group[16] and can now be considered as useful evidence of the presence of this moiety. Preliminary Xα molecular orbital calculations indicate the absorptions in the visible and ultraviolet regions of the spectrum to be due to ligand to metal charge-transfer transitions.[16]

Acknowledgment. This work was supported by PHS Grant CA24344. An allotment of computer time from the Boston University Computing Center is gratefully acknowledged by M.E.K. We are grateful to Drs. S. Srivastava and A. Packard of Brookhaven National Laboratory for making available preprints of several papers and to Dr. E. Deutsch and collaborators (University of Cincinnati), who verified the synthetic method and indicated the presence of a previously unnoticed absorption band.

Registry No. *trans*-[$O_2(en)_2Tc$]I, 80720-95-2; *trans*-[$O_2(en)_2Tc$]Cl, 37473-42-0; (n-Bu_4N)$TcOCl_4$, 71341-65-6.

Supplementary Material Available: Tabulations of structure factor amplitudes for *trans*-[$O_2(en)_2Tc$]Cl, thermal parameters and atomic coordinates for hydrogen atoms in the chloride salt, calculated hydrogen positions, atomic coordinates and thermal parameters, bond lengths and angles for the iodide salt, and absorption maxima and molar absorptivities for electronic transitions, an ORTEP drawing of the complex in the iodide salt, and the infrared spectrum of the chloride salt (16 pages). Ordering information is given on any current masthead page.

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Electronic Structures of Copper(II) Complexes with N_4 and S_4 Ligand Fields

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Received September 9, 1980

The relation between unique natures of some copper complexes and the Cu–S bonding nature in conjunction with the geometry of the ligand field is studied by use of molecular orbital calculations. It is ascertained that unique spectral features of blue-copper proteins (BCP's) as well as several copper complexes can be understood in terms of the two potentials V_{as} and V_{sp}. V_{as} equally ascends all energy levels of d electrons, and V_{sp} splits them. The Cu–S bonding nature is compared with that of Cu–N. Analysis of E_{AB} shows that the former has more covalent nature than the latter.

Introduction

It has been known that blue-copper proteins (BCP's) have unique spectral features in comparison with those of other copper complexes,[2] i.e., (a) an unusually large extinction coefficient of the absorption near 600 nm (ϵ 1000–5000), (b) an abnormally small copper hyperfine coupling constant ($A_{\parallel}$ = (30–100) × 10^{-4} cm^{-1}), and (c) a remarkably positive redox potential ($E_{1/2}$ = +0.2–0.8 V).

Recent investigations of BCP's by resonance Raman spectra,[3] CD,[4] MCD,[5] and XPS[6] suggested the coordination of a cysteine thiol sulfur and two histidine imidazole nitrogens to the central Cu in the distorted ligand field. The X-ray crystallographic analysis of poplar plastocyanin and *Pseudomonas aeruginosa* azurin confirmed the coordination of the methionine thioether sulfur as the fourth ligand.[7] Brill et al. used the ligand field theory (LFT) for azurin and calculated 12.5° for the angle of the distortion from square-planar symmetry.[8] Solomon et al. also discussed the three features by use of LFT.[9] Roberts et al. investigated the relation between the coordination geometry and the natures of (a) and (b) according to the results of ENDOR.[10]

On the other hand, low-molecular-weight Cu(II) complexes that can mimic the characteristic properties in these proteins have been investigated. Rorabacher et al. synthesized some polythioether–Cu(II) complexes with properties (a) and (c).[11] They insisted that the two properties did not primarily depend on the distortion of the coordination geometry. On the contrary, the relation between the distorted environment around Cu and the small $A_{\parallel}$ value was pointed out by Betes et al.[12] The study of complexes Cu(P2A-H)$_2$ and Cu(P2A$_2$-B) (A and B = H, CH_3, C_2H_5, etc.) proved the importance of this condition for properties (b) and (c).[13] By ^{60}Co γ irradiation of the crystal of the Cu(I) analogue,[14] Sakaguchi and Addison obtained the complex $Cu(S{=}C(CH_3)NH_2)_4^{2+}$, which has the distorted ligand field and small $A_{\parallel}$ value. Recently, the complex $Cu(pea)^{2+}$ with two thioether sulfur donors and distorted geometry was synthesized.[15] The complex shows properties similar to those of BCP's except for the $A_{\parallel}$ value. Sugiura et al. also obtained several copper–sulfur complexes with properties similar to those of BCP's, though their detailed structures are unknown.[16] Miskowski et al. observed the absorption near 450 nm in some Cu(II) complexes with sulfur

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[1] Faculty of Pharmaceutical Science.

[2] (a) Peisach, J.; Aisen, P.; Blumberg, W. E. "Biochemistry of Copper"; Academic Press: New York, 1966. (b) Malkin, R.; Malmstrong, B. G. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1970**, *33*, 177.

[3] (a) Siiman, O.; Young, N. M.; Carey, P. R. *J. Am. Chem. Soc.* **1974**, *96*, 5583.

[4] Solomon, E. I.; Hare, J. W.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 1389.

[5] Solomon, E. I.; Rawlings, J.; McMillin, D. R.; Stephen, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 8040.

[6] Solomon, E. I.; Clendening, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3987.

[7] (a) Coleman, P. M.; Freeman, H. C.; Murata, M.; Norris, V. A.; Ramshaw, J. A. M.; Venkatappa, M. P. *Nature (London)* **1978**, *273*, 319. (b) Adman, E. T.; Stenkap, R. E.; Seker, L. C.; Jensen, L. H. *J. Mol. Biol.* **1978**, *128*, 35.

[8] Brill, A. S.; Bryce, G. F. *J. Chem. Phys.* **1968**, *48*, 4398.

[9] Solomon, E. I.; Hare, J. W.; Doley, D. M.; Dawson, J. H.; Stephen, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 168.

[10] Roberts, J. E.; Brown, T. G.; Hoffman, M. B.; Peisach, J. *J. Am. Chem. Soc.* **1980**, *102*, 825.

[11] (a) Jones, T. E.; Rorabacher, D. B.; Ochrymocyz, L. A. *J. Am. Chem. Soc.* **1975**, *97*, 7485. (b) Dockel, R. R.; Jones, T. E.; Sokol, W. F.; Engerer, R. J.; Rorabacher, D. B.; Ochrymocyz, L. A. *Ibid.* **1976**, *98*, 4322.

