Contribution from the Dipartimento di Chimica Inorganica e Metallorganica, Università di Milano, 20133 Milano, Italy

Synthetic Approach to the Type 1 Active Site of Copper Proteins. Copper(I), Copper(II), and Zinc(II) Complexes with N_2SS^* Ligand Donor Sets

LUIGI CASELLA

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The copper(I), copper(II), and zinc(II) complexes of the ligand formed by condensation of 1-phenyl-3-formyl-2(1*H*)-pyridinethione and 4-{[(2-aminoethyl)thio]methyl}-5-methylimidazole, pyt-N,S-im, with an N_2SS^* donor set, have been synthesized and characterized. These are apparently the first complexes with such a donor set that have been reported. While the free ligand exhibits typical thione character, it is bound to the metal ions in its tautomeric thiolate form. This behavior has been established by examining the electronic spectra and especially, for copper(I) and zinc(II), the ^1H NMR spectra of the complexes. These also indicated that while zinc(II) prefers to bind somewhat more strongly to the imine nitrogen donor, copper(I) appears to be bound more strongly to the thioether sulfur donor of the ligand. The copper(II) complex of pyt-N,S-im represents one of the few stable copper(II)–thiolate systems that have been reported. The spectroscopic properties of this complex indicate an approximate tetragonal stereochemistry and are largely determined by the presence of the thiolate sulfur donor. Binding by the other donor atoms could only be inferred by comparison with the spectra of the copper(II) complexes derived from 4-{[(2-aminoethyl)thio]methyl}-5-methylimidazole and its *N*-salicylidene analogue (N_2OS^* ligand donor set). The UV–vis and ESR spectra of these copper(II) complexes have been rationalized in terms of the ligand donor sets and discussed in relation to other systems containing nitrogen and sulfur ligand donors.

Introduction

The attempt to duplicate at least some of the spectral properties peculiar to the type 1 active site of the oxidized forms of a variety of "blue" copper proteins[1-3] has produced a wealth of studies on synthetic model complexes. The available structural studies on the blue proteins have shown that the spectral properties of the type 1 site are essentially determined by the unusual combination of a highly distorted tetrahedral N_2SS^* coordination about copper(II) and the binding of a mercaptide sulfur atom to the metal,[4-6] though also the imidazole and thioether donor groups give some nonnegligible contribution. Model studies have thus mainly focused on ligand donor systems containing thiolate,[7-16] thioether,[15-30] or thiocarboxylate[31] sulfur donor atoms, while imidazole binding is often simulated by imine groups or ni-

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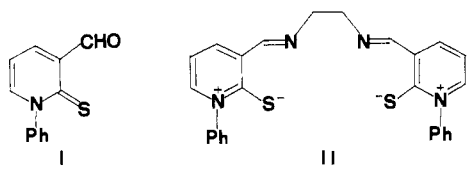
Table I. Proton NMR Data for the Ligands and Diamagnetic Complexes[a]

compd	α	β	δ	γ	ϵ	py	Ph	Im	NH	$J_{\beta\delta}$	$J_{\delta\epsilon}$
N,S-im	2.15	2.41–2.85[b]		3.64				7.35	3.3[c]		
pyt-N,S-im	2.17	2.77	3.78	3.69	9.04	8.00 (H-6)[d] 7.92 (H-4)[d] 6.83 (H-5)[d]	7.2–7.6		*e*	6.6	1.2
[Cu(pyt-N,S-im)][ClO_4]	2.17	2.89[c]	3.77[c]		8.49		7.1–8.4		10.4	~6	
[Zn(pyt-N,S-im)][ClO_4]$_2$	2.17	2.85	4.23	3.64	8.84		7.3–8.5		10.8	6.0	1.1

[a] The labeling scheme for the proton resonances is given in Figure 2; coupling constants are given in Hz. [b] AA'BB' system centered at δ 2.62. [c] Broad. [d] J_{45} = 6.7 Hz, J_{46} = 1.8 Hz, J_{56} = 7.2 Hz. [e] Signal not observed. It is probably extensively broadened and collapsed due to tautomeric exchange between the two imidazole nitrogen atoms and nuclear quadrupole relaxation by the ^{14}N nuclei.

trogen heterocyclic bases. To date, however, no synthetic system with a ligand donor set analogous to that found in the blue proteins has been reported. Our interest has been stimulated by the recent report[32] that in the imine complexes of 1-phenyl-3-formyl-2(1*H*)-pyridinethione (I) the ligand (II)

