

Fast Atom Bombardment Mass Spectrometry of Related Cu(I) and Cu(II) Chelates

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The reactions of a series of Cu(I) and Cu(II) complexes containing pyrazolyl or dimethylpyrazolyl residues in the ligands during the ionization process were studied by fast atom bombardment mass spectrometry. Complexes with a +1 charge produce intact cations. Those with a higher charge yield +1 cations by formal reduction or by clustering with anions, sometimes by several simultaneous processes. Neutral complexes are protonated to give +1 ions.

Introduction

Copper-containing proteins serve vital functions in many biological systems, including binding and activation of molecular oxygen [1, 2]. This activity has prompted modeling studies of the metal site in such proteins, for which most of the compounds in this report have served. They also offer a chance to compare the behavior of different oxidation states of the same metal, similarly coordinated, under desorption conditions in mass spectrometry. Such studies by fast atom bombardment are uncommon [3]. We recently have reported studies of neutral and cationic Re, Rh, and Os coordination complexes and have uncovered tentative rules for predicting the behavior of complexes [4]. These rules are tested and confirmed here.

Experimental

Samples were dissolved in glycerol, or if only slightly soluble in glycerol, in N,N-dimethylformamide to which glycerol was then added. The solutions were placed on an Al foil over the tip of a stainless steel probe and analyzed on a VG 7070 mass spectrometer outfitted for fast atom bombardment. The instrument was fitted with a modified saddlefield ion source (Ion Tech Ltd.) to serve as the atom beam

gun. The primary beam was Xe; a primary current of 1 mA at 4–8 keV provided acceptable sample ion intensities.

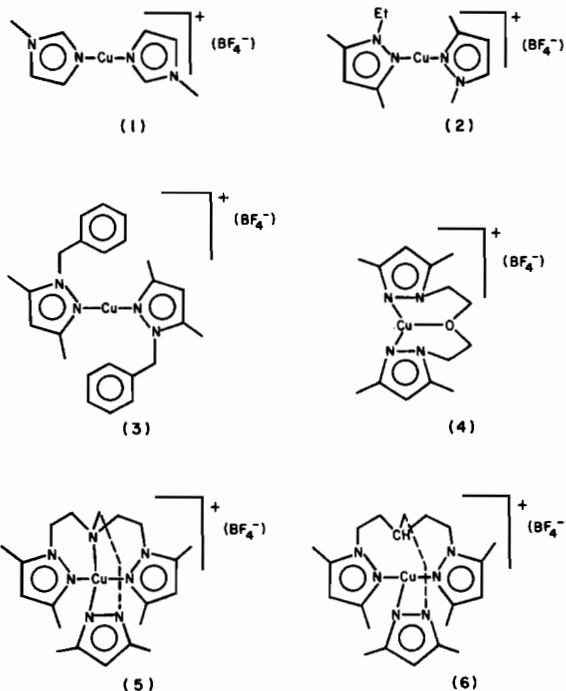
The preparation of samples is referenced at the appropriate discussion in the text.

Results and Discussion

The m/z values of only the ions composed of the principal isotopes of constituent atoms are given in the text and tables.

Complexes with Monodentate Ligands

Several Cu(I) complexes of monodentate ligands related to the chelating agents that form the major part of this discussion were studied first. The spectra of bis(N-methylimidazole)copper(I) tetrafluoroborate



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TABLE I. Fast Atom Bombardment Mass Spectra of Bis(alkylimidazole)copper(I) Complexes.^a

Compound	m/z (relative intensity)						
	Cu ⁺	LH ⁺	CuL ⁺	CuL ₂ ⁺	CuLgly ⁺	CuL ₂ gly ⁺	other
1	63(12)	83(13)	145(50)	227(100)		319(5)	CuL ₃ ⁺ , 309(6)
2	63(4)		187(35)	311(100)	279(3)	393(5)	
3	63(5)		249(100)	435(78)	341(13)		C ₇ H ₇ ⁺ , 91(60)