[12] Betes, C. A.; Moore, W. S.; Standley, K. J.; Steven, K. W. H. *Proc. Phys. Soc., London* **1962**, *72*, 73.

[13] Yokoi, H.; Addison, A. W. *Inorg. Chem.* **1977**, *16*, 1341.

[14] Sakaguchi, U. U.; Addison, A. W. *J. Am. Chem. Soc.* **1977**, *99*, 5190.

[15] Karlin, K. D.; Dahlstrom, P. L.; Standord, M. L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1974**, 465.

[16] (a) Sugiura, Y.; Hirayama, Y.; Tanaka, H.; Ishizu, K. *J. Am. Chem. Soc.* **1975**, *97*, 5777. (b) Sugiura, Y.; Hirayama, Y. *Inorg. Chem.* **1967**, *15*, 697. (c) Sugiura, Y.; Hirayama, Y. *J. Am. Chem. Soc.* **1977**, *99*, 1581.

0020-1669/82/1321-2040$01.25/0

Table I. Calculated and Observed Transition Energies (eV) of Some Copper Complexes

complex	obsd E (log ϵ)	calcd E (f)[a]	assign	exptl
$Cu(NH_3)_6^{2+}$	1.39	1.30	$^2A_{1g}\ z^2 \rightarrow x^2-y^2$	$^2A_{1g}$
	2.03	2.05	$^2E_g\ xz,yz \rightarrow x^2-y^2$	^2E_g, $^2B_{2g}$
		2.18	$^2B_{2g}\ xy \rightarrow x^2-y^2$	
	4.74	4.04	$^2E_u\ n_{NH_3} \rightarrow x^2-y^2$	$n_{NH_3} \rightarrow d$
$Cu(P2A\text{-}H)_2$	2.23	2.06	^2A_g d → d	
		2.32	^2B_g d → d	
	2.54	2.44	^2B_g d → d	
		2.58	^2A_g d → d	
		3.24 (0.207)	$n_N \rightarrow d$	
		4.36 (0.442)	$n_N \rightarrow d$	
		3.46 (1.343)	$\pi \rightarrow \pi^*$	
$Cu(MNT)_2^{2-}$	1.03 (1.94)	1.85	$\pi_S \rightarrow d$	d → d
		2.54	^2A_g d → d	
		2.64	$^2B_{3g}$ d → d	
		2.89	$^2B_{2g}$ d → d	
		3.22 (0.611)	$n_S \rightarrow d$	
		3.63 (0.612)	$n_S \rightarrow d$	
		3.06 (0.729)	$\pi \rightarrow \pi^*$	
$Cu(14\text{-}ane\text{-}S_4)^{2+}$	2.17 (3.28)	2.30 (0.665)	$n_{S_1} \rightarrow$ SOMO	
	3.18 (3.91)	2.39 (0.569)	$n_{S_2} \rightarrow$ SOMO	
		3.46 (0.096)	ligand → SOMO	

[a] Values in parentheses are those of the calculated oscillator strengths. They are estimated by following the equation $f = 0.087|r|^2$, where r is the transition moment calculated.[39]

and/or nitrogen donors.[17] They assigned the band to the Cu–S-type charge-transfer (CT) transition. Bosnich and his co-workers also synthesized several complexes with different combinations of donor atoms: CuS_4, CuS_2N_2, and $CuSN_3$.[18] They observed the CT transition near 400 nm and discussed the relation between the donor set and the absorption.

These studies have given much information and a better interpretation of the unique natures of BCP's; i.e., the absorption near 600 nm is assigned to the S–Cu CT transition, and properties (b) and (c) are understood in terms of the donor set and the coordination geometry. It is clear that these unique features come from sulfur atoms in the distorted ligand field. Therefore, it is very interesting to disclose the characteristic role of sulfur atoms in the ligand field and the bonding properties of the Cu–S bond with some covalent nature. From the CD and ESR results, Solomon et al.[9] recently discussed theoretically these properties on the basis of LFT. As is well-known, the theory is essentially a qualitative one for the electronic structure of d orbitals of a central metal perturbed by the electrostatic field of ligands. Hence, it is not always suitable for a discussion of quantitative features such as the assignment of CT bands, ESR parameters, and the redox potential or the covalent nature of the Cu–S bond. The properties are well described by molecular orbital (MO) theory. For instance, the electronic spectra observed can be assigned by the transition energies and moments calculated. ESR parameters (g and $A_{\parallel}$ values) are estimated by eq 2–4 in the text. The redox potential can be related to the energy of the single occupied (SO) MO. Therefore, several copper complexes are calculated in order to estimate the relation between unique spectral features and the ligand field. They are (a) hexaaminecopper(II), $Cu(NH_3)_6^{2+}$, (b) bis(pyrrole-2-carboxaldiminato)copper(II), $Cu(P2A\text{-}H)_2$, (c) bis(maleonitriledithiolato)copper(II), $Cu(MNT)_2^{2-}$, and (d) (1,4,8,11-tetrathiacyclotetradecane)copper(II), $Cu(14\text{-}ane\text{-}S_4)^{2+}$.

The purpose of the present paper is to disclose the Cu–S bonding natures as well as to analyze spectroscopic properties of Cu(II) model complexes of BCP's. The unique natures of BCP's are also discussed in connection with results of model Cu(II) complexes treated here.

Method of Calculations

For the calculations of model complexes, we used the INDO-type semiempirical method[19] based on Roothaan's open-shell theory.[20] Orbital exponents are taken from the work of Pople et al.[21] for ligand atoms and that of Gouterman et al. for Cu.[22] For ligands, one-center Coulomb repulsion integrals, one-center exchange integrals, and ionization potentials estimated by Hinze et al.[23] are adopted. For Cu, these values are taken from Di Sipio's data.[24]

