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Tetrahalo- and (Mixed-tetrahalo)cuprates of the Piperazinium Dication. Coordination Geometry Changes in Some CuX_4^{2-} Anions

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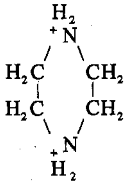
Some halo- and (mixed-halo)cuprates of the type $(pipzH{\cdot}HX)_2CuY_4$ (X = Y = Cl, Br; X = Cl, Y = Br), $(pipzH{\cdot}HCl)_2CuCl_3Br$ ($pipzH{\cdot}HX$ = piperazinium monocation hydrohalide), $(pipzH_2)CuCl_4$, $(pipzH_2)CuCl_3Br$, $(pipzH_2)CuCl_2Br_2$, $(pipzH_2)CuBr_4$, and $(pipzH_2)Cu_2Cl_6$ ($pipzH_2$ = piperazinium dication) were prepared and characterized by means of far-ir, ir, and near-ir spectroscopy, magnetic moments, and conductivity measurements. For the $(pipzH{\cdot}HX)_2CuY_4$ and $(pipzH{\cdot}HCl)_2CuCl_3Br$ complexes, which are thermochromic, an approximately square-planar geometry may be suggested, while for the $(pipzH_2)CuX_mY_n$ ($m + n = 4$) complexes a distorted tetrahedral geometry may be suggested from the room-temperature spectroscopic properties of these compounds, compared to those of other tetrahalocuprates of known structure. The planar geometry is probably stabilized by extensive N–H···Cl hydrogen-bonding interactions, as is demonstrated by the change in the coordination geometry from square planar to distorted tetrahedral when the compounds are heated at 80–95 °C or dissolved in dimethylformamide. In fact a weakening of the hydrogen-bonding network, caused by the increasing disorder due to the thermal motion or by a solvent effect, is responsible for the coordination geometry change. A band at 19 000 cm^{-1}, which appears only in the $(pipzH_2)Cu_2Cl_6$ complex, is characteristic of $Cu_2Cl_6^{2-}$ dimer species. Also for this complex an approximately square-planar geometry is suggested.

Introduction

Our interest in the coordination properties of substances such as piperazine, piperidine, and morpholine, which are of great importance as biologically active materials and as constituents in many complex organic compounds of practical importance, was recently extended to the study of the chemical behavior of their hydrohalide salts. The trichloro-, tetrahalo-, and (mixed-tetrahalo)cuprates of the piperidinium and morpholinium cations[1] examined, which have nearly identical dimensions but different hydrogen-bonding abilities, present different CuX_4^{2-} geometries, but no thermochromic behavior.

In view of the great interest in the halocuprate(II) coordination geometries, we have now considered the complexes formed between the piperazinium dication (hereafter abbreviated $pipzH_2$) and the copper halides. The piperazinium dication (I) has dimensions similar to those of piperidinium and morpholinium cations, but the two positive charges lend it greater hydrogen-bonding possibilities.



This work is also encouraged by the fact that with another dication, such as the ethylenediammonium cation, interesting geometries of the tetrahalocuprate anions were found.[2,3]

Experimental Section

Preparation of the Piperazinium Hydrohalides. The piperazinium dihydrohalide salts were prepared by adding drop by drop a concentrated hydrogen halide solution to a concentrated ethanolic solution of the amine until complete neutralization of the amine, accompanied by nearly complete precipitation of the salt, was reached.

The piperazinium monohydrohalide salts were obtained by adding drop by drop a stoichiometric amount of concentrated hydrohalide solution to a concentrated ethanolic solution of the amine. The solution was heated until a clear solution was obtained. By adding ethyl ether the piperazinium monohydrohalide salt (pipzHX) precipitated. The same compounds were prepared by adding a stoichiometric amount of piperazine in ethanol to an ethanolic solution of the piperazinium dihydrohalide salt, by heating the mixture until the piperazinium dihydrohalide salt was dissolved, and by adding ethyl ether.