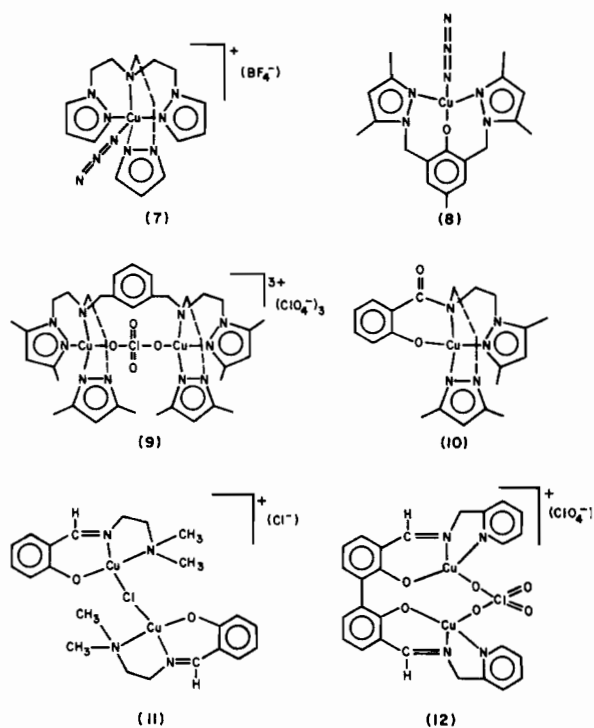
^aPrincipal isotopes.

(1) [5], bis(3,5-dimethyl-N-ethylpyrazole)copper(I) tetrafluoroborate (2) [5], and bis(3,5-dimethyl-N-benzylpyrazole)copper(I) tetrafluoroborate [5] (3) are given in Table I. The spectra are each characterized by a major peak for the intact cation and another for the singly ligated metal ion. The other peaks vary. In the first case, small peaks due to Cu⁺ and protonated ligand appear at m/z 63 and 83 respectively; a glycerol attachment peak CuL₂gly⁺ at m/z 319 and a ligand attachment peak CuL₃⁺ at m/z 309 attest to ion-molecule reactions, whether in solution or the gas phase. In the second, the glycerol attachment peak (m/z 393) is accompanied by a glycerol displacement peak CuLgly⁺, m/z 279. In the third, a similar displacement peak at m/z 341 is accompanied by C₇H₇⁺, m/z 91.

We have observed that high resolution techniques may be applied successfully to fast atom bombardment analysis of coordination complexes if appropriate standards are chosen [4]. Considering that the complex presents a lipophilic surface to solvent, we chose other singly charged ions with non-polar surfaces as standards to confirm previous observations. Our choices were tetraphenyl-, triphenylalkyl-, and tetraalkylphosphonium and -arsonium salts. Peak matching of the m/z 249 ion of 1, CuC₁₂H₁₄N₂⁺, against the tetrabutylphosphonium ion (m/z 242.2848) gave a value of 249.050 ± 0.006 vs. the expected value of 249.045, for example. We consider this accuracy sufficient to distinguish the formula from all reasonable alternatives.

Complexes with Multidentate Ligands

The spectra of tetrafluoroborate salts of Cu(I) complexes of three related ligands, bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] ether [6], tris[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine [7], and tris[2-(3,5-dimethyl-1-pyrazolyl)ethyl]methane [8], 4, 5, and 6 respectively, are given in Table II. The first of these contains only peaks corresponding to the intact complex ion and free Cu⁺. The other two spectra are similar; the major peaks differ by one mass unit (N vs. CH). The intact cation (N: m/z 446; CH: m/z 445) dominates the spectrum. The loss of the elements of dimethylpyrazole accounts for the fragment of highest mass (N: m/z 350; CH: m/z 349). The