The E_{AB} value, which is defined as the contribution of the A–B bond to the total energy, is used to estimate the bond strength between Cu and donor atoms. As complexes have open shells, the expression of E_{AB} is slightly different from that of the closed-shell system:

$$E_{AB} = \sum_r^{A}\sum_s^{B}[4p_{rs}H_{rs} - 2p_{rs}^2(rr|ss)] - \sum_r^{A}\sum_s^{B}(2p_{rr} - n_r)(2p_{ss} - n_s)(rr|ss) + \sum_r^{A}\sum_s^{B}[4fq_{rs}H_{rs} - (bf^2q_{rs}^2 + 2fp_{rs}q_{rs})](rr|ss) + \sum_r^{A}\sum_s^{B}[4(af^2q_{rr}q_{ss} + fp_{rr}q_{ss} + fp_{ss}q_{rr}) - 2f(n_rq_{ss} + n_sq_{rr})](rr|ss) \quad (1)$$

where

$$p_{rs} = \sum_i C_{ir}C_{is} \qquad p_{rs} = \sum_m C_{mr}C_{ms}$$

f, a, and b are the constants for each spin state, and the other notations are the same as those in ref 19 and 20. The first two terms are the same as those of the closed-shell system. The last two terms are the contribution of the open shell to the total energy and the interaction between the open shell and the closed one. The first and the third terms are considered as the covalent components and the second and fourth ones as the electrostatic components. The former terms are divided into each type of interaction such as $E_{d_{xy}-n_s}$, E_{sp-n_S} and so on.[25]

Geometries of the complexes calculated are shown in Figure 1. Their bond lengths and angles are taken from their

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(17) Miskowski, V. M.; Thich, J. A.; Solomon, R.; Schuger, M. J. *J. Am. Chem. Soc.* **1976**, *98*, 8344.

(18) Amudsen, A. R.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6730.

(19) Kato, H.; Morokuma, K.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1749.

(20) Roothaan, C. C. J. *Rev. Mod. Phys.* **1960**, *32*, 179.

(21) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

(22) Gouterman, M.; Zerner, M. *Theor. Chim. Acta* **1966**, *4*, 44.

(23) Hinze, J.; Jaffe, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540.

(24) Di Sipio, L.; Tondello, E.; De Michelis, G.; Oleari, L. *Chem. Phys. Lett.* **1971**, *11*, 287.

(25) Sakaki, S.; Hori, K.; Ohyoshi, A. *Inorg. Chem.* **1978**, *17*, 3183.

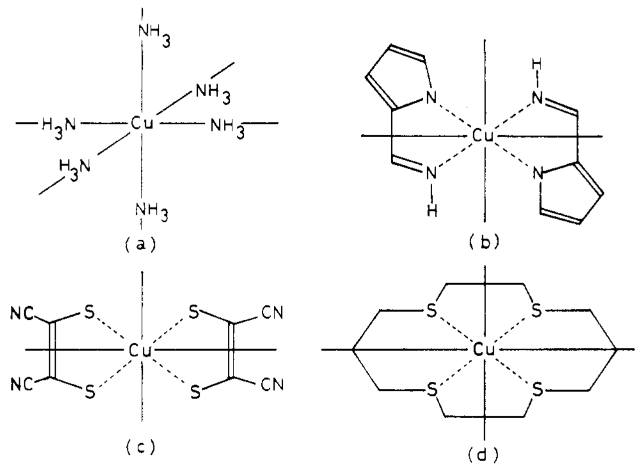

Figure 1. Geometries of copper complexes calculated: (a) Cu$(NH_3)_6^{2+}$; (b) $Cu(P2A\text{-}H)_2$; (c) $Cu(MNT)_2^{2-}$; (d) $Cu(14\text{-}ane\text{-}S_4)^{2+}$.

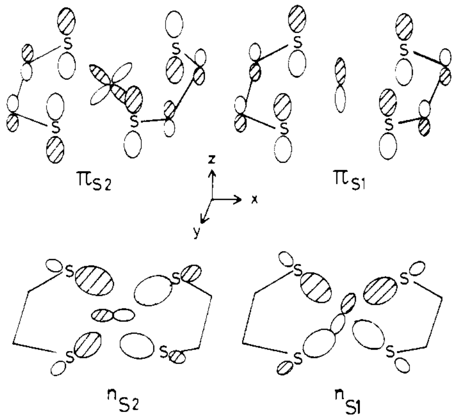

Figure 2. Two types of lone-pair orbitals in $Cu(MNT)_2^{2-}$.

crystallographic data[26] except for $Cu(NH_3)_6^{2+}$. Its geometry is the same as that used by Roos.[27]

Results and Discussions

Electronic Spectra of Copper Complexes. Table I summarizes the transition energies calculated for several copper complexes.

$Cu(NH_3)_6^{2+}$. Transition energies of $^2A_{1g}$, $^2B_{2g}$, and ^2E_g are calculated to 1.30, 2.18, and 2.05 eV, respectively. The d-d-type transitions are observed at 1.39 and 2.03 eV.[28] The former transition is assigned to $^2A_{1g}$ and the latter to ^2E_g and $^2B_{2g}$. The CT band from the lone-pair orbital of NH_3 ligands is calculated to be 4.04 eV and observed at 4.74 eV. These transition energies are in good agreement with each other.

$Cu(P2A\text{-}H)_2$. Two d–d-type bands of 2.23 and 2.54 eV are observed in the complex.[13] The first and the second bands are assigned to ^2A_g, ^2B_g (2.06 and 2.32 eV) and ^2B_g, ^2A_g (2.44 and 2.58 eV), respectively. The CT transitions from the lone-pair orbitals of nitrogen donors to Cu are calculated to be 3.24 and 4.36 eV. The π–π^*-type transition of the pyrrole ring in P2A-H ligands is calculated to be 3.46 eV. This value is close to that observed in pyrrole itself (3.82 eV).[29]

Table II. Calculated and Observed ESR Parameters of Some Copper Complexes

		$g_\parallel$	$g_\perp$	$A_\parallel$, 10^{-4} cm^{-1}	α[a]
$Cu(NH_3)_6^{2+}$	SCF	2.222	2.061	151	0.786
	CI	2.222	2.061	151	
	exptl	2.210	2.060	150	
$Cu(P2A\text{-}H)_2$	SCF	2.106	2.033	218	0.756
	CI	2.174	2.049	159	
	exptl	2.182	2.049	192	
$Cu(MNT)_2^{2-}$	SCF	2.056	2.021	176	0.654
	CI	2.082	2.034	166	
	exptl	2.086	2.020	162	
$Cu(14\text{-}ane\text{-}S_4)^{2+}$	SCF	2.033	2.010	142	0.451
	CI	2.038	2.010	141	
	exptl	2.088	2.026	172	

[a] Coefficient of the d orbital in SOMO.