Preparation of the Complexes. $(pipzH_2)CuCl_4$ and $(pipzH_2)CuCl_3Br$ were obtained by adding an ethanolic solution of $CuCl_2{\cdot}2H_2O$ to a boiling solution of $pipz(HCl)_2$ and pipz(HCl)(HBr) respectively, with a metal to ligand molar ratio of 1:1. Upon addition of ethyl ether and cooling at 5 °C for some hours a solid crystalline compound precipitated.

$(pipzH_2)CuCl_2Br_2$, $(pipzH_2)_2CuBr_6$, and $(pipzH_2)_2CuCl_2Br_4$ were also prepared as cited above, by starting from $CuBr_2{\cdot}3H_2O$ and $pipz(HCl)_2$, $pipz(HBr)_2$, and pipz(HCl)(HBr), respectively.

$(pipzH_2)_2CuCl_6$ and $(pipzH_2)_2CuCl_5Br$ were obtained by adding $CuCl_2{\cdot}2H_2O$ in ethanol to a boiling solution containing $pipz(HCl)_2$ or pipz(HCl)(HBr), respectively, in methanol.

$(pipzH_2)CuBr_4$ was obtained by mixing $CuBr_2{\cdot}3H_2O$ and pipzHBr in methanol at room temperature with a metal to ligand molar ratio of 8:1.

$(pipzH_2)Cu_2Cl_6$ was prepared by mixing $CuCl_2{\cdot}2H_2O$ and pipzHCl in the minimum amount of boiling methanol with a metal to ligand molar ratio of 8:1.

Physical Measurements. The electronic spectra of the solid compounds were recorded with a Beckman DK 1A spectrophotometer in the temperature range 290–380 K. Samples were prepared by grinding the complexes on a filter paper as support. The infrared spectra of KBr pellets were recorded with a Perkin-Elmer 521 (4000–250 cm^{-1}) and the far-infrared spectra of Nujol mulls with a Perkin-Elmer FIS 3 (400–60 cm^{-1}) spectrophotometer.

The room-temperature magnetic moments were measured with the Gouy method by using $HgCo(NCS)_4$ or $Ni(en)_3S_2O_3$ as calibrants and correcting for diamagnetism with the appropriate Pascal constants.

The conductivities of the complexes in *N,N'*-dimethylformamide (DMF) solution were measured with a WTW (Wissenschaftlich-Technische Werkstatten) D 812 conductivity meter, LBR, at 25 °C.

Analyses. Nitrogen, carbon, and hydrogen were analyzed by Mr. G. Pistoni using a Perkin-Elmer 240 elemental analyzer.

Results and Discussion

The analytical results are reported in Table I. All of the compounds are crystalline, stable in air, and slightly soluble in common organic solvents.

The isolated compounds have two types of stoichiometry corresponding (a) to the complexes with empirical formulas $(pipzH_2)_2CuX_6$ (X = Cl, Br) and $(pipzH_2)_2CuX_5Y$ and (b) to the complexes with empirical formulas such as $(pipzH_2)CuX_4$, $(pipzH_2)CuX_3Y$, $(pipzH_2)CuX_2Y_2$, and $(pipzH_2)CuY_4$ (X = Cl, Y = Br). A compound of formula $(pipzH_2)Cu_2Cl_6$ was also prepared.

The electronic, infrared, and far-infrared spectra of the type a complexes indicate that in all of these complexes tetrahalocuprate species are present and their true formulas may be indicated as reported in Tables II and III. In particular since the $(pipzH{\cdot}HX)_2CuBr_4$ (X = Cl, Br) complexes have the same charge-transfer spectra, being the CT spectra characteristic of the ligands bonded to the Cu^{2+}, this means that both salts have the $CuBr_4^{2-}$ ion and that $(pipzH_2)$-

