plexation site to the carbonyl group. The shift to lower wavenumber in the 2:1 Guo and Ino complexes is intermediate between the values for the individual 1:1 adducts. Little change in $\nu(C_6{=}O)$ between the 2:1 and 3:1 $MeHg^{II}$–Ino derivatives is observed, supporting the idea that the third binding site in the latter case is removed from the carbonyl group.

Concluding Remarks. It has frequently been the case in studies of metal ion complexation by nucleic acid constituents that single site specificity is not encountered and chelate formation results. Invariably, the effect of coordination on any given site is thus comprised of more than one contributing factor, and as a result the spectral properties, for example, reflect the *net* effect of chelation. Nevertheless, many examples of the successful identification of binding sites from spectroscopic considerations can be found in the literature (see for example the recent review by Marzilli[32]). However, in the present study, the use of the unidentate $MeHg^{II}$ cation has made it possible to probe *individual* binding sites in the purine nucleosides Guo and Ino.

It has been found possible to isolate the solid complexes which were previously predicted as existing in aqueous solution,[14-16] by selecting appropriate conditions under which complex formation was attempted. ^1H NMR, ^{13}C NMR, and IR spectroscopy have confirmed the identity of the complexes as being as suggested by Simpson.[14] However, in addition, activation of the C_8–H bond by prior $MeHg^{II}$ coordination to N_7 has led to the identification of a novel C-bonded $MeHg^{II}$–nucleoside derivative.

Each of the above-mentioned techniques has fulfilled a role in assigning and confirming the $MeHg^{II}$ binding site(s). Most valuable has been ^1H NMR through which effects of coordination on both the purine and the metal ion have been monitored, as well as confirming the stoichiometry of the complexes. Since it is not always possible to identify individual proton resonances (e.g., if overlapping or solvent-obscured regions exist in the spectrum), ^{13}C NMR can usefully supplement the proton data. In this way, binding to the ribose portion of the nucleoside has been discounted in the present work; thus N_1 and N_7 coordinations lead to specific shifts in the C_6/C_2 and C_8 resonances, respectively. From the effect on the $C_6{=}O$ stretching frequency, further confirmation of N_1 binding has been demonstrated, as has the presence in some of the complexes of the NO_3^- counterion.

In terms of the interaction of $MeHg^{II}$ with the guanine and hypoxanthine residues of nucleic acids at the molecular level, even though the strongest coordination site is believed to be N_1, since this site is already protonated at physiological pH, it is likely that N_7 will be the preferred position for binding. As is apparent from the ^1H NMR spectra of the complexes $[MeHg(GuoH_2)]NO_3$ and $[MeHg(InoH_2)]NO_3$, N_7 coordination has the effect of weakening the N_1–H bond, thereby either (i) facilitating deprotonation of N_1, so allowing reaction with further electrophiles at N_1, as in the case of the formation of the 2:1 complexes in the present work, or (ii) relaxing the hydrogen-bonding tendency of N_1–H, perhaps leading to a disruption of base-pairing capabilities of Guo and Ino. Furthermore, following N_7 coordination, C_8–H bond activation could lead to subsequent reactions at C_8, implying that the mutagenic nature of organomercurials (and heavy-metal ions in general) may be more far reaching than was at first envisaged.

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Registry No. $[MeHg(GuoH)]NO_3$, 68629-63-0; MeHg(GuoH), 68630-40-0; $[(MeHg)_2(GuoH)]NO_3$, 68629-65-2; $[MeHg(InoH_2)]NO_3$, 75311-39-6; MeHg(InoH), 75311-47-6; $[(MeHg)_2(InoH)]NO_3$, 75332-09-1; $[(MeHg)_3(Ino)]NO_3$, 72951-44-1; $GuoH_2$, 118-00-3; $InoH_2$, 58-63-9; $MeHgNO_3$, 2374-27-8.

Supplementary Material Available: Figures 6 and 7, infrared spectral data (1800–1400 cm^{-1}) for the methylmercury(II)–guanosine and methylmercury(II)–inosine complexes, respectively (2 pages). Ordering information is given on any current masthead page.

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Copper Complexes of the "Tripod" Ligand Tris(2-benzimidazolylmethyl)amine: Five- and Six-Coordinate Copper(II) Derivatives and Some Copper(I) Derivatives

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A series of five-coordinate trigonal-bipyramidal and six-coordinate pseudooctahedral copper(II) complexes of the title ligand are reported. These systems are characterized by analytical data, IR, far-IR, ESR, and electronic spectra and magnetic susceptibility measurements. Although six-coordinate structures may pertain in some cases, in the solid state, all the compounds appear to have trigonal-bipyramidal structures in solution in methanol, where characteristic ESR spectra are observed, with $g_{\parallel} < g_{\perp}$ and low values of $|A_{\parallel}|$. Cyclic voltammetry and rotating platinum electrode dc polarography indicate the accessibility of stable copper(I) species in solution, which may have five-coordinate structures. Carbonyl adducts of these copper(I) complexes are formed in both MeCN ($K = 10\ atm^{-1}$) and DMF ($K = 30\ atm^{-1}$). Solid copper(I) complexes can be obtained under reducing conditions from the corresponding copper(II) compounds and also by reacting the ligand with copper(I) salts.

Introduction

Histidine imidazole plays a key role in the coordination of metals at the active sites of numerous proteins. Its prevalence (but not ubiquity[2]) as a donor in copper proteins is evidenced by resonance Raman,[3] electron spin resonance,[4,5] and spin–echo[6] results, as well as by the crystallographic models for

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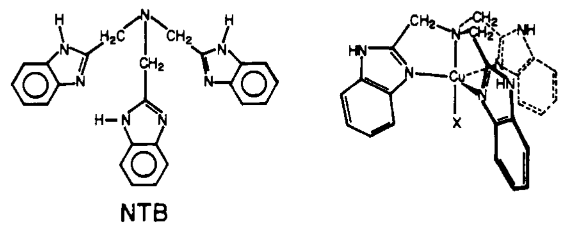

Figure 1. Structural representation of a trigonal-bipyramidal copper complex of NTB.

bovine superoxide dismutase,[7] *Populus nigra italica* plastocyanin,[8] and *Pseudomonas aeruginosa* azurin.[9]

The irregularly tetrahedral or trigonal coordination geometry involving imidazole, currently proposed in the last two cases,[8,9] has prompted us to investigate the appropriate properties of trigonally[10] and pseudotetrahedrally[11] coordinated copper(II) model compounds. These situations are accessible with "tripod" type ligands[12,13] containing aromatic nitrogen donors mimetic of histidine imidazole.

Because of the probable electron-transfer functions of the copper in many of the proteins,[14] an assessment of the redox properties of such systems, including studies of the chemistry of the copper(I) species, would provide an important insight into the structure of reduced copper redox centers and also the possible redox mechanisms in these systems.[15]

In previous papers[10,16] we have investigated the coordinating ability of the polyfunctional benzimidazole ligand tris(2-benzimidazolylmethyl)amine (NTB) (Figure 1) with such metals as cobalt(II), nickel(II), copper(II), and zinc(II) and have found a preference in all cases, with the exception of nickel, for the formation of trigonal-bipyramidal derivatives. Several copper complexes were reported,[10] which were all found to exhibit ESR and electronic spectra in solution typical of trigonal-bipyramidal copper(II). However, in the solid state certain derivatives appeared to be five-coordinate (Figure 1) while others were assigned six-coordinate structures on the basis of spectral evidence.