$Cu(MNT)_2^{2-}$. The MNT ligand has two types of lone-pair orbitals as shown in Figure 2. Those are σ-type ones in the S_4 plane, n_S, and π-type ones, π_S. Therefore, the complex would show two kinds of CT bands. The π_S–d-type transition is calculated to be 1.85 eV. The absorption observed at 1.03 eV, which had been assigned to the d–d-type transition by Maki et al.[30] would then be assigned to this transition. The other two ones from n_S to Cu are calculated to be 3.22 and 3.63 eV. These values are similar to the new band at 3.41 eV in Cu(cyclam)SR, which was assigned to the RS^-–Cu CT transition.[17] Therefore, the strong band due to the n_S–Cu CT transition must be observed within 300–400 nm in the complex. The d–d-type absorptions are calculated to be 2.54 (^2A_g), 2.63 ($^2B_{3g}$), and 2.89 eV ($^2B_{2g}$).

$Cu(14\text{-}ane\text{-}S_4)^{2+}$. Much interest has been concentrated to these kinds of complexes because they have the characteristic 600-nm absorption as well as a 400-nm one with large extinction coefficients and positive redox potentials. These complexes, however, show completely different ESR parameters from BCP's.

SOMO of the complex is characterized by the small contribution of d_{xy} of Cu and the large contribution of the lone-pair orbital constructed with sulfur donors (see Figure 6b), showing the large orbital interaction between them. Orbitals immediately below the SOMO are σ-type lone-pair orbitals in the S_4 plane, n_{S1} and n_{S2}. There are no π-type lone-pair orbitals in the complex due to the geometry of the ligand. Therefore, two transitions from n_{S1} and n_{S2} to SOMO would be expected and their energies are calculated to be 2.30 and 2.39 eV, respectively. Thus, two intense bands observed in the complex are assigned to the transition from n_{S1}, n_{S2} to SOMO.

ESR Parameters of Copper Complexes. Analysis of the ESR parameters of copper complexes is based on the perturbation method introduced by Abragam and Pryce.[31] When the SOMO of a complex with the d^9 configuration is mainly constructed with d_{xy}, ESR parameters are expressed by eq 2–4.

$$g_\parallel = g_e - 8\lambda\alpha^2\sum_i \beta_i^2/\Delta_\parallel^i \quad (2)$$

$$g_\perp = g_e - 2\lambda\alpha^2\sum_i \gamma_i^2/\Delta_\perp^i \quad (3)$$

$$A_\parallel = -P[\kappa + 4\alpha^2/7 + (g_e - g_\parallel) + 3(g_e - g_\perp)/7] \quad (4)$$

where

$$\Delta^i = \epsilon_m - \epsilon_i + (mm|mm)/2 - (mm|ii) + 3(mi|mi)/2 \quad (5)$$

$$P = g_e\beta_e g_N\beta_N\langle r^{-3}\rangle_{3d} \quad (6)$$

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[26] (a) Plumlee, K. W.; Hoffman, B. M.; Ibers, J. A.; Soons, Z. G. *J. Chem. Phys.* **1975**, *63*, 1962. (b) Glick, M. D.; Gavel, D. P.; Diaddrario, L. L.; Rorabacher, D. B. *Inorg. Chem.* **1976**, *15*, 1190. (c) Hall, D.; Sheat, S. V.; Waters, T. N. *J. Chem. Soc.* **1968**, 460.

[27] Roos, P. *Acta Chem. Scand.* **1966**, *20*, 1637.

[28] Elliot, H.; Hathaway, B. J. *Inorg. Chem.* **1966**, 885.

[29] "Organic Electronic Spectral Data"; Interscience: New York, 1957; Vol. 1, p 25.

[30] Maki, A. H.; Edelstein, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580.

[31] (a) Abragam, A.; Pryce, M. H. L. *Proc. R. Soc. London, Ser. A* **1951**, *205*, 135. (b) Case, D. A.; Karplus, M. *J. Am. Chem. Soc.* **1977**, *99*, 6182.

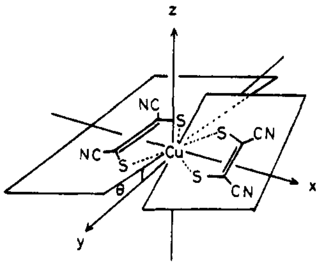

Figure 3. Geometries of the distorted complex $Cu(MNT)_2^{2-}$. The dihedral angle between the two CuS_2 planes is 2θ.

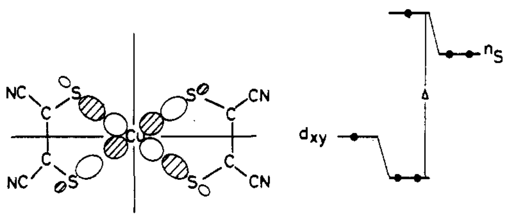

Figure 4. Schematic representation of the orbital interaction between d_{xy} and n_S.

λ is the spin–orbital coupling constant. α is the coefficient of d_{xy} in the SOMO. β_i and γ_i are those of $d_{x^2-y^2}$ and $d_{xz,yz}$ in the doubly occupied (DO) MO. $\Delta_{\|}{}^{i}$ are transition energies from these orbitals to SOMO estimated by eq 5. ϵ_m and ϵ_i denote orbital energies of SOMO *m* and DOMO *i*, respectively. $(mm|mm)$, $(mm|ii)$, and $(mi|mi)$ are the Coulomb integrals (the first two terms) and the exchange integral (the last term), respectively. κ is the Fermi contact contribution, and *P* has the form in eq 6. $\langle r^{-3}\rangle_{3d}$ is the value of the radial integral. We regard *P* and κ as parameters and use 0.035 cm^{-1} and 0.325, respectively.[31] Table II summarizes ESR parameters, both observed and calculated, by using simple SCF wave functions and those after CI calculations. Values calculated are in good agreement with those observed. The improvement of the estimation of the transition energy by the CI method resulted in a better agreement of the observed and calculated ESR parameters.[32]

Effect of the Tetrahedral Distortion. It is well-known that the tetrahedral distortion of the ligand field has some influence on the electronic spectra, the redox potential, and magnetic properties. For a clarification of the effect of this distortion, $Cu(MNT)_2^{2-}$ was calculated with different values for the dihedral angle, θ (Figure 3). Transition energies, ESR parameters, the orbital energies of SOMO, etc. are summarized in Table III.