Table I. Analytical Results

	Color	% Cu		% C		% H		% N		Mp, °C	μ_{eff}, μ_B	λ_M (DMF)
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found			
(pipzH$_2$)CuCl$_4$	Yellow	21.65	21.83	16.36	16.98	4.12	4.35	9.54	9.92	220 dec	1.80	59
(pipzH$_2$)$_2$CuCl$_6$	Green-yellow	14.04	14.01	21.22	21.52	5.35	5.50	12.38	12.30	160 dec	1.81	63
(pipzH$_2$)CuCl$_3$Br	Orange	18.80	18.33	14.20	14.23	3.58	3.35	8.29	8.09	200 dec	1.71	72
(pipzH$_2$)CuCl$_2$Br$_2$	Red	16.62	16.09	12.55	13.19	3.16	3.25	7.32	7.62	210 dec	1.72	76
(pipzH$_2$)$_2$CuCl$_5$Br	Red-orange	12.79	12.83	19.32	20.32	4.87	5.40	11.27	10.67	150 dec	1.83	98
(pipzH$_2$)CuBr$_4$	Violet	13.48	13.44	10.18	10.58	2.57	2.58	5.94	5.75	320–323	1.78	78
(pipzH$_2$)$_2$CuCl$_2$Br$_4$	Red	10.08	9.69	15.23	15.18	3.84	4.23	8.89	8.59	125 dec	1.81	154
(pipzH$_2$)$_2$CuBr$_6$	Red-violet	8.83	8.76	13.34	13.59	3.36	3.74	7.79	7.78	130 dec	1.79	177
(pipzH$_2$)Cu$_2$Cl$_6$	Red	29.69	30.61	11.22	11.46	2.83	2.70	6.55	6.63	220–223	1.78	70

Table II. Electronic Spectra of the Tetrahalo- and (Mixed-tetrahalo)cuprates (cm^{-1})[a]

	T, K	d–d bands	Charge-transfer bands
(pipzH·HCl)$_2$CuCl$_4$	298	11 490	23 810 sh, 27 400
	373	6760 sh, 10 640	
(pipzH·HCl)$_2$CuCl$_3$Br	298	11 560	27 780
	373	6660 sh, 10 530	20 410 sh
(pipzH·HCl)$_2$CuBr$_4$	298	11 430	17 390 sh, 20 830, 23 810 sh
	373	7520, 10 200	17 240 sh, 20 410
(pipzH·HBr)$_2$CuBr$_4$	298	11 360	17 390 sh, 20 620, 23 810
	373	7410, 10 200	17 240 sh, 20 000
(pipzH$_2$)CuCl$_4$	298	6850, 9620	25 320
(pipzH$_2$)CuCl$_3$Br	298	6060, 7350, 9950	25 970
(pipzH$_2$)CuCl$_2$Br$_2$	298	6130, 7250 sh, 9480	20 830 sh
(pipzH$_2$)CuBr$_4$	298	6060, 9520	16 130 sh, 18 870, 24 390 sh
(pipzH$_2$)Cu$_2$Cl$_6$	298	11 690	18 870, 24 390 sh

[a] The ligands and the complexes show some bands at ~4350, ~4650, ~5130, and ~6760 cm^{-1} which do not change on deuteration, while on heating the band at ~5130 cm^{-1} disappears.

CuCl$_2$Br$_4$ is correctly formulated as (pipzH·HCl)$_2$CuBr$_4$ and not as (pipzH·HBr)$_2$CuCl$_2$Br$_2$ or the mixed salt.

Electronic Spectra and Magnetic Moments. One of the most common geometries found for the CuX$_4^{2-}$ anion is that often referred to as the "flattened" tetrahedron with nearly or exactly D_{2d} symmetry, which is intrinsically more stable than a complex with either T_d (regular tetrahedron) or D_{4h} (square plane) symmetry.[4–6] The geometry of the CuX$_4^{2-}$ species in the solid state depends on many factors, including crystal field stabilization, ligand–ligand repulsion, Jahn–Teller distortion, hydrogen bonding, and van der Waals forces. It has been predicted theoretically that the electronic absorption spectrum of the D_{2d} CuX$_4^{2-}$ complex should be sensitive to the amount of "flattening" or distortion that has occurred; in particular, the maximum d–d transition should increase in energy as the geometry distorts from a regular tetrahedron toward a square plane.[7]