In the present study we have synthesized further examples of both five- and six-coordinate copper(II) complexes, utilizing NTB. Redox studies on certain of the trigonal-bipyramidal complexes, with soft axial ligands, e.g., NCS^- and Br^-, show quasireversible couples and provide evidence for the formation of a 1:1 Cu(I)–carbonyl adduct. Copper(I) complexes of NTB can be produced by direct synthetic routes and by reduction of copper(II) complexes. Some copper(I) compounds are discussed here, but a more detailed study of these systems will be described elsewhere.

Experimental Section[17]

The ligand NTB was prepared as described previously.[16]

Copper(II) Complexes. $[Cu(NTB)X]PF_6 \cdot yH_2O$ (X = Cl, $y = 1$ (I); X = Br, $y = 1.5$ (II)). NTB (0.50 g, 1.2 mmol) was dissolved in 100 mL of hot methanol and added to a solution of $CuCl_2 \cdot 2H_2O$ (0.21 g, 1.2 mmol) in 20 mL of methanol. Addition of 3 mL of saturated aqueous $NaPF_6$ followed by reduction in volume led to the formation of yellow-buff crystals. The product was recrystallized from acetone–methanol (50/50) and dried in vacuo (0.1 mmHg) at 100 °C for 10 h to give a green powder. The bromide complex was prepared similarly.

$[Cu(NTB)I]BF_4 \cdot 2CH_3OH \cdot 4H_2O$ (IV) and $[Cu(NTB)(NCS)](BF_4) \cdot H_2O$ (V). NTB (0.50 g, 1.2 mmol) was dissolved in 100 mL of hot ethanol. $Cu(BF_4)_2 \cdot 6H_2O$ (0.42 g, 1.2 mmol) was dissolved in 30 mL of hot ethanol and filtered into the solution of NTB. Addition of excess NH_4NCS, dissolved in a minimum volume of ethanol, led to the formation of lime green crystals. The product was recrystallized from ethanol and dried in vacuo (0.1 mmHg) at 80 °C for 3 h. The iodo complex was prepared similarly in methanol, by using NEt_4I, and recrystallized from methanol–TEOF (triethyl orthoformate) (95/5).

$[Cu(NTB)(N_3)]N_3 \cdot 3MeOH$ (VI). The product was obtained as yellow-green crystals by addition of excess NaN_3, dissolved in 50/50 methanol–water, to a methanolic solution of $[Cu(NTB)(H_2O)](BF_4)_2$, prepared as described previously.[10] The complex was recrystallized from methanol and dried in vacuo (0.1 mmHg) at room temperature for 3 h.

$[Cu(NTB)(NMeIz)](BF_4)_2 \cdot MeNO_2 \cdot {}^1/_2MeOH$ (VII). NTB (1.0 g, 2.4 mmol) and *N*-methylimidazole (0.20 g, 2.4 mmol) were dissolved in 100 mL of methanol containing 5 mL of TEOF. $Cu(BF_4)_2 \cdot 6H_2O$ (0.85 g, 2.5 mmol) was dissolved in 50 mL of methanol and filtered into the ligand solution. The mixture was warmed and filtered and reduced to a volume of 5 mL. Large green crystals were deposited on standing for 1 week. The product was recrystallized from nitromethane and dried in vacuo (0.1 mmHg) at room temperature for 3 h.

$[Cu(NTB)(NO_3)]NO_3 \cdot H_2O$ (VIII). NTB (0.81 g, 2.0 mmol) was dissolved in 50 mL of hot ethanol and added to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2.0 mmol) in a mixture of 10 mL of absolute ethanol and 2 mL of TEOF. Crystallization occurred on cooling at room temperature, and the green product was filtered off, washed with absolute ethanol and diethyl ether, and dried in vacuo (0.1 mmHg) at 80 °C for 6 h.

$[Cu(NTB)(NO_3)(H_2O)]NO_3 \cdot H_2O$ (IX). NTB (0.81 g, 2.0 mmol) was dissolved in 50 mL of hot methanol and added to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2.0 mmol) in 10 mL methanol (no TEOF added). Crystallization occurred on cooling at room temperature, and the green product was filtered off, washed with methanol and diethyl ether, and dried in vacuo (0.1 mmHg) at 80 °C for 6 h. Additional drying in vacuo at 160 °C for 48 h did not change the complex according to elemental analysis, infrared, and ligand field spectra.

Other Copper(II) Complexes (III, X–XV). NTB (0.81 g, 2.0 mmol) was dissolved in 50 mL of hot absolute ethanol and added to a solution of a mixture of two Cu(II) salts (1.0 mmol of each salt) in 10 mL of absolute ethanol and 2 mL of TEOF. Crystallization occurred on cooling to room temperature, and the products were isolated by filtration, washed with absolute ethanol and diethyl ether, and dried in vacuo (0.1 mmHg) at 80 °C for 6 h. The Cu(II) salts used were $CuCl_2 \cdot 2H_2O$, $CuBr_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $Cu(BF_4)_2 \cdot 6H_2O$, and $Cu(ClO_4)_2 \cdot 6H_2O$.

Several of the mixed-anion complexes could be obtained in two stereochemistries (octahedral or trigonal bipyramidal according to their solid-state ligand field spectra). Rapid cooling of the reaction mixture in the refrigerator produced octahedral systems, while slow

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(17) Abbreviations: ESR = electron spin resonance; DMF = *N,N*-dimethylformamide; NTB = tris(2-benzimidazolylmethyl)amine; TEOF = triethyl orthoformate; NMeIz = *N*-methylimidazole; RPE = rotating platinum electrode; IR = infrared, tren = tris(2-aminoethyl)amine; R_6tren = tris[2-(dialkylamino)ethyl]amine; SCE = saturated calomel electrode.

cooling at room temperature produced five-coordinate derivatives. No differences were observed in the elemental analyses of these systems.

Copper(I) Complexes (XVI–XX). Cu(NTB)Cl (XVI) and Cu_2(NTB)Br_2 (XVII). These complexes were prepared by stirring a suspension of 2 mmol of Cu(NTB)$X_2 \cdot H_2O$ (X = Cl, Br)[10] with excess copper turnings in acetonitrile (30 mL). After 2 weeks a white solid was produced. The white product was filtered under nitrogen (excess copper turnings removed by decanting), washed with acetonitrile and diethyl ether, and dried in vacuo (0.1 mmHg) at 80 °C for 6 h.

Cu(NTB)ClO_4 (XVIII). $Cu(ClO_4)_2 \cdot 6H_2O$ (0.41 g, 1.1 mmol) was reacted with NTB (0.81 g, 2.0 mmol) and an excess of copper turnings in 30 mL of acetonitrile. A white product was obtained after stirring for 1 day and treated as described above.