SOMO of $Cu(MNT)_2^{2-}$ is the antibonding orbital constructed with σ-type lone-pair orbitals of MNT ligands and d_{xy} (Figure 4). The antibonding nature of the orbital is the largest at θ = 0.0° because the overlapping between them is the largest with this angle. It becomes smaller with the increase of the dihedral angle, which weakens the interaction between them, and the splitting, Δ, becomes small. Therefore, the energy level of SOMO goes down due to the distortion. It is calculated that the complex $Cu(MNT)_2^{3-}$, which is the reduced complex of the divalent analogue, gets more stable with the increase of the tetrahedral distortion though $Cu(MNT)_2^{2-}$ becomes unstable. These results suggest that the more the ligand field of the complex is distorted, the more it is easily reduced, and it comes to have a higher redox potential.[33] As the orbital pattern of SOMO is similar to that of other tetragonal complexes, for example, $Cu(NH_3)_6^{2+}$ in Figure 6a, it is expected that the energy level of SOMO descends by the increase of the tetrahedral distortion of the ligand field and that these distorted complexes will therefore have higher redox potentials than the planar complexes. Indeed, such a tendency is observed in experimental $E_{1/2}$ values, which get higher in terms of the tetrahedral distortion made by changing the alkyl group in $Cu(P2A\text{-}R)_2$ or $Cu(P2A_2\text{-}B)$.[13]

Table III. Change of ESR Parameters, Transition Energies, ϵ_m, Etc. as the Function of the Dihedral Angle, θ, in $Cu(MNT)_2^{2-}$

	θ, deg		
	0.0	30.0	40.0
$g_{\|}$	2.084	2.187	2.269
$g_{\perp}$	2.034	2.074	2.097
$A_{\|}$, 10^{-4} cm^{-1}	166	140	116
ϵ_m, eV	0.46	−0.60	−1.14
ϵ_{DOMO}, eV[a]	−3.75, −3.49	−3.83, −3.55	−3.97, −3.39
$E_{n_{S_1}-d}$, eV[b]	3.22 (0.173)	2.24 (0.252)	1.84 (0.234)
$E_{n_{S_2}-d}$, eV	3.63 (0.612)	3.26 (0.138)	2.58 (0.116)
$(mm\|mm)$, eV	7.65	8.58	9.05
$(mm\|ii)$, eV	5.32, 5.24	5.36, 5.58	5.40, 5.37
α[c]	0.645	0.714	0.740

[a] Values for DOMO in the table is that for n_{S_1} and n_{S_2}.
[b] Values in parentheses are calculated oscillator strengths.
[c] Coefficient of d_{xy} in SOMO.

Table III also shows transition energies and moments of the CT bands as the function of the dihedral angle. The main part of the transitions are those from n_{S1} and n_{S2} to SOMO even though values listed in the table are those obtained by CI calculations. It means that the transition energies are roughly estimated by eq 5. As previously mentioned, the orbital energy of SOMO, ϵ_m, decreases with the increase of the distortion, while those of n_{S1} and n_{S2} are almost unchanged (ϵ_{S1} = −3.75 and −3.97 eV for θ = 0 and 40°, respectively). It is attributed to the fact that n_{S1} and n_{S2} orbitals interact little with those of the central metal atom as shown in Figure 2. Of the other three terms in eq 5, only $(mm|mm)$ is largely dependent on the dihedral angle and becomes large. Such an increment, however, contributes to the CT transition energy less than the stabilization of SOMO because only half of the former contributes. Consequently, the red shift of the n_S–d-type transition is mainly due to the stabilization of SOMO induced by the tetrahedral distortion.

In the case of $Cu(P2A\text{-}R)_2$, it has been observed that the *g* values get large while the $A_{\|}$ values get small with increase of the torsional angle. The same trend is obtained from the present MO calculations of $Cu(MNT)_2^{2-}$. Equations 2 and 3 show that *g* values are strongly dependent on the coefficient of d_{xy} in SOMO (α) and the d–d transition energies. The former becomes large while the latter gets small with increase of the dihedral angle. For example, the transition energy assigned to ^2A_g ($d_{x^2-y^2}$–d_{xy}) changes as follows: 2.54 (0.0°), 1.72 (30.0°), and 1.35 eV (40.0°). The change of the ligand field absorptions is also attributed to the stabilization of SOMO. Therefore, *g* values of the complex with θ = 40.0° are fairly large. On the other hand, the $A_{\|}$ value estimated by eq 4 is dependent on α and *g* values in which they have contributions opposite to each other. Both of them become large by the distortion. However, the influence of the former is considered to be smaller than that of the latter because the former contributes to it with the square form. These are reasons why the characteristic ESR parameters are calculated for the complex with the distortion.

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(32) The expression of *g* values with use of CI wave functions is similarly derived as

$$g_{\|} = g_e - 8\lambda\alpha^2\sum_n\sum_j c_{nj}{}^2\beta_j{}^2/\Delta_{\|}{}^n \qquad g_{\perp} = g_e - 2\lambda\alpha^2\sum_n\sum_j c_{nj}{}^2\gamma_j{}^2/\Delta_{\perp}{}^n$$

where c_{nj}'s are coefficients of configurations and Δ^n's are the transition energies estimated by the CI calculation.

(33) Yamabe, S.; Minato, T.; Arai, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2143.

Table IV. Comparison of the Properties Calculated for $Cu(MNT)_2^{2-}$ at $\theta = 40.0°$ with Those Observed in Complexes with Tetrahedral Ligand Fields

	$Cu(MNT)_2^{2-}$	$Cu(PPh_2NPPh_2S)$	$Cu(pea)^{2+}$[a]
$g_\parallel$	2.269	2.170	2.210
$g_\perp$	2.097	2.030	
$A_\parallel$, 10^{-4} cm^{-1}	116	119	173
E_{d-d}, eV	1.35, 1.46	0.72, 1.32	1.1
E_{n_S-d}, eV	1.84, 2.58	2.16, 2.93	1.38

[a] pea = (2-pyridylethyl)bis[2-(ethylthio)ethyl]amine. This complex has a positive redox potential (+0.5 V).