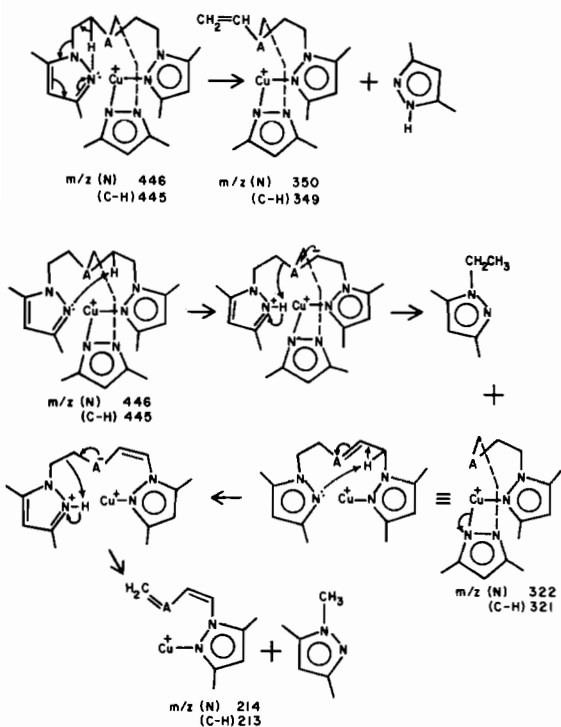


fragment (N: m/z 322; CH: m/z 321) corresponds to a loss of the elements of dimethylpyrazole and ethylene from the intact cation, and (N: m/z 214; CH: m/z 213) corresponds to a further loss of trimethylpyrazole from (N: m/z 322; CH: m/z 321). Thus the same processes occur whether the apical group of the ligand is N or CH; this correspondence suggests that this nitrogen has virtually no role in directing fragmentation. This is quite unlike the conventional role of aliphatic nitrogen in organic ions, where it usually controls fragmentation almost to the exclusion of other atoms. The complexation of Cu⁺ by the lone pair of the apical N, of course, renders them unusable for controlling fragmentation, according to simple pictures of reactivity of organic ions. These reactions may be summarized in Scheme 1.

The spectrum (Table II) of azido[tris(2-(1-pyrazolyl)ethyl)amine]copper(II) tetrafluoroborate (7) [8], conversely, does not contain a peak for the intact

TABLE II. Fast Atom Bombardment Mass Spectra of Three- and Four-coordinate Complexes of Copper(I) and (II).

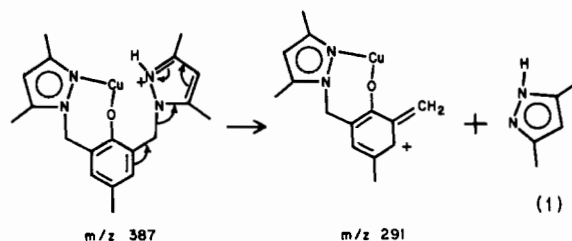
Compound	m/z (relative intensity)		
	Cu ⁺	CuL ⁺	other
4	63(17)	325(100)	
5	63(12)	446(100)	[CuL - C ₅ H ₈ N ₂] ⁺ , 350(23) [CuL - C ₇ H ₁₂ N ₂] ⁺ , 322(20) [CuL - C ₁₃ H ₂₂ N ₄] ⁺ , 214(50)
6		445(100)	[CuL - C ₅ H ₈ N ₂] ⁺ , 349(20) [CuL - C ₇ H ₁₂ N ₂] ⁺ , 213(25) [CuL - C ₁₃ H ₂₂ N ₄] ⁺ , 213(47)
7	63(30)	362(100)	[CuL - C ₃ H ₄ N ₂] ⁺ , 294(12) [CuL - C ₅ H ₈ N ₂] ⁺ , 266(18) [CuL - C ₉ H ₁₄ N ₄] ⁺ , 188(21)
8			CuLH ⁺ , 387(100) [CuLH - C ₅ H ₈ N ₂] ⁺ , 291(60)



Scheme 1.

cation, which would appear at m/z 404. Instead, the most massive ion is $[M - N_3]^+$, m/z 362; the Cu(II) has formally been reduced to Cu(I), and the fragmentations to m/z 294, m/z 266, and m/z 188 correspond to processes of Scheme 1 (except that the ligand contains pyrazole, not dimethylpyrazole). The related neutral complex azido[2,6-bis((3,5-dimethyl-1-pyrazolyl)methyl)-4-methylphenoxy]copper(II) [8] (8) gives $[M - N_3 + H]^+$ as the ion of highest mass;

the proton presumably comes from glycerol. Cationization of a neutral coordination complex by protonation from solvent has precedent [4]. The fragment at m/z 291 is formed by loss of the elements of dimethylpyrazole and can easily be accounted for if the protonation has occurred on a pyrazole N (eqn. 1).



The complex {1,3-bis[bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]aminomethyl]benzene}-dicopper(II) perchlorate [8] (9) produced a spectrum with the peak of highest mass at m/z 850 (Table III). This behavior suggests that the species desorbs under fast atom bombardment by reduction of both Cu(II) centers to Cu(I) and by transport of one perchlorate. The ion at m/z 687 corresponds to complexation of a single Cu(I) by a protonated ligand. These are probably formed on bombardment by different routes from the species in solution. The ions m/z 322 and m/z 214 are the same fragments as noted above in Scheme 1.

Several derivatives containing salicylate fragments were also studied (Table IV). The spectrum of {*o*-hydroxybenzoyl-bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine} copper(I) [8] (10) gives, as expected for a neutral complex, the protonated molecule (m/z 444) at highest mass; the peak at m/z 324 may arise by the process shown in eqn. 2. It is analogous to the loss of water from the molecular ion of salicylic acid,

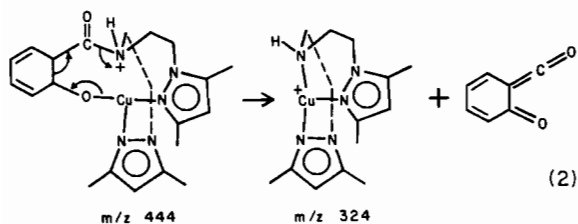
TABLE III. Fast Atom Bombardment Mass Spectra of Binuclear Complexes of Copper(II).