Cu(NTB)$NO_3 \cdot H_2O$ (XIX) and Cu(NTB)$BF_4 \cdot H_2O$ (XX). $CuNO_3$ was prepared by reacting $Cu(NO_3)_2 \cdot 3H_2O$ (0.24 g, 1.0 mmol) with an excess of copper powder in 10 mL of acetonitrile and the solution filtered under nitrogen into a refluxing solution of NTB (0.81 g, 2.0 mmol) in 100 mL of ethanol. After cooling and evaporation of some of the solvent by blowing a stream of nitrogen over the solution a white precipitate formed which was filtered, washed with ethanol and diethyl ether, and dried in vacuo (0.1 mmHg) at 80 °C for 6 h.

The tetrafluoroborate complex was prepared in a similar fashion by using an acetonitrile solution of $[Cu(CH_3CN)_4]BF_4$.

No suitable solvent has been found for the recrystallization of these Cu(I) compounds. The complexes appear to be quite stable as dry solids, even on exposure to air.

Analyses. C, H, and N analyses were carried out by Atlantic Microlab, Inc., Atlanta, GA, and by the Organisch Chemisch Instituut TNO Utrecht. Copper analyses were carried out by standard EDTA titration and by Atomic Absorption (Varian Techtron AA-5). Satisfactory C, H, N, and Cu analyses were obtained for all new complexes reported.

Physical Measurements. Electronic spectra were recorded with a Cary 17 spectrometer (mulls and solutions) and a Beckman DK-2 ratio recording spectrometer furnished with a reflectance attachment. Infrared spectra were recorded as Nujol mulls between KCl, CsI, and polyethylene disks by using a Perkin-Elmer 283 spectrometer (4000–200 cm^{-1}) and as pressed polyethylene disks by using a Beckman IR-720 interferometer (500–100 cm^{-1}). ESR powder spectra (room temperature) and solution spectra (77 K) were recorded on Varian instruments at X-band frequency. (Magnetic field strengths were calibrated with an NMR probe and with Mn(II) in MgO powder.) Magnetic susceptibilities were measured at room temperature by using a Cahn Model No. 7600 Faraday magnetic susceptibility system coupled to a Cahn gram electrobalance and to 4.2 K with a PAR vibrating-sample magnetometer.

Cyclic voltammetry and RPE dc polarography at a horizontal disk electrode (0.300 cm^2) were performed at 25 ± 0.2 °C in solutions deoxygenated by bubbling research grade nitrogen. The instrumentation utilized included a PAR-173 potentiostat and PAR-176 i/E converter with an iR-correcting feedback network. Voltammetric scan data were captured with a Nicolet Explorer-III digital oscilloscope and plotted on an X-Y recorder. Current (i) vs. charge (q) plots were obtained by using the current's time integral (McKee-Pedersen MP1012A integrator) and the capacitively damped current as inputs for the X-Y recorder. The three-electrode cell utilized as the reference an Ag(s)/$[AgClO_4]$ (0.01 M), $[NEt_4ClO_4]$ (0.1 M), MeCN electrode. We have measured this as being 0.30 V positive of the SCE in acetonitrile at 25 °C. MeCN for use in electrochemistry was distilled from P_4O_{10} under nitrogen, while DMF was usually used directly as the spectroscopic grade supplied.

Results and Discussion

In a previous paper[10] several copper(II) complexes of NTB were reported which were all shown to have trigonal-bipyramidal solution structures, according to electronic spectra and ESR spectra. However, it was apparent that in the solid state five-coordinate species existed in certain cases, while pseudooctahedral structures occurred in others. The complexes Cu(NTB)$X_2 \cdot H_2O$ (X = Cl, Br) were assigned dimeric pseudooctahedral halogen-bridged solid-state structures involving tetradentate ligands, on the basis of electronic spectra and infrared spectra. A reexamination of these systems shows no magnetic exchange down to 4.2 K, far-infrared data consistent with the presence of terminal metal–halogen bonds (ν(Cu–Cl) 263 cm^{-1}, ν(Cu–Br) 214 cm^{-1}) and ESR parameters consistent with a monomeric pseudooctahedral system in the solid state. In the light of these new data the chloride and bromide complexes appear to have monomeric six-coordinate structures involving at least one coordinated halogen, the other coordination site being occupied by either halide or a water molecule.

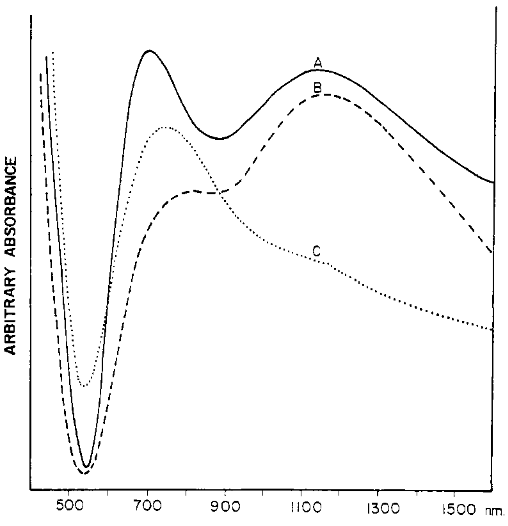

Figure 2. Electronic spectra (mull transmittance): A, [Cu(NTB)Br]$PF_6 \cdot 1.5H_2O$; B, [Cu(NTB)Cl]$PF_6 \cdot H_2O$; C, [Cu(NTB)(NCS)]$BF_4 \cdot H_2O$.

Ligand Field and Electron Spin Resonance Spectra. The copper complexes of NTB are in general characterized by a rather broad absorption in their electronic spectra, exhibiting either a low- or high-energy shoulder or in some cases two distinct absorption maxima (Figure 2, Table I). In many cases it has been shown that the presence of a single absorption with a high-energy shoulder is typical of a trigonal-bipyramidal stereochemistry for copper.[10,18,19] Caution should be exercised before application of observations of this sort as a general criterion for distinction between five- and six-coordinate copper systems, especially in the solid state.[20] A recent X-ray structure on the copper nitrate complex of the benzothiazole analogue of NTB, $[Cu(NTBT)(NO_3)_2] \cdot {}^1/_2H_2O$ (NTBT = tris(2-benzothiazolylmethyl)amine), revealed a distorted trigonal-bipyramidal structure involving a tetradentate ligand and monodentate nitrate in the metal coordination sphere.[21] This system was characterized, though, by an absorption maximum with a low-energy shoulder in its mull transmittance electronic spectrum, which, in many cases, is considered typical of six-coordinate systems. In another example the complex Cu(1,2-dimethylimidazole)$_3Cl_2$, which has a distorted trigonal-bipyramidal structure and a symmetry lower than C_{3v}, exhibits a diffuse reflectance electronic spectrum with a main band at 13 200 cm^{-1} and a shoulder at 10 500 cm^{-1}.[22,23]