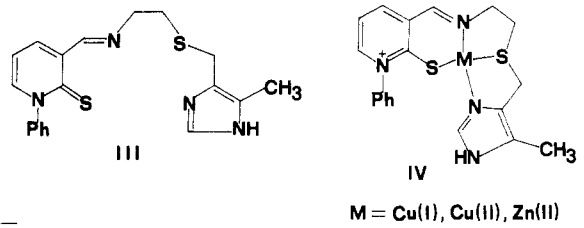


I II

may possess thiolate character in the C–S bond and pyridinium character in the ring. A current problem in developing the chemistry of bioinorganic models is the difficulty of preparing stable copper(II) thiolate systems. The strong electron-withdrawing substitution of mercaptides such as II should make less oxidizable the ligand and, therefore, enhance the stability of the mercapto–copper(II) bond with respect to that of an aliphatic mercaptan, and in addition, phenyl substitution at the pyridine nitrogen in II is expected to provide considerable steric hindrance to the generally easy coupling of copper(II) thiolate residues to produce disulfide units:[14,33]

$$2RS^- + 2Cu(II) \rightarrow 2Cu(I) + R\text{–}S\text{–}S\text{–}R$$

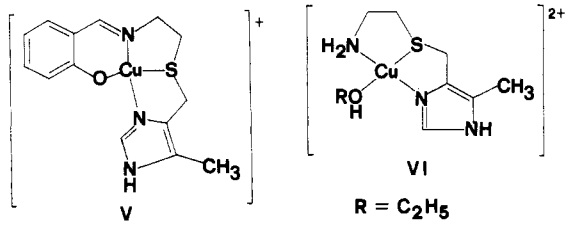
Therefore, although the electronic structure of the thiolate chromophore in II is somewhat different from that of an aliphatic mercaptide such as the cysteinate residue in the blue proteins, 1-phenyl-3-formyl-2(1*H*)-pyridinethione can provide an easily conjugable frame to form stable mercapto–copper(II) complexes. This paper reports the synthesis and spectral properties of the copper(I), copper(II), and zinc(II) complexes of the ligand pyt-N,S-im (III),[34] derived from the condensation



III IV

M = Cu(I), Cu(II), Zn(II)

of I and 4-{[(2-aminoethyl)thio]methyl}-5-methylimidazole, an intermediate in the synthesis of the antiulcer drug cimetidine.[35] If the thiolate structure of the ligand, as depicted in IV, is accessible to these systems and if the analogy between the conjugated imine and the imidazole nitrogen donors is allowed, the N_2SS^* donor set of this ligand represents a simulation of the copper donor set found in plastocyanin and azurin.[4-6] For comparison purposes the copper(II) complexes of 4-{[(2-*N*-salicylideneimino)ethyl)thio]methyl}-5-methylimidazole (V)[34] and 4-{[(2-aminoethyl)thio]methyl}-5-methylimidazole (VI),[34] with CuN_2OS^* cores, were also synthesized.



V VI

R = C_2H_5

Experimental Section

Physical Measurements. Elemental analyses (C, H, N) were from thee microanalytical laboratory of the Universitâ di Milano; copper analyses were made by atomic absorption. Infrared spectra were recorded on a Nicolet MX-1E FT-IR instrument; a standard resolution of 2.0 cm^{-1} was used in the measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda-5 spectrophotometer. Proton NMR spectra were recorded at 80 MHz on a Bruker WP-80 spectrometer using the pulsed Fourier transform technique; all chemical shift data are downfield from Me_4Si. ESR spectra were obtained at X-band frequencies on a Varian E-109 instrument and were calibrated with diphenylpicrylhydrazyl. Mass spectra were recorded on a Varian MAT 112 spectrometer at 70 eV. Conductivity measurements were performed on acetonitrile solutions of the complexes with use of a Philips Model PR 9500 conductimeter.