The room-temperature electronic spectra (Table II) suggest for the type a complexes an approximately square-planar configuration[7–9] and for the type b complexes a distorted tetrahedral configuration. The effect of the crystal field stabilization evidently prevails in the type a complexes, since extensive NH···Cl hydrogen bonding reduces the effective charge on the chlorine atoms.[10,11a] Ligand–ligand repulsions, which offset the crystal field stabilization,[10,11a] prevail in the type b complexes by the diminished hydrogen-bonding possibility for an increase in the disorder of the hydrogen bonding.[2,12]

An important role for NH···Cl hydrogen bonding in stabilizing the planar geometry is probable, as all of the type a complexes upon heating to 80–95 °C convert to a more intensely colored form (the electronic spectra dramatically change), with a shift to longer wavelengths of the d–d transitions. In Figure 1 the near-ir spectral region at tem-

Table III. Far-Ir Spectra (600–60 cm^{-1}) of the Dihydrohalide Salts, Their Tetrahalo- and (Mixed-tetrahalo)cuprates, and Some Tetrahalocuprates of Known Geometry

	Approx geom	ν(CuCl)	ν(CuBr)	δ(CuX)	Other far-ir bands
pipz(HCl)$_2$					570 vs, 390 m, 270 vs, 176 vs, 150 vs, 90 s
pipz(HBr)$_2$					560 vs, 390 m, 330 m, 264 s, 137 vs, b, 86 ms
(pipzH·HCl)$_2$CuCl$_4$	D_{2h}	298 sh, 282 vs		182 vs, b	580 sh, 571 vs, 388 w, 252 ms, 158 s, 126 s, 87 m
(pipzH·HCl)$_2$CuCl$_3$Br	C_{2v}[a]	293 sh, 278 vs	218 w	182 vs, b, 132 sh	571 vs, 254 sh, 160 vs, 125 m
(pipzH·HCl)$_2$CuBr$_4$	D_{2h}		214 sh, 208 ms	136 m, b	567 vs, 390 w, 303 sh, 280 m
(pipzH·HBr)$_2$CuBr$_4$	D_{2h}		214 sh, 210 ms	130 m, b	568 vs, 300 w, 277 m, 150 m, b, 100 w, 74 w
(pipzH$_2$)CuCl$_4$	D_{2d}	303 vs, 264 vs, 233 m		187 sh, 172 vs, b	556 vs, 390 m, 233 m, 122 s, 77 m
(pipzH$_2$)CuCl$_3$Br	C_s[b]	300 vs, 288 vs, 263 vs	200 m	180 m, 123 s	555 vs, 235 sh, 165 m, 78 m
(pipzH$_2$)CuCl$_2$Br$_2$	C_{2v}[b]	285 sh, 270 vs, b	230 sh, 194 m	160 m, b	556 vs, 395 w, 108 m
(pipzH$_2$)CuBr$_4$	D_{2d}		242 s, 220 m	140 s, 130 sh	545 vs, 557 vs, 388 w, 277 m, 164 m, 93 w, 75 m
(pipzH$_2$)Cu$_2$Cl$_6$	D_{2h}	292 vs, 273 vs		183 ms	564 vs, 390 w, 163 s, 138 s, 117 sh, 104 m, 81 ms, 65 w
A$_2$CuCl$_4$[c]	D_{2h}	278–295 sh, 281–294		182–186	
B$_2$CuCl$_4$[d]	D_{2d}	267–292, 237–260		136–149, 118–128	
(Et$_4$N)$_2$CuBr$_4$[e]	D_{2d}		248 sh, 222	174	

[a] Planar C_{2v} symmetry for which are predicted three ir-active Cu–Cl and one ir-active Cu–Br stretching modes.[19] [b] Tetrahedral C_s symmetry for which are predicted three ir-active Cu–Cl and one ir-active Cu–Br stretching modes; tetrahedral C_{2v} symmetry for which are predicted two ir-active Cu–Cl and two ir-active Cu–Br stretching modes.[19] [c] A = $C_2H_5NH_3$, $(CH_3)_2CHNH_3$ (at 20 kbars and room temperature), and $(C_2H_5)_2NH_2$ (at low temperature).[11] [d] B = Cs, Me$_4$N, and Et$_4$N.[17,18,20] [e] References 18, 20.