No clear pattern emerges in the solid-state spectra of compounds I–VII (Table I). In some cases high-energy shoulders are observed, while in others two bands of comparable intensity are observed. Other data for these systems are, however, indicative of five-coordinate solid-state structures. The solid-state spectra of the remaining complexes VIII–XV all exhibit low energy shoulders, possibly suggesting six-coordinate solid-state species. In solution high-energy shoulders are ob-

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Table I. Electronic Spectra (cm^{-1})

no.	compd		d-d^g	CT
I	[Cu(NTB)Cl]PF$_6$·H$_2$O	*a*	8500, [12500]	
		b	8800, [12500]	
		c	8500 (101), [11500] (55)	
		d	8600, [11600]	
		e	8700, [11800]	
II	[Cu(NTB)Br]PF$_6$·1.5H$_2$O	*a*	8700, 13900	
		b	8900, 14500	
		c	8300 (105), [11800] (67)	
		e	8500, [11900]	
III	[Cu(NTB)Br]ClO$_4$	*b*	9000, 14100	
		c	8300 (110), [11800] (68)	
IV	[Cu(NTB)I]BF$_4$·2CH$_3$OH·4H$_2$O	*a*	7900, 12100	
		f	[9300] (98), 14300 (295)	22000 (1370)
V	[Cu(NTB)(NCS)]BF$_4$·H$_2$O	*a*	[8700], 13300	
		c	9500 (119), [12500] (100)	
		e	9700 [12500]	
VI	[Cu(NTB)(N$_3$)]N$_3$·3MeOH	*a*	11900, [14000]	
		c	9700 (212), 13150 (235)	
VII	[Cu(NTB)(NMeIz)](BF$_4$)$_2$·MeNO$_2$·0.5MeOH	*a*	11200	
		c	11800 (120), [14300] (90)	
VIII	[Cu(NTB)(NO$_3$)]NO$_3$·H$_2$O	*b*	[9800], 14800	
		f	10300 (83), 13300 (81)	
IX	[Cu(NTB)(NO$_3$)(H$_2$O)]NO$_3$·H$_2$O	*b*	[9900], 13700	
		f	10300 (85), 13300 (82)	
X	[Cu(NTB)Cl(NO$_3$)]	*b*	[8000], 13800	
		c	8400 (115), [11800] (57)	
XI	[Cu(NTB)Cl(H$_2$O)]BF$_4$	*b*	[7700], 13300	
		c	8500 (118), [11800] (59)	
XII	[Cu(NTB)Cl(ClO$_4$)]	*b*	[8000], 13300	
		c	8400 (115), [11800] (60)	
XIII	[Cu(NTB)Br(NO$_3$)]	*b*	[8400], 13200	
		c	8300 (110), [11800] (68)	
XIV	[Cu(NTB)Br(H$_2$O)]BF$_4$	*b*	[8400], 13300	
		c	8400 (130), [11800] (77)	
XV	[Cu(NTB)Br(ClO$_4$)]	*b*	[8300], 13500	
		c	8400 (113), [11800] (68)	

[a] Mull transmittance. [b] Diffuse reflectance. [c] Acetone solution. [d] Acetonitrile solution. [e] Dimethylformamide solution. [f] Methanol solution. [g] Brackets indicate a shoulder; ϵ (molar extinction coefficient) is in parentheses.

served in almost all cases, indicating the probability of a common trigonal-bipyramidal stereochemistry in solution. For compounds VIII–XV this may involve a change in stereochemistry. It is clear that an X-ray structural investigation is required to completely rationalize the data for the solid state.

In acetone compounds X–XII have identical electronic spectra, which are very similar to that of compound I, suggesting the presence of the cation [Cu(NTB)Cl]$^+$ in solution. Compounds XIII–XV also have identical acetone spectra, which are the same as that of compound II, suggesting [Cu(NTB)Br]$^+$ as the solution species in these cases. For solubility reasons the solution electronic spectra of the nitrate complexes VIII and IX were run in methanol, and even though in the solid state different species appear to exist, the same species exist in solution according to electronic spectra. Conductance data for IX in methanol[10] suggest a 1:1 solution species, and so a trigonal-bipyramidal system with a coordinated nitrate is proposed.

[Cu(NTB)Cl(H$_2$O)]BF$_4$ (XI) and [Cu(NTB)Br(H$_2$O)]BF$_4$ (XIV) have solid-state spectra which are very similar to those reported for the complexes Cu(NTB)X$_2$·H$_2$O (X = Cl, Br).[10] In acetone solution the corresponding spectra are almost identical. These observations indicate that the complexes reported previously[10] probably involve the six-coordinate species [Cu(NTB)(H$_2$O)X]Y (Y = Cl, Br).

The copper complexes of NTB exhibit ligand field spectra typical of nitrogen donor systems and although the d–d bands observed fall in the same general region as those observed for the copper proteins, little can be inferred with respect to protein stereochemistry. However NTB is unique in that it provides the copper center with a polyimidazole, histidine-like environment.

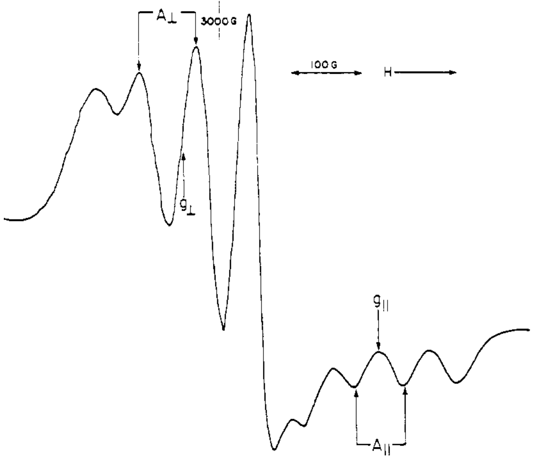

Figure 3. Electron spin resonance spectrum (X band) of frozen solution of [Cu(NTB)(N$_3$)]N$_3$·3MeOH in methanol at 77 K.

ESR spectra of powdered samples have been recorded at ambient temperature at X-band frequency. For compounds X–XIV, three g values are observed (Table II) consistent with six-coordinate systems involving a rhombic distortion. For the nitrato complexes (VIII, IX) $g_\perp$ is not split, while for [Cu(NTB)Br(ClO$_4$)] (XV) no $g_\parallel$ peak can be found. For compounds I–VII, single g values are observed. These pure solids are presumably not magnetically dilute enough to yield ESR spectra which are indicative of the solid-state stereochemistry.

