by using a vacuum line under argon and employing standard Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques under argon. IR spectra were recorded on a FT Bomem Michelson 100 spectrometer from samples prepared on KBr disks. NMR (^1H, ^{13}C, ^{31}P) spectra were recorded on a Bruker AM 250 instrument, and chemical shifts are relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). Data (^{31}P, ^{13}C) are proton decoupled, reported downfield positive with respect to the reference standard. Elemental analyses were performed by the microanalyses service of CNRS, Vernaison, France.

$[Co_2(CO)_6(CH{\equiv}CCH_2SMe_2)]BF_4$ (1a). A solution of an excess of SMe_2 (2 mL) was added to a suspension of $[(Co_2(CO)_6(CH{\equiv}CCH_2)]BF_4$ (424 mg, 1.03 mmol) in 10 mL of CH_2Cl_2. The mixture was stirred under argon for 1 h; later 10 mL of diethyl ether was added, providing an orange-red bright microcrystalline compound. Complex **1a** was washed several times with ether and recrystallized from CH_2Cl_2/diethyl ether. Yield: 88% (429 mg). Anal. Calcd for $C_{11}H_9O_6SBF_4Co_2$: C, 27.84; H, 1.89; S, 6.75. Found: C, 27.95; H, 1.66; S, 6.66. ^1H NMR (CD_3CN): δ 6.51 (CH–, s, 1 H), 4.81 ($-CH_2-S$, s, 2 H), 2.94 (CH_3-S, s, 6 H).

[†] UA 403-CNRS ENSCP.

[‡] Université Pierre et Marie Curie.

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