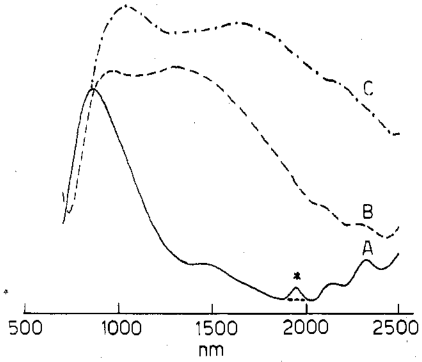


Figure 1. d–d spectra of the $CuBr_4^{2-}$ ion in $(pipzH{\cdot}HBr)_2CuBr_4$ below (25–90 °C) (A) and above (95 °C) (B) the phase transition and in $(pipzH_2)CuBr_4$ (C). The band labeled with an asterisk disappears on heating.

peratures above and below the transition temperature are shown by taking the $(pipzH{\cdot}HBr)_2CuBr_4$ complex as an example. The experimental evidence supports an interpretation of the thermocromic behavior of these compounds as the result of a phase transition involving a change in the coordination geometry, which is favored by a weakening of the hydrogen-bonding network as a result of the increasing disorder due to the thermal motion.

The high-temperature forms of the type a compounds present a more distorted tetrahedral symmetry than the type b complexes, as the shift of the d–d bands to higher energies of the former indicates.

The color change is reversible and also the electronic spectrum of the room-temperature form is restored after several hours.

Similar behavior is observed for the $[(C_2H_5)_2NH_2]_2CuCl_4$ complex. Its electronic spectrum below 315 K (9900 and 12 900 cm^{-1} at 9.2 K and ~12 000 cm^{-1} at 315 K) is considered indicative of a distorted square-planar geometry, while above 315 K (7300 and 10 200 cm^{-1} at 317 K) it is considered indicative of a distorted tetrahedral symmetry.[11b]

For the types M_2CuCl_4 and $MCuCl_4$ (where M is a uni- or divalent cation) a distorted tetrahedral anion of D_{2d} symmetry is expected when M is a large bulky cation which prevents the CuX_4^{2-} ions from interacting to produce distorted square-pyramidal or octahedral coordination.[7] Our cation is quite large to form distorted tetrahedral CuX_4^{2-} ions (type b complexes); hence, in the type a complexes the presence of two cations should furthermore decrease the ability of the CuX_4^{2-} ions to interact, hindering the five- or six-coordination, and the change in the coordination geometry of these complexes, with respect to the type b complexes, may be only due to the increased hydrogen-bonding possibility.

Further evidence of the role of the NH···Cl hydrogen bonding in stabilizing the planar geometry of the type a complexes in the solid state is the fact that in DMF solution, for the abatement of the NH···Cl hydrogen bonding (by effect of the solvent) and for the axial solvent perturbation,[13] the distorted tetrahedral geometry is restored. This is demonstrated as the electronic spectra in DMF solution of the type a complexes, identical with those of the type b complexes, show a single maximum at 9200–9600 cm^{-1} with a broad tail extending at lower energy. In DMF solution the type b complexes act as 1:1 electrolytes, while in the type a complexes only the $(pipzH{\cdot}HX)_2CuBr_4$ (X = Cl, Br) complexes show molar conductivities characteristic of 2:1 electrolytes.[14] The increasing conductivities of the complexes with an increasing number of bromide atoms, particularly pronounced in the type a complexes, may be due to a decreasing outer coordination sphere association dependent on the charge density on the halide.

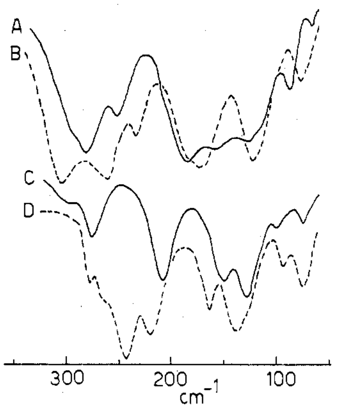


Figure 2. Exemplifying far-ir spectra of complexes with approximately square-planar geometry as $(pipzH{\cdot}HCl)_2CuCl_4$ (A) and $(pipzH{\cdot}HBr)_2CuBr_4$ (C) and with a distorted tetrahedral geometry as $(pipzH_2)CuCl_4$ (B) and $(pipzH_2)CuBr_4$ (D).