On the other hand, in methanol glass (77 K) compounds I–VII exhibit spectra typical of trigonal-bipyramidal species.[10,24-26] Figure 3 illustrates the methanol glass (77 K)

Table II. Magnetic Moment and ESR Data

no.	compd	μ,[a] μ_B	$\langle g \rangle$[b]	g_1[b]	g_2[b]	g_3[b]	$g_\parallel$[c]	$g_\perp$[c]	$\lvert A_\parallel \rvert$[c]	$\lvert A_\perp \rvert$[c]
I	$[Cu(NTB)Cl]PF_6 \cdot H_2O$	1.9	2.16				1.996	2.233	60	84
II	$[Cu(NTB)Br]PF_6 \cdot 1.5H_2O$	1.8	2.14				1.970	2.208	53	97
III	$[Cu(NTB)Br]ClO_4$	1.9	2.13				1.970	2.224	58	100
IV	$[Cu(NTB)I]BF_4 \cdot 2CH_3OH \cdot 4H_2O$	1.8	2.10							
V	$[Cu(NTB)(NCS)]BF_4 \cdot H_2O$	1.9	2.11				2.006	2.222	69	99
VI	$[Cu(NTB)(N_3)]N_3 \cdot 3MeOH$	2.0	2.10				2.004	2.211	69	89
VII	$[Cu(NTB)(NMeIz)](BF_4)_2 \cdot MeNO_2 \cdot 0.5MeOH$	1.9	2.11					2.236		113
VIII	$[Cu(NTB)(NO_3)]NO_3 \cdot H_2O$	2.0		2.27	2.12			2.218		95
IX	$[Cu(NTB)(NO_3)(H_2O)]NO_3 \cdot H_2O$	1.9		2.29	2.12		2.014	2.229	75	98
X	$[Cu(NTB)Cl(NO_3)]$	1.8		2.26	2.14	2.05	2.002	2.235	60	85
XI	$[Cu(NTB)Cl(H_2O)]BF_4$	1.8		2.29	2.15	2.05		2.224		86
XII	$[Cu(NTB)Cl(ClO_4)]$	1.9		2.26	2.14	2.05		2.223		85
XIII	$[Cu(NTB)Br(NO_3)]$	1.9		2.23	2.13	2.04	2.009	2.218	70	98
XIV	$[Cu(NTB)Br(H_2O)]BF_4$	1.9		2.25	2.14	2.04	2.020	2.219	80	100
XV	$[Cu(NTB)Br(ClO_4)]$	1.9			2.15	2.04	1.980	2.209	75	100

[a] 300 K. [b] Spin-Hamiltonian parameters for powders at room temperature. [c] Spin-Hamiltonian parameters for frozen methanol solutions (−196 °C). All hyperfine coupling constants in units of 10^{-4} cm^{-1}.

Table III. Infrared Spectra (cm^{-1})

no.	compd	ν(Cu–Cl)	ν(Cu–Br)	other
I	$[Cu(NTB)Cl]PF_6 \cdot H_2O$	290		
II	$[Cu(NTB)Br]PF_6 \cdot 1.5H_2O$		230	
III	$[Cu(NTB)Br]ClO_4$		235	
V	$[Cu(NTB)(NCS)]BF_4 \cdot H_2O$			ν(CN(NCS)) 2094
VI	$[Cu(NTB)(N_3)]N_3 \cdot 3MeOH$			$\nu(N_3)$ 2049, 2028
VIII	$[Cu(NTB)(NO_3)]NO_3 \cdot H_2O$			$\nu_1 + \nu_4(NO_3)$ 1725, 1755, 1765
IX	$[Cu(NTB)(NO_3)(H_2O)]NO_3 \cdot H_2O$			$\nu_1 + \nu_4(NO_3)$ 1740, 1753, 1768
X	$[Cu(NTB)Cl(NO_3)]$	270		$\nu_1 + \nu_4(NO_3)$ 1745, 1775
XI	$[Cu(NTB)Cl(H_2O)]BF_4$	270		
XII	$[Cu(NTB)Cl(ClO_4)]$	270		$\nu_1(OClO_3)$ 920
XIII	$[Cu(NTB)Br(NO_3)]$		219	$\nu_1 + \nu_4(NO_3)$ 1757, 1785
XIV	$[Cu(NTB)Br(H_2O)]BF_4$		216	
XV	$[Cu(NTB)Br(ClO_4)]$		218	$\nu_1(OClO_3)$ 920
XVI	Cu(NTB)Cl	187		

spectrum of $[Cu(NTB)(N_3)]N_3 \cdot 3MeOH$. Copper complexes of tren, Me$_6$tren, and Et$_6$tren, which have trigonal-bipyramidal structures, have $g_\parallel < g_\perp$ and $|A_\parallel|$ in the range ~65–100 ($\times 10^{-4}$ cm^{-1}). Spin-Hamiltonian parameters for our five-coordinate copper/NTB systems (I–VII) are reported in Table II. The $|A_\parallel|$ values are generally low ($<100 \times 10^{-4}$ cm^{-1}), and the value for the bromo complex (II) is the lowest one so far reported. In the case of the *N*-methylimidazole complex (VII) the lack of hyperfine splitting in the parallel portion of the spectrum prevented determination of $g_\parallel$ and $A_\parallel$. In nitromethane this compound behaves as a 1:2 electrolyte (Λ_M = 153 Ω^{-1} mol^{-1} cm^2 at ~10^{-3} M), and since electronic spectral bands are comparable with those of the azide complex and occur at somewhat higher energy than in the other five-coordinate systems, a trigonal-bipyramidal species involving coordinated *N*-methylimidazole seems reasonable.

The methanol glass spectrum of the iodo complex (IV) is unusual in that there appears to be superposition of the spectra of two slightly different trigonal-bipyramidal species (Figure 4). A similar observation was made by Barbucci et al.[26] for the ESR spectrum of polycrystalline [Cu(Me$_6$tren)I]I doped into its isomorphous zinc salt, and this doubling of the peaks in the $g_\perp$ and $g_\parallel$ regions was observed to persist in frozen methanol at 133 K.[25] In the system $[Cu(NTB)I]^+$, while apparent doubling of peaks does occur in both the $g_\parallel$ and $g_\perp$ regions, only six are observed in each case: this is most straightforwardly rationalized by presuming some overlap of two sets of resonances. However, a full analysis of this spectrum awaits further study, including simulation.

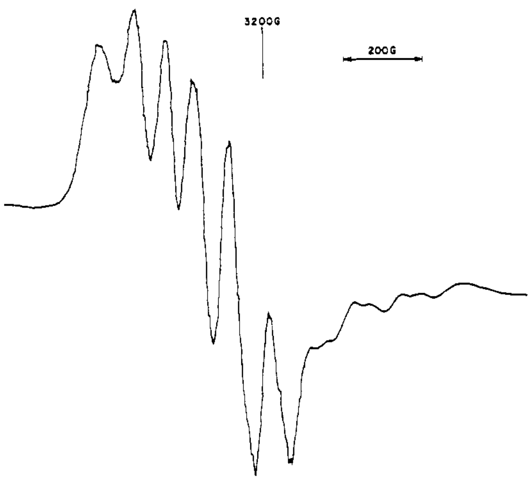

Figure 4. Electron spin resonance spectrum (X band) of frozen solution of $[Cu(NTB)I]BF_4 \cdot 2CH_3OH \cdot 4H_2O$ in methanol at 77 K.