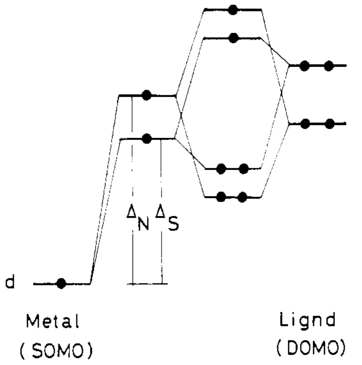


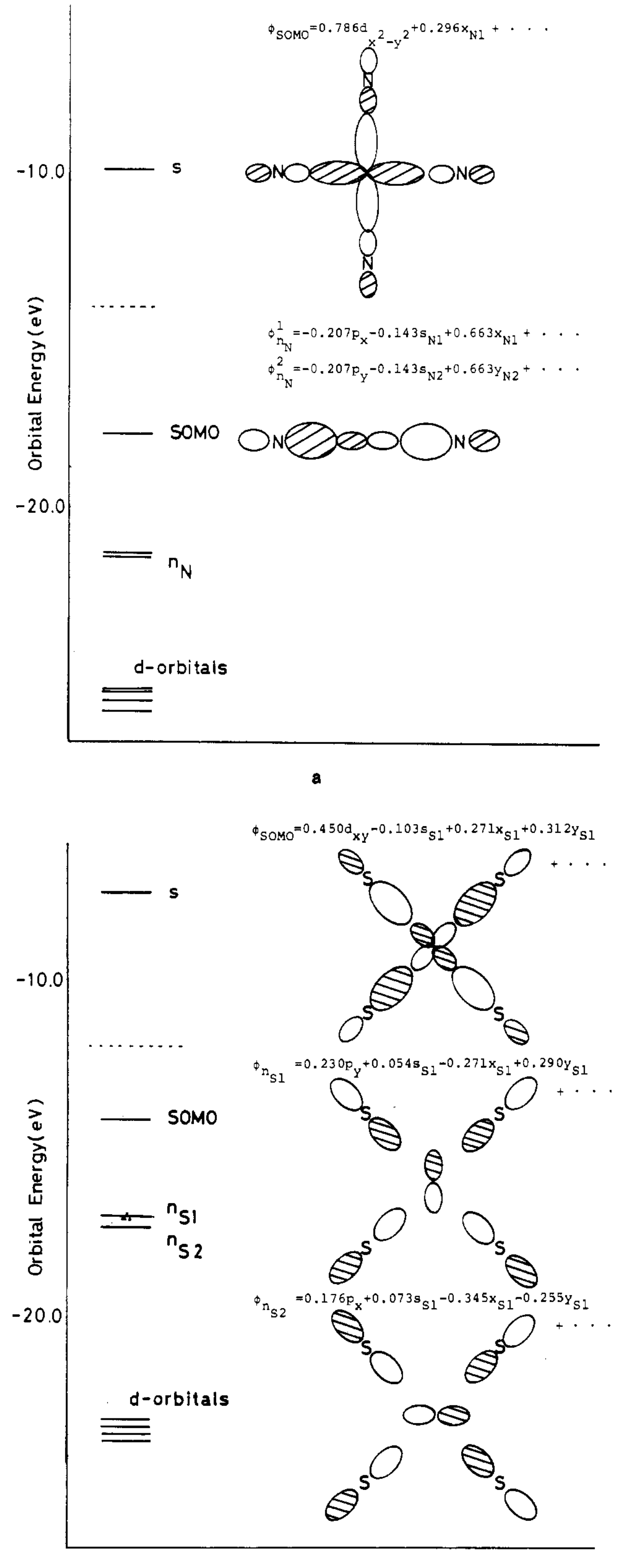
Figure 5. Schematic representation of the interaction between a metal d orbital and the ligand field.

These relationships between the properties and the distortion of the ligand field are seen in experimental results. Table IV summarizes the properties observed in the complex with the tetrahedral ligand field and sulfur donors together with those calculated for $Cu(MNT)_2^{2-}$ with $\theta = 40.0°$. The absorption bands of $Cu(SPPh_2NPPh_2S)_2$ are very similar to these calculated values. These two complexes are considered to have the same ligand field as each other. Absorptions are observed at 2.16 ($\epsilon = 3600$) and 2.93 eV ($\epsilon = 4100$), which are assigned to n–π^* and n–σ^* by Bereman et al.[34] CT transitions were calculated to be 1.84 and 2.58 eV for $Cu(MNT)_2^{2-}$. Therefore, the bands observed in the complex are probably assigned to the n_S–d CT transitions. Bereman et al. assigned the transitions at 0.72 and 1.32 eV to d–d transitions, which are calculated to be 1.35 and 1.46 eV. The g values calculated are a little larger than those observed, but the $A_\parallel$ values are close to each other. It is interesting to note here that these features are not dependent on the whole ligand but on atoms coordinated to the central metal. $Cu(pea)^{2+}$ also shows properties similar to those of BCP's except for the $A_\parallel$ value. It may be attributed to the fact that the complex has two thioether sulfur atoms coordinated to the central metal.

Bonding Nature between Cu(II) and the Sulfur Donor. Through the present MO calculations as well as experimental evidence, it is clear that the unique natures of Cu(II) complexes are closely related to the existence of the Cu–S bond and the coordination geometry of ligands. It is, therefore, valuable to investigate the Cu–S bonding nature in conjunction with the geometry of the ligand field in detail. Results of MO calculations for two complexes, $Cu(NH_3)_6^{2+}$ and $Cu(14\text{-ane-}S_4)^{2+}$, which have the N_4 and S_4 fields, respectively, are compared with each other.

According to the crystal field theory, the effect of the crystal field, V_{cryst}, on d electrons of the central metal is divided into two terms:[35]

$$V_{cryst} = V_{as} + V_{sp} \qquad (7)$$



b

Figure 6. MO diagrams of copper complexes (a) $Cu(NH_3)_6^{2+}$ and (b) $Cu(14\text{-ane-}S_4)^{2+}$. Other orbitals that are constructed with ligand orbitals are not drawn in these figures. ϕ_{SOMO}, ϕ_{S1}, etc. are the MO's obtained. $d_{x^2-y^2}$, p_x, p_y and s_{N1}, x_{N1} show atomic orbitals of the central metal and ligand atoms, respectively. Only the coefficients of atomic orbitals of a ligand atom are represented in the figure.

The first term, V_{as}, is the spherical potential, which raises the energies of d electrons. The second term, V_{sp}, is the potential that splits them according to the symmetry of the field. In

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(34) Bereman, R. D.; Wang, F. F.; Najdzionek, J.; Braitsch, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 7266.

(35) Ballhausen, C. "Introduction to Ligand Field Theory"; McGraw-Hill: New York, 1961.