Compound	m/z (relative intensity)	
	Cu ₂ L(ClO ₄) ⁺	other
9	850(100)	CuLH ⁺ , 687(37); 322(95) ^a ; 214(95) ^a
12	645(60)	Cu ₂ LH ⁺ , 547(100) [Cu ₂ LH - C ₅ H ₆ N] ⁺ , 467(50) [Cu ₂ LH - C ₆ H ₇ N] ⁺ , 454(35) [Cu ₂ LH - C ₁₁ H ₁₁ N ₂] ⁺ , 376(90)

^a See 5, Table I, Scheme 1.

TABLE IV. Fast Atom Bombardment Mass Spectra of Salicyl Copper Complexes.

Compound	m/z (relative intensity)
10	CuLH ⁺ , 444(56) [CuLH - C ₇ H ₄ O ₂] ⁺ , 324(100) 214(20) ^a LH ₂ ⁺ , 382(18) [LH ₂ - C ₇ H ₄ O ₂] ⁺ , 262(14)
11	C ₃ H ₆ N ⁺ , 58(100) Cu ⁺ , 63(75) Cu ₂ L ₂ Cl ⁺ , 543(20) CuL ⁺ , 254(57)

^a See 5, Table I, Scheme 1.

a loss which is a paradigm of the *ortho* effect [9, 10]. In that case, the charge remains on the fragment which presumably has the lower ionization potential, that is, the organic fragment, not water; here the charge remains on the fragment with the lower ionization potential, the metal-containing fragment. Peaks at m/z 382 and 262 attest to the same process in the ions in which H⁺ has replaced Cu(I). The m/z 214 is the same fragment as noted in Scheme 1. The spectrum of [1-(N,N-dimethylamino)-2-salicyliminoethane]copper(II) chloride [8] (11) has m/z 543 as the peak of highest mass; this corresponds to a chloride-bridged ion such as the one indicated in the formula for 10. The ion at m/z 254 is the intact complex cation [CuC₁₁H₁₅N₂O]⁺, in which Cu(II) has been reduced to Cu(I). Consequently single charged ions are produced by two independent routes from 11.

Finally, the bombardment of [2,2'-dihydroxy-3,3'-bis(2-pyridylmethyliminomethyl)biphenyl]dicopper(II) perchlorate [8] (12) likewise produces ions by two routes. The peak at highest mass (m/z 645) corresponds to a binuclear complex plus a perchlorate ion; perhaps it is bridging. The ion of m/z 547 can be formed by reduction of both Cu(II) ions to Cu(I) and then, because the complex is now neutral, protonation by solvent. The fragment at m/z 467 corresponds to the loss of the elements of a dihydropyridyl radical, and that at m/z 454 to the loss of the elements of methylpyridine, from the m/z 547 ion. The m/z 376 ion is accounted for by the loss of C₆H₄N from m/z 454. Mechanisms justifying these losses by the formation of extended conjugated systems can be written.

Conclusions

Spectra of complexes of monodentate ligands with Cu(I) with a +1 charge contain the intact cation and peaks corresponding to successive losses of ligands. Spectra of +1 complexes of a multidentate ligand with Cu(I) contain the intact cation and peaks due to rearrangements within the ligand; at least two consecutive rearrangements can occur. If the complex has zero charge, the ion is formed by protonation by the fast atom bombardment glycerol.

Complexes with a charge greater than +1 have not produced spectra directly. The ions observed are produced from reduction of Cu(II) to Cu(I) by loss of an anionic ligand as a radical, from reduction of Cu(II) by addition of an electron, and from combination of two Cu(II) centers with an anion in order to produce a cluster of net charge +1. Samples containing two Cu(II) ions are apparently reduced formally at both metal centers in sputtering, and no process has yet been observed at which only one of these Cu(II) ions is reduced. While this failure to observe coordination complexes of unreduced Cu(II) is undoubtedly a function of the systems studied, it does point out that facile routes to reduction are available, and that caution must be taken in the inter-

pretation of mass spectra of unknown systems. In particular, three examples were found in which the ions observed are formed by two routes from the solution species, so that one cannot explain all of the peaks in the spectrum as fragments of the ion with highest mass.

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