The solution electronic spectra of compounds VIII–XV suggest the presence of trigonal-bipyramidal species, and this is supported by ESR evidence. In frozen methanol glass, spectra typical of trigonal-bipyramidal species are observed, although in some cases parallel features are too weak to assign values of $g_\parallel$ and $A_\parallel$.

While the trigonal-bipyramidal copper derivatives of NTB have low $A_\parallel$ values, comparable with those observed for some "blue" copper proteins,[14] other ESR parameters differ markedly. This implies that the copper coordination sphere in the NTB complexes differs from that present in, e.g., plastocyanin[8] and azurin,[9] for which pseudotetrahedral CuN$_2$S$_2$

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Table IV. Redox Properties of Some NTB Complexes

no.	compd[f]	solvent[a]	potential[b]	$i_L/C\omega^{1/2}$ [c]	process[d]
	$Cu(ClO_4)_2 \cdot 6H_2O$	DMF	$E_{i/2}$ −0.55	22	R, $n = 2$, i
	$[Cu(NTB)(H_2O)](ClO_4)_2 \cdot H_2O$	DMF	$E_{p,c}$ −0.42		R, $n = 1$, i
	$[Cu(NTB)(H_2O)](BF_4)_2$	DMF	$E_{i/2}$ −0.43	7.8	R, $n = 1$, i
	$[Cu(NTB)(H_2O)](BF_4)_2$	MeCN	$E_{1/2}$ −0.15		R, $n = 1$, r
	$[Cu(NTB)(H_2O)](BF_4)_2$	MeCN	$E_{1/2}$ −0.14[e]		R, $n = 1$, r
	$[Cu(NTB)(H_2O)](ClO_4)_2 \cdot H_2O$	MeCN	$E_{1/2}$ −0.15	29	R, $n = 1$, r
I	$[Cu(NTB)Cl]PF_6 \cdot H_2O$	DMF	$E_{p,c}$ −0.61		R, $n = 1$, i
I	$[Cu(NTB)Cl]PF_6 \cdot H_2O$	MeCN	$E_{p,c}$ −0.45, $E_{p,a}$ −0.09	15	R, $n = 1$, i
			$E_{i/2}$ +0.18	19	O, $n = 1$, i
II	$[Cu(NTB)Br]PF_6 \cdot 1.5H_2O$	DMF	$E_{1/2}$ −0.45	9.0	R, $n = 1$, q
			$E_{i/2}$ +0.68	13	O, $n = 1$, i
V	$[Cu(NTB)(NCS)]BF_4 \cdot H_2O$	DMF	$E_{1/2}$ −0.49	11	R, $n = 1$, q
			$E_{i/2}$ +0.75	11	O, $n = 1$, i

[a] NEt_4ClO_4 supporting electrolyte unless otherwise noted. [b] In volts, vs. the nonaqueous Ag reference electrode described in text. $E_{1/2}$ values are $^1/_2(E_{p,c} + E_{p,a})$; those prefixed $E_{i/2}$ are estimated from E at $i = {}^1/_2 i_L$ in the RPE polarogram. [c] mA $s^{1/2}$ M^{-1} $rad^{-1/2}$. [d] R = reduction; O = oxidation; r = Nernstian; i = irreversible; q = quasireversible ($E_{p,a} - E_{p,c} > 60$ mV; $i_{p,a}/i_{p,c} > 0.9$). [e] NEt_4PF_6. [f] The complexes $[Cu(NTB)(H_2O)]X_2 \cdot nH_2O$ ($X = ClO_4$, $n = 1$; $X = BF_4$, $n = 0$) have been described previously.[10]

centers have been proposed on the basis of X-ray studies.

Magnetic Measurements. Magnetic moments measured at ambient temperature (Table II) fall in the range 1.8–2.0 μ_B and are normal for five- and six-coordinate copper(II). Low-temperature susceptibility measurements down to 4.2 K indicate no appreciable magnetic exchange in these systems ($|J| < -2$ cm^{-1}), supporting the proposed monomeric structures.

Infrared Spectra. In the far-infrared region, bands due to ν(Cu–Cl) and ν(Cu–Br) have been assigned (Table III), confirming the presence of copper–halogen bonds in compounds I–III and X–XV. A CN stretching absorption at 2094 cm^{-1} for compound V confirms the presence of a thiocyanato N linkage, while two bands at 2049 and 2028 cm^{-1} for compound VI can be associated with ionic and coordinated azide groups, respectively. These two bands could also be associated with a cis octahedral bis(azide) structure, were it not for the presence of a high-energy shoulder in the solid-state electronic spectrum, which is indicative of a trigonal-bipyramidal structure.

The nitrato complexes VIII and IX both have two absorptions in the range 800–850 cm^{-1} associated with nitrate fundamentals, indicating the presence of two different nitrate groups. Combination bands (Table IV) suggest the presence of ionic and bidentate nitrate for VIII, ionic and monodentate nitrate for IX, and monodentate nitrate for X and XIII.[27] In compounds XII and XV an absorption at 920 cm^{-1} is attributed to the ν_1 vibration of monodentate perchlorate. The ν_3 fundamental, which often splits into two components on coordination of perchlorate as a monodentate ligand, appears only to be broadened. This may be due to overlap with ligand bands in this region or may result from hydrogen bonding to neighboring N–H groups. In the bromo complex III the perchlorate appears to be ionic with no splitting or broadening of ν_3 and no ν_1 band, and in compounds I, II, V, XI, and XIV the hexafluorophosphate and tetrafluoroborate groups are also ionic.

The infrared spectra of the Cu(I) compounds do not differ significantly from the Cu(II) compounds with respect to NTB absorptions, and the compounds Cu(NTB)X (X = ClO_4, NO_3, and BF_4) (XVIII–XX) show almost identical infrared spectra. The only differences are the anion absorptions and the H_2O absorptions in the NO_3 and the BF_4 compounds. There is no infrared evidence for the coordination of the anions in these three compounds. In the case of the Cu(NTB)Cl (XVI), on the other hand, a strong far-infrared absorption at 187 cm^{-1} (absent in all other compounds) strongly suggests the presence of a Cu–Cl stretching frequency. It is not clear whether this band should be assigned to a bridging or terminal Cu–Cl vibration, because the geometry around Cu(I) is not known. However, such a low frequency may suggest a bridging group. The far-infrared spectrum of $Cu_2(NTB)Br_2$ (XVII) is too complicated to allow any assignments although several bands below 200 cm^{-1} could be due to Cu–Br stretching vibrations. The stoichiometry of this compound in fact already suggests Cu–Br bonds.

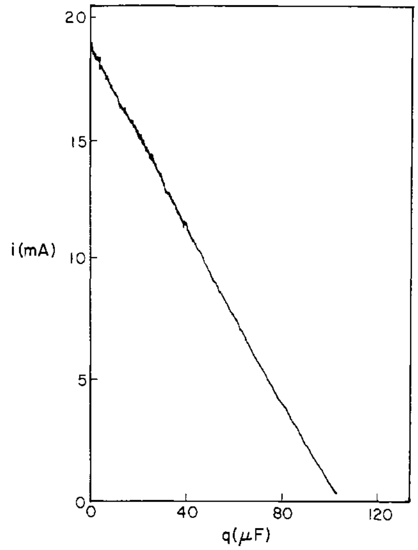

Figure 5. Coulometry of $[Cu(NTB)(NCS)]BF_4 \cdot H_2O$ (104 μmol) in DMF–NEt_4ClO_4 at a Pt mesh cathode at −0.75 V vs. the nonaqueous silver reference electrode.