Table V. Electron Density and E_{AB} Values Calculated for $Cu(NH_3)_6{}^{2+}$ and $Cu(14\text{-ane-}S_4)^{2+}$

	$Cu(NH_3)_6{}^{2+}$	$Cu(14\text{-ane-}S_4)^{2+}$
	Electron Density	
Cu α[a]	0.786	0.451
d_{xy}[b]	1.38	1.80
sp	0.63	0.82
total	10.00 (1.00)[c]	10.54 (0.46)
X[d]	5.62 (−0.62)	5.96 (0.04)
	E_{AB} Values (eV)	
d_{xy}-n_X	−1.02	−0.68
sp-n_X	−3.83	−5.03
ES[e]	−3.42	0.02
total	−8.04	−6.01

[a] Coefficient of the d orbital in SOMO. [b] SOMO in $Cu(NH_3)_6{}^{2+}$ is mainly constructed with $d_{x^2-y^2}$. [c] Values in parentheses are the charge density on each atom. [d] X indicates the donor atom of each complex, that is, nitrogen and sulfur for $Cu(NH_3)_6{}^{2+}$ and $Cu(14\text{-ane-}S_4)^{2+}$, respectively. [e] ES shows the electrostatic contribution of E_{AB} (the sum of the second and fourth components in eq 1).

MO calculations, these two effects are substantially included in the estimation of Fock matrix elements. Especially, the latter effect is described by orbital interactions between MO's of the metal and of the ligands. The schematic representation of the d orbital level through these potentials is shown in Figure 5, and MO diagrams of the two complexes are shown in Figure 6. In general, the Cu–S bond distance is longer than the Cu–N one. The lone-pair electrons of a sulfur atom are more diffused than those of a nitrogen atom. Moreover, the net charge on a nitrogen atom in $(NH_3)_6$ (0.70−) is more negative than that of a sulfur atom in 14-ane-S_4 (0.23−). The electrostatic repulsion in the N_4 field would be stronger than that in the S_4 one. In other words, the magnitude of the level shift of d electrons in the former, Δ_N, is expected to be larger than that in the latter, Δ_S. Of the resulting two orbitals after the interaction between the lone-pair orbital of NH_3 ligands, n_N, and a d orbital lifted by V_{as}, the upper one largely has the nature of $d_{x^2-y^2}$ as indicated by its large coefficient (0.786) in SOMO (Figure 6a). The lower one is mainly constructed with lone-pair orbitals. This suggests that the raised d orbital lies at a position higher than that the original lone-pair orbitals. According to the present calculations, the net charge on Cu in $Cu(NH_3)_6{}^{2+}$ is 1.0+ indicating that one electron on the ligands is transferred to sp and $d_{x^2-y^2}$ orbitals of Cu. Nevertheless, the net charge of nitrogen atoms is almost unchanged. It means that the charge transfer occurs from hydrogen atoms of NH_3 ligands to Cu. Anyway, such a negative charge on nitrogen atoms leads to the larger ascending effect of d orbitals and gives large electrostatic stabilization for the complex formation as indicated by E_{AB} values in Table V.

In the case of $Cu(14\text{-ane-}S_4)^{2+}$, on the other hand, the energy level of d orbitals lifted by the S_4 field is considered to be still lower than that of the lone-pair orbitals of 14-ane-S_4, n_S, because the level shift of d orbitals is smaller as previously mentioned and the energy level of n_S is higher than that of n_N. Therefore, SOMO in the field is mainly composed of n_S with a small contribution of d_{xy} (0.450). In other words, the unpaired electron is delocalized over sulfur donors rather than positioned on the metal (density of an unpaired electron: 0.205 on Cu, 0.128 × 4 on sulfur atoms). The orbital reduction factors, $K_\parallel$ and $K_\perp$, have been calculated to be 0.31 and 0.16, respectively, for plastocyanin by Solomon et al.[9] The values are much smaller than those calculated for copper peptide complexes.[36] The contribution of the d orbital to SOMO in the protein appears to be relatively small. The trend is very similar to that obtained by present MO calculations.

The redox potential is closely related to the energy level of SOMO. Figure 5 suggests that SOMO in the S_4 field is lower than that in the N_4 field.[37] As a result, $Cu(14\text{-ane-}S_4)^{2+}$ has a higher redox potential than $Cu(NH_3)_6{}^{2+}$ because a complex with a low-lying SOMO is considered to be easily reduced. Thus, the small increase of d energy levels results in the positive redox potential observed in the complex. It has been reported that the replacement of an oxygen donor with a sulfur donor promotes the anodic shift of ~0.4 V in the Cu(II)/Cu(I) potential.[38] When oxygen donors are substituted for sulfur donors, the ascending effect for the d energy level becomes small, i.e., the redox potential gets higher. Therefore, the change of the redox potential can be interpreted by considering the potential that relates to the increase of the energy level of d electrons. On the other hand, the ligand field theory as well as MO calculations predicts that the tetrahedral distortion in copper complexes affects the change of the redox potential. Solomon et al. indicated that the ligand field stabilization energy (LSFE) associated with the tetrahedral copper site makes an important contribution to the redox potential. However, it is impossible to explain only by LSFE why the positive redox potential is observed in the complex $Cu(14\text{-ane-}S_4)^{2+}$ though other complexes with the same symmetry show much lower values. The explanation for the high redox potential requires two effects. One is the spherical potential, V_{as}, and the other is the distortion of the ligand field that relates to the symmetry of the field, V_{sp}.

It should be noted here that there is an appreciable amount of electron density in sp orbitals in both complexes, which largely contributes to the bonding between ligands and Cu as indicated by E_{sp-n_X} in Table V. Such a contribution has the nature of a covalent bond. The sum of the value and $E_{d_{xy}-n_X}$ of the Cu–S bond is larger than that of the Cu–N one. On the other hand, the total E_{AB} value of the latter is smaller than that of the former because of the large electrostatic contribution (ES = −3.42 eV). Thus, it can be concluded that the stabilization of $Cu(14\text{-ane-}S_4)^{2+}$ is mainly due to the covalent nature of the Cu–S bond, while that of $Cu(NH_3)_6{}^{2+}$ is attributed to both the covalent and the electrostatic natures of the Cu–N bond.

Concluding Remarks

By the existence of sulfur donors in the ligand field, the Cu(II) complexes discussed are given some features different from those without a Cu–S bond. One is SOMO, which does not have the large contribution of a d orbital of Cu. The trend is consistent with the fact that these complexes generally show small *g* values. The small orbital reduction factors are obtained for plastocyanin in spite of its relatively large *g* values. The absorption near 600 nm is assigned to the S–Cu(II) CT bands. However, it is concluded that the absorption has a nature different than that observed in complexes with nitrogen or other donors.