The $(pipzH_2)Cu_2Cl_6$ complex shows an electronic spectrum very similar to those of the room-temperature type a complexes for which an approximately square-planar stereochemistry is suggested and to those obtained for the $Cu_2Cl_6^{2-}$ dimers and for other approximately square-planar $CuCl_4^{2-}$ ions.[8,9] While the position of the d–d bands does not change during transition from the square-planar monomeric species to the dimer, there being no strong perturbation of the electronic environment involved in the formation of the dimer, a new band appears at ~19 000 cm^{-1} only in the latter. This band, noted in $Cu_2Cl_6^{2-}$ dimers,[8,9] also appears in our $(pipzH_2)Cu_2Cl_6$ complex.

The room-temperature magnetic moments of the solid complexes agree well with the proposed configuration.[15,16]

Far-Infrared Spectra. The far-ir spectra for the complexes and the appropriate starting amine hydrohalide salts are listed and assigned in Table III.

The frequencies of the ν(Cu–X) modes in the complexes (type a) with approximately square-planar geometry are significantly different from those found in complexes with a distorted tetrahedral symmetry (Figure 2). In particular the $(pipzH{\cdot}HCl)_2{\cdot}CuCl_4$ and $(pipzH{\cdot}HX)_2{\cdot}CuBr_4$ (X = Cl, Br) complexes show peaks at 282 cm^{-1}, with a shoulder at 298 cm^{-1}, and at 209–210 cm^{-1}, with a shoulder at 214 cm^{-1}, respectively, corresponding to the b_{2u} and b_{3u} modes in D_{2h},[11a] and an absorption at 182–184 and 130–136 cm^{-1}, respectively, corresponding to the out-of-plane b_{1u} bending mode.[11a]

In the complexes with nearly D_{2d} symmetry such as $(pipz{\cdot}H_2){\cdot}CuX_4$ (X = Cl, Br) the splitting of the e vibration mode at 303, 264 and 241, 220 cm^{-1}, respectively, and of the bending mode at 187, 172 and 140, 130 cm^{-1}, respectively, indicates that some distortion from D_{2d} symmetry must be present.

The strong band in the hydrohalide salts at ~270 cm^{-1} appears in all of the $CuBr_4^{2-}$ complexes almost unchanged in position but attenuated in intensity, for which, in the complexes containing the Cu–Cl bond, this band may be overlapped and masked by the strong ν(Cu–Cl) absorption.

For comparative purposes, in Table III we have also given the far-ir spectra of compounds of known geometry.[17,18]

The far-ir spectra of the $(pipzH{\cdot}HCl)_2{\cdot}CuCl_3Br$, $(pipzH_2){\cdot}CuCl_3Br$, and $(pipzH_2){\cdot}CuCl_2Br_2$ are interpreted on the basis of planar C_{2v}, tetrahedral C_s, and tetrahedral C_{2v} symmetries, respectively.[19]

In the $[Cu_2Cl_6]^{2-}$ spectrum the 292-cm^{-1} band must be due to terminal ν(CuCl) and the 273-cm^{-1} band could be bridging ν(CuCl). The difficulty of assigning the bridging ν(CuCl) dimers derives from the fact that its range is severely overlapped by that of terminal ν(CuCl).[20]

Hydrogen Bonding. In the parent amine dihydrohalides, a complex series of absorptions is found at 2600–2800 (very strong) and 2400–2600 cm^{-1} (strong), which became attenuated on deuteration, indicating that the N–H motion is involved.[21] The positions of these bands are in agreement with the piperidinium and morpholinium salts[1] and other secondary amine hydrohalides.[21,22] Furthermore a medium-intensity band appears at 3200–3250 cm^{-1}.