Structurally these Cu(I) compounds are difficult to interpret, and it is not clear how NTB is coordinated to the metal centers. The general insolubility of these systems suggests the possibility of polymeric species, possibly involving bridging NTB groups. Preliminary results on methyl-substituted NTB ligands indicate much better solubility in organic solvents, which may allow NMR studies in solution for structural elucidation. This is left for future investigation.

Redox Measurements. Redox data are summarized in Table IV. The numbers of electrons involved in the redox processes have been deduced from RPE polarography of the complexes, by assuming diffusion control of i_L at a potential well beyond $E_{1/2}$. Diffusion coefficients in DMF were usually ca. 6×10^{-6} cm^2 s^{-1} and in MeCN about 1.6×10^{-5} cm^2 s^{-1}, yielding $D\eta \simeq 5.0 \times 10^{-8}$ g cm s^{-2} for most of the complexes. Since the diffusion coefficients of the oxidized and reduced species are likely to be very similar (vide infra), the values reported in

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Table IV as $E_{1/2}$ may be considered to be formal potential (E_f) values. For confirmation of the n values, coulometry was performed on $[Cu(NTB)(NCS)]BF_4 \cdot H_2O$ (V) in DMF–NEt_4ClO_4, at a reduction potential 260 mV more negative than $E_{1/2}$. The i–q plot[28] (Figure 5) is quite linear, indicating diffusion-controlled coulometry and extrapolates to passage of 0.98 F mol^{-1} at $i = 0$. The consequent bleaching of the solutions betokens the redox process to be the reduction of Cu(II) to Cu(I). The irreversible $n = 1$ oxidation processes observed for the Cl, Br, and NCS complexes (I, II, and V) were not pursued in detail, as these are considered more likely to involve oxidation of ligand rather than metal.

The reduction potentials correspond to non-Nernstein processes for the majority of the compounds investigated. However, the values show that all the copper(II) compounds should be reducible to Cu(I) in MeCN or DMF by reagents with $E°$ values close to that of the standard hydrogen electrode, the potential of which is about −0.5 V vs. the nonaqueous reference electrode used here.

When the Cu(II) $\rightleftharpoons$ Cu(I) redox process involves exchange of ligand(s) with the medium, this may be reflected most obviously in the cyclic voltammograms, if the rates of such processes are slow relative to the scan rate. This situation appears to apply to a number of compounds studied here. The reductions of $[Cu(NTB)(H_2O)]X_2$[10] ($X = BF_4$, ClO_4) in DMF and of $[Cu(NTB)Cl]PF_6$ (I) in both DMF and MeCN are followed by anodic peaks (cyclic voltammetry) at potentials shifted positively enough (~200 mV) to betray the formation of Cu(II) species whose coordination spheres differ from those prior to reduction. A broad anodic peak observed for $[Cu(NTB)Cl]^+$ in MeCN is close (±20 mV) to the observed position of the anodic peak for $[Cu(NTB)(H_2O)]^{2+}$, suggesting that the chloride ion is lost from the copper(I) complex under these conditions. For $[Cu(NTB)(H_2O)]^{2+}$ a Nernstian reduction may be observed in MeCN–NEt_4ClO_4 ($i_a/i_c = 1.00$, $E_{p,a} - E_{p,c} = 60$ mV),[29] and the electronic spectrum and ESR spectrum of $[Cu(NTB)(H_2O)]^{2+}$ in MeCN indicate a five-coordinate solvated species, supporting the conclusion that H_2O is lost in *both* oxidation states. It might thus be anticipated that loss of the fifth (anion) ligand in the reduced (cuprous) states would render all the systems irreversible in their cyclic voltammetric behavior. However, when complexes with the ligands NCS^- and Br^-, of "softer" or more class b character,[30] were examined in DMF–NEt_4ClO_4, the Cu(II) $\rightleftharpoons$ Cu(I) voltammograms were quasireversible. In DMF the optical absorption spectra of these species showed that Br^- and NCS^- were still bound to Cu(II). This implies that these anions are also bound in the Cu(I) state and therefore that MeCN (a good Cu(I) ligand) is likely to be bound also when $[Cu(NTB)(H_2O)]^{2+}$ is reduced. These Cu(I) species could therefore be pentacoordinate—a situation with ample precedent for Cu(I) chelates with at least one "soft" ligand.[31,32] However, tetracoordinate Cu(I) is not precluded, since this could conceivably result through scission of one of the Cu(I)–NTB linkages (e.g., to the tertiary amine nitrogen). As expected, the voltammograms of the perchlorate and tetrafluoroborate salts of $[Cu(NTB)(H_2O)]^{2+}$ in MeCN–NEt_4ClO_4 were superimposable and not significantly affected by substitution of NEt_4ClO_4 by NEt_4PF_6 as supporting electrolyte.

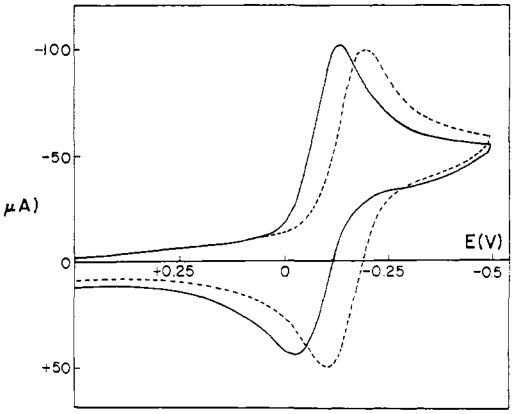

Figure 6. Cyclic voltammograms of $[Cu(NTB)(H_2O)](BF_4)_2$ (1.28×10^{-3} mol dm^{-3}) in MeCN: 0.1 mol dm^{-3} in NEt_4ClO_4 under CO (full line) and N_2 (broken line). Potential is referred to nonaqueous reference electrode (scan rate 0.1 V s^{-1}).