The tetrahedral distortion of the ligand field, which is related to V_{sp} in eq 7, largely influences the energy level of SOMO. But it is impossible to explain the positive values of the redox potential in BCP's or its difference between CuN_4 and CuS_4 complexes in terms of LSFE. The difference of the value in various Cu(II) complexes can be interpreted by considering the potential that raises all of the energy levels of d electrons, V_{as}. The magnitude of the raising effect by sulfur donors is

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(36) Bryce, G. F. *J. Phys. Chem.* **1966**, *70*, 3549.

(37) Although the orbital energy of SOMO in the S_4 field is expected to be lower than that in the N_4 one, the opposite is true. This curious result is attributed to the semiempirical method we used. The order of SOMO is explained only by the ab initio calculation.

(38) Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257.

(39) Ishitani, A.; Nagakura, S. *Theor. Chim. Acta* **1966**, *4*, 263.

smaller than that by nitrogen or oxygen donors.

The *g* values of Cu(II) complexes with sulfur donors are relatively small under the square-planar symmetry. The stabilization of SOMO achieved by the distortion of the copper environment results in the large *g* values in spite of the small contribution of a d orbital in SOMO. The existence of the Cu–S bond in the distorted ligand field is the origin of the small $A_{\parallel}$ value.

Acknowledgment. Permission to use the M-200 computer at the Data Processing Center at Kyoto University is gratefully acknowledged. We thank Professor I. Fisher-Hjalmars and Dr. A. Henriksson-Enflo for informative discussions at the Third International Congress of Quantum Chemistry.

Registry No. $Cu(NH_3)_6^{2+}$, 14946-73-7; $Cu(P2A\text{-}H)_2$, 15170-36-2; $Cu(MNT)_2^{2-}$, 19562-26-6; $Cu(14\text{-ane-}S_4)^{2+}$, 57673-86-6.

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Theoretical Study on Dinitrogen Complexes. Change of the Electronic Structure of the N_2 Moiety due to Protonation

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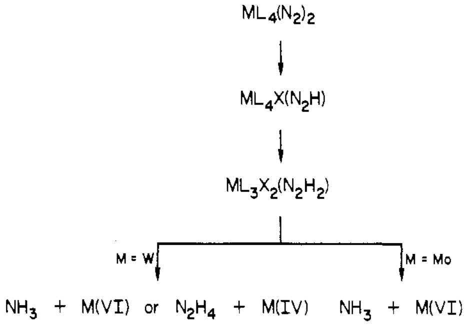
Received June 25, 1981

This paper concerns the effect of protonation to dinitrogen complexes. It is ascertained that protonation causes a remarkable rearrangement of the electron distribution of N_2 complexes. The d_π orbital as HOMO is one of the most characteristic features of the Cr complex. This orbital relates to the charge transfer from the N_2 moiety to the hydrogen 1s orbital as well as to the large protonation energy. The d_π–π^* type polarization is also effective in forming the N–H bond. The change of atomic bond population of the Cr–N and N–N bonds due to protonation is consistent with the experimental results that the M–N bond is strengthened and the N–N bond is weakened by protonation.

Introduction

Since the first dinitrogen complex (N_2 complex) was synthesized,[1] one of its main purposes for chemists has been to reduce the nitrogen molecule under mild conditions by use of transition-metal complexes. It is, however, difficult to reduce them to NH_3 and N_2H_4 because the N–N bond is not largely weakened by coordination.[2] In 1972, Chatt et al. succeeded in reducing N_2 complexes to protonated ones, $M(dppe)_2X_2N_2H_2$ (M = Mo or W, dppe = $PPh_2CH_2CH_2PPh_2$, and X = Cl or Br).[3] Subsequently, similar complexes, $ML_2(N_2H_n)$ (L = dppe, etc., n = 1 or 2; hereafter, they are represented by N_2H and N_2H_2 complexes, respectively),[4,5] were synthesized by using different ligands and reaction conditions. Moreover, Chatt et al. found that NH_3 was given by the treatment of $ML_4(N_2)_2$ (M = Mo or W, L = $PMePh_2$ or PMe_2Ph) with H_2SO_4 in alcoholic solution.[6] They also found that W complexes produce both NH_3 and N_2H_4 with high yields. They proposed two different mechanisms for the reactions:



Using HCl as acid, Takahashi et al.[7] obtained N_2H_4 as well as NH_3 from Mo dinitrogn complexes. In both cases, N_2H and N_2H_2 complexes were considered as important intermediates for the formation of the reduction products.

Crystallographic analysis of these protonated complexes showed that the MNN fragment was almost linear and hydrogen atoms were attached to the terminal nitrogen (N_T).[8] They usually have a longer N–N bond by ca. 0.2 Å and a shorter M–N bond by ca. 0.2 Å than those of parent dinitrogen complexes. These results suggest that the nature of the N_2 complex is largely changed by protonation. Therefore, it is very interesting to investigate the change of the electronic structure in the N_2 moiety because it will influence the reaction mechanism. It is known that this trend is well described by molecular orbital (MO) calculations. Dubois et al.[9] discussed the stable conformation of the N_2H fragment by use of extended Hückel calculations. However, they did not discuss

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(1) Allen, A. D.; Senoff, C. V. *Chem. Commun.* **1965**, 621.

(2) (a) Kahn, M. M. T.; Martel, A. E. "Homogenous Catalysis by Metal Complexes"; Academic Press: New York; Vol. 1. (b) Stiefel, E. S. *Prog. Inorg. Chem.* **1977**, *22*, 1. (c) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

(3) (a) Chatt, J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1972**, 1010. (b) Chatt, J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074.

(4) Hidai, M.; Kodama, T.; Sato, M.; Harakawa, M.; Uchida, Y. *Inorg. Chem.* **1976**, *15*, 2694. (b) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, M.; Hidai, M. *J. Am. Chem. Soc.* **1979**, *101*, 3405.

(5) Chatt, J.; Pearmann, A. L.; Richards, R. L. *J. Organomet. Chem.* **1975**, *101*, C45; *J. Chem. Soc., Dalton Trans.* **1976**, 1520.

(6) Chatt, J.; Pearmann, A. L.; Richards, R. L. *Nature (London)* **1975**, *253*, 39.

(7) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *103*, 7461.

(8) (a) Heath, G. A.; Marson, R.; Thomas, K. M. *J. Am. Chem. Soc.* **1974**, *96*, 259. (b) Day, V. W.; George, T. A.; Iske, S. D. A. *Ibid.* **1975**, *97*, 4127.

(9) Dubois, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1978**, *1*, 497.

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