The bending N–H mode at 1612, 1540 and 1618, 1568, 1532 cm^{-1} in dihydrochloride and dihydrobromide salts, respectively, which disappears on deuteration, is not sensitive to the CuX_4^{2-} geometry contrary to that found with piperidinium and morpholinium cations.[1] Instead, the bending N–H modes appearing at 914–930 and at 560–570 cm^{-1} in the dihydrohalide salts, which disappear on deuteration, are shifted to higher energies (990 and 570 cm^{-1}, respectively) in the complexes which approach square-planar configuration and remain stationary or are slightly lowered in energy (910 and 550 cm^{-1}, respectively) in the complexes with a distorted tetrahedral symmetry, in accordance with a stronger hydrogen bond in the former.

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Registry No. (pipzH_2)$CuCl_4$, 59830-85-2; (pipzH_2)$_2CuCl_6$, 59830-86-3; (pipzH_2)$CuCl_3Br$, 59872-30-9; (pipzH_2)$CuCl_2Br_2$, 59872-32-1; (pipzH_2)$_2CuCl_5Br$, 59830-87-4; (pipzH_2)$CuBr_4$, 59830-88-5; (pipzH_2)$_2CuCl_2Br_4$, 59830-89-6; (pipzH_2)$_2CuBr_6$, 59830-90-9; (pipzH_2)Cu_2Cl_6, 59872-33-2; (pipz)(HCl)$_2$, 142-64-3; (pipz)(HBr)$_2$, 59813-05-7; (pipz)(HCl)(HBr), 59813-06-8; pipzHBr, 59813-07-9; pipzHCl, 6094-40-2.

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Nitrogen Charge Distributions in Free-Base Porphyrins, Metalloporphyrins, and Their Reduced Analogues Observed by X-Ray Photoelectron Spectroscopy[1a]

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The metal, N 1s, and C 1s XPS binding energies for the free-base compounds (H_2OEP, H_2TPrP, H_2TPP, H_2TPC, H_2TPBC), the metalloporphyrins (MgTPP, ZnTPP, CoTPP, CuTPP, NiTPP, AgTPP), and the metallochlorins (MgTPC, ZnTPC, CoTPC, CuTPC, NiTPC, AgTPC) are reported. The N 1s binding energies plus additional information from theoretical calculations and NMR, uv–vis, and ir spectroscopy show that reduction of the free bases slightly decreases the electron density of the nitrogen and only subtly changes their XPS spectra. The replacement of the free-base protons by a metal ion to form the metalloporphyrin increases the symmetry of the molecule and also introduces an electron-withdrawing group into the center of the ligand which increases the N 1s binding energy as the metal ion electronegativity increases. Finally these results are used to show that both effects are found in metallochlorins. In both metalloporphyrins and metallochlorins differences in the spectral features of paramagnetic and diamagnetic ions are noted.

Introduction

The comparison of data derived from several spectroscopic methods has been a standard modus operandi for establishing the structure and bonding in metal chelates. To this end nearly every available technique has been applied to porphyrins and their derivatives. Most of the early studies were primarily concerned with defining the effect of the porphyrin structure and substituents on the ultraviolet–visible absorption[2–8] and emission[9,10] spectral patterns. However, ESR,[11–14] ir,[15–18] x-ray crystallographic,[19–21] ^{1}H,[22] ^{13}C,[23] and ^{15}N,[24] NMR, Raman,[25,26] and electrochemical[27–30] techniques have all been used to study the porphyrin macrocycle. In most cases these studies were combined with molecular orbital calculations to support the measurements. The results of these experiments and calculations have shown the porphyrin ring is a planar, aromatic macrocycle which behaves as a quadridentate, soft-base ligand.[31]

In Figure 1, some of the variations available with the porphyrin ligand are illustrated. As indicated in Figure 1a, the β carbons (C_β)[32] may incorporate ethyl substituents to form the molecule of 1,2,3,4,5,6,7,8-octaethylporphyrin free base. Alternately as shown in Figure 1b the central porphine skeleton may be substituted on the meso carbon positions (C_m) to form $\alpha,\beta,\gamma,\delta$-*meso*-tetraphenylporphyrin. Finally, as shown in Figure 1c and d, the ring may be reduced to the corresponding chlorin or bacteriochlorin. Formally, the reduction occurs on the β carbons on ring IV to form the chlorin and on rings II and IV to form the bacteriochlorin. Although