The availability of a coordination site on the Cu(I) species $[Cu(NTB)X]^{n+}$ for exogenous ligands is further demonstrated by Figure 6 which depicts the shift in potential of the cyclic voltammogram for $[Cu(NTB)(H_2O)](ClO_4)_2 \cdot H_2O$ in MeCN–NEt_4ClO_4 when the nitrogen atmosphere is replaced by carbon monoxide. This effect is readily reversed by flushing the cell with nitrogen. The increase in the system's $E_{1/2}$ is due to the binding of carbon monoxide to the reduced Cu(I) form of the complex, in competition with the solvent. The couple is quasireversible in the presence of carbon monoxide, and from the shift in the cathodic peak potential we are able to estimate K for a 1:1 binding[31,32]

$$[Cu(NTB)(MeCN)]^+ + CO \rightleftharpoons [Cu(NTB)(CO)]^+ + MeCN$$

to be ca. 10 atm^{-1}. This system thus provides a further example of a carbonyl adduct of a copper(I) chelate. Such adducts have recently become firmly established for tri-,[28] tetra-,[33] and pentacoordinate[32] systems. For $[Cu(NTB)(H_2O)](ClO_4)_2 \cdot H_2O$ in DMF–NEt_4ClO_4, the shift of $E_{p,c}$ effected by carbon monoxide is greater (90 mV, $K \simeq 30$ atm^{-1}) than in MeCN, in keeping with the lesser ability of "harder"[34] DMF (compared with MeCN) to compete with carbon monoxide for Cu(I). The CO-binding constant in DMF is comparable with those observed for a number of systems in which Cu(I) is chelated by oximate and imine nitrogens from equatorially tetradentate macrocyclic ligands.[35] This was surprising to us, as we expected the poorly basic benzimidazole donors not to promote donation of metal electron density to the π acceptor, CO, in these cationic systems. However, the possibility that departures from (tetragonally) symmetric coordination promote π-acceptor binding appears to be consistent with the limited amount of structural and binding data presently available. It is noteworthy that significant CO binding can occur with a dominantly imidazole-coordinated copper(I) and that no ("softer") sulfur donor is necessary. Imidazoles have been classified as "borderline" in the HSAB approach,[30] and their copper(II) complexes have ESR parameters (particularly $g_{\parallel}$ and $A_{\parallel}$) similar to those with oxygen donors,[4] while on the other hand the E and C values for N-methylimidazole appear to be those of a strong, rather "soft" base.[36] Native and modified hemocyanins bind CO,[37] while

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the available spectroscopic evidence suggests[4,37] the absence of sulfur and dominance of nitrogen in the copper coordination sphere.

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Registry No. I, 75267-56-0; II, 75267-58-2; III, 75267-59-3; IV, 75330-96-0; V, 75267-61-7; VI, 75267-63-9; VII, 75284-08-1; VIII, 75267-65-1; IX, 75267-67-3; X, 75267-68-4; XI, 765299-13-7; XII, 75284-09-2; XIII, 75284-10-5; XIV, 75284-12-7; XV, 75284-13-8; XVI, 75284-14-9; XVII, 75420-67-6; XVIII, 75284-15-0; XIX, 75284-16-1; XX, 75267-70-8; $[\mathrm{Cu(NTB)(H_2O)}](\mathrm{BF_4})_2$, 67269-67-4; $\mathrm{Cu(ClO_4)_2{\cdot}6H_2O}$, 15333-31-0.

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Photolabilization and Bond Indices in Hexacoordinated Transition-Metal Complexes: The D_{2h} Case

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Bond indices I(ML) are introduced for the ground and the excited states of hexacoordinated transition-metal complexes. The formalism is developed for the general case where the three orthogonal axes are characterized by different ligand field parameters. It is shown that photolabilization and photosubstitution reactions can be summarized by the simple rule that the leaving ligand is the one characterized by the smallest value of the bond index I^*(ML).

Introduction

Adamson's rules[1] on the photolabilization of hexacoordinated transition-metal complexes have been discussed extensively in the recent literature.[2-5] So far, all the complexes under consideration were characterized by a real or an effective D_{4h} symmetry. The bond-breaking process is accordingly classified either as axial labilization or as equatorial labilization. Recently, a few cases were reported[6-9] where the effective symmetry of the hexacoordinated species was only D_{2h} (three *different* orthogonal axes). It is the purpose of this work to extend the previously developed I^* model[4,5] to this class of complexes.

Definition of the Bond Indices I and I^*

Let V represent the ligand field Hamiltonian; let d_i and ϵ_i be the five eigenstates and eigenvalues of the one-electron perturbation matrix, constructed on the d-orbital manifold (i = 1–5). This means that $\epsilon_i = (\mathrm{d}_i|V|\mathrm{d}_i)$ are the d-orbital destabilization energies. In what follows, the ligand orbital stabilization is assumed to be equal to the corresponding metal d destabilization. Figure 1 shows the example of a schematic energy level diagram for an octahedral complex.

If the state function under consideration Ψ can be described by one single configuration (as in Figure 1), the total one-electron bonding energy is given by

$$I = -(\Psi|V|\Psi) = \sum_i h_i\epsilon_i \qquad (1)$$

where h_i is the number of holes in the ith d orbital.

Since the ligand field Hamiltonian can be written as a sum of individual ligand perturbations

$$V = \sum_L V_L$$

the contribution of the Lth ligand to I is given by

$$I(\mathrm{ML}) = \sum_i h_i(\mathrm{d}_i|V_L|\mathrm{d}_i) \qquad (2)$$

It should be stressed that the quantities I and I(ML) are not necessarily acceptable approximations for the thermodynamic bond energies. For instance, they should certainly not be used to compare the bond strength from one metal to another one (having a different number of d electrons). But they can be useful in a more limited context: for instance, the "bond indices" I(ML) might provide a comparative measure of the different bond strengths *within one given state of a complex*.

If the relevant state function is constructed on the basis of several configurations, the extension of eq 1 is quite straightforward. One particular case, that will be of some interest in the next section, arises when the state function is a linear combination of two determinants, differing in only one spin orbital. A wavefunction of this type can obviously be rearranged into one single determinant, whose spin orbitals are *not* diagonal in V. In this case, it is easy to show that the quantity I can still be obtained from eq 1, but now the summation does not run over the five eigenorbitals of V but over the orbitals in the determinant and their orthogonal counterparts.

For instance, consider the $\mathrm{t_{2g}^3}$, $^4\mathrm{A_{2g}}$ ground state and the $\mathrm{t_{2g}^2e_g^1}$, $^4\mathrm{T_{2g}}$ excited state of an octahedral d^3 system; the wave functions (corresponding to $M_S = {}^3/_2$ for instance) are given by eq 3. In O_h, $\epsilon(\mathrm{t_{2g}}) = 4\pi$ and $\epsilon(\mathrm{e_g}) = 3\sigma$; therefore, the

$$\Psi_0 = |xz\ yz\ xy|$$

$$\Psi_1 = |xz\ yz\ x^2 - y^2|$$

$$\Psi_2 = (3^{1/2}/2)|xz\ xy\ z^2| + (1/2)|xz\ xy\ x^2 - y^2|$$

$$\Psi_3 = (3^{1/2}/2)|yz\ xy\ z^2| - (1/2)|yz\ xy\ x^2 - y^2| \qquad (3)$$

ground state $I = 3\epsilon(\mathrm{t_{2g}}) + 4\epsilon(\mathrm{e_g}) = 12\sigma + 12\pi$, and each $I(\mathrm{ML}) = 2\sigma + 2\pi$. For $^4\mathrm{T_{2g}}$ the three functions lead to the expression $I^* = 4\epsilon(\mathrm{t_{2g}}) + 3\epsilon(\mathrm{e_g}) = 9\sigma + 16\pi$, and all I^*(ML)

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