Reagents and Preparations. All reagents were of the highest grade commercially available. Acetonitrile-d_3 was dried and stored over molecular sieves (3 Å). 1-Phenyl-3-formyl-2(1*H*)-pyridinethione was prepared from the sodium salt of glutacondialdehyde[36] and phenyl isothiocyanate according to a published procedure.[37,38] 4-{[(2-Aminoethyl)thio]methyl}-5-methylimidazole dihydrochloride was a gift from Prodotti Chimici Sabbatini (Milano). Tetrakis(acetonitrile)copper(I) perchlorate was prepared by following the usual method.[39]

Preparation of py-N,S-im. 4-{[(2-Aminoethyl)thio]methyl}-5-methylimidazole was freed from its dihydrochloride salt (1 mmol)

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(34) Abbreviations: 1-phenyl-3-{[(3-thia-4-(5-methylimidazol-4-yl)butyl)-imino]methyl}-2(1*H*)-pyridinethione = pyt-N,S-im (III); 4-{[(2-(*N*-salicylideneimino)ethyl)thio]methyl}-5-methylimidazole = sal-N,S-im; 4-{[(2-aminoethyl)thio]methyl}-5-methylimidazole = N,S-im; imidazole = Im; phenyl = Ph; pyridine = py.
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(38) Spectral data of 1-phenyl-3-formyl-2(1*H*)-pyridinethione (I) are as follows. IR (Nujol mull, cm^{-1}): 3080 vw, 1673 vs, 1605 w, 1588 vw, 1533 s, 1487 m, 1460 m, 1453 m, 1444 m, 1389 m, 1360 s, 1249 s, 1203 m, 1152 w, 1142 m, 1133 m, 1069 m, 1022 m, 867 w, 836 vw, 796 m, 760 m, 737 w, 721 w, 713 vw, 670 m. ^1H NMR (CD_3CN): δ 10.67 (s, 1 H, CHO), 8.01 (dd, J_{56} = 6.5 Hz, J_{46} = 1.8 Hz, 1 H, H-6), 7.87 (dd, J_{45} = 7.3 Hz, 1 H, H-4), 7.2–7.7 (m, 5 H, Ph), 6.87 (~t, $J \approx 7$ Hz, 1 H, H-5). UV–Vis (CH_3CN; λ_{max}, nm (ϵ): 425 (3000), 323 (12 500), 240 sh (8000), 214 (17 000). MS (*m/e* (%)): 215 (M^+, 22), 187 (23), 186 (100), 154 (10), 127 (6), 115 (8), 95 (9), 77 (24), 57 (15), 51 (26).
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by stirring in absolute ethanol–chloroform (4:1 v/v, 50 mL) with the appropriate amount of methanolic ~1 N sodium hydroxide. After filtration of the precipitate of sodium chloride, evaporation to dryness of the solution gave a light yellow solid. This was dissolved in absolute ethanol (30 mL), and 1-phenyl-3-formyl-2(1*H*)-pyridinethione (1 mmol) was added. The mixture was refluxed until all the thione had dissolved; then the solution was cooled to room temperature and 3-Å molecular sieves were added and allowed to react for 15 min. Upon removal of the sieves by filtering, evaporation to dryness gave an orange oil. This was stirred in dry diethyl ether, giving an orange powder of the Schiff base that was filtered, washed with diethyl ether, and dried under vacuum. Anal. Calcd for $C_{19}H_{20}N_4S_2$: C, 61.92; H, 5.47; N, 15.21. Found: C, 61.91; H, 5.67; N, 14.97. IR (Nujol mull, cm^{-1}): 3100 w (broad), 1630 m, 1607 w, 1592 w, 1558 vw, 1536 s, 1506 vw, 1488 m, 1362 m, 1328 vw, 1257 m, 1219 vw, 1159 w, 1139 m, 1071 m, 1022 w, 972 vw, 955 vw, 888 vw, 761 m, 721 w, 693 m. UV–vis (CH_3CN; λ_{max}, nm (ϵ)): 408 (4000), 318 (12 200), 245 sh (10 500), 222 (25 000). MS (*m/e* (%)): 368 (M^+, 0.3), 290 (2), 275 (5), 274 (37), 241 (21), 233 (7), 232 (7), 231 (10), 214 (25), 213 (64), 200 (22), 186 (7), 181 (8), 171 (9), 154 (9), 142 (18), 137 (10), 128 (21), 127 (28), 122 (29), 96 (64), 95 (100). The proton NMR data for N,S-im and pyt-N,S-im are reported in Table I.

Preparation of the Complexes.[34] The synthesis of the pyt-N,S-im complexes was carried out according to the following procedure (the copper(I) complex was prepared under nitrogen). A solution of 4-{[(2-aminoethyl)thio]methyl}-5-methylimidazole (1 mmol, freed from the dihydrochloride salt as described above) and 1-phenyl-3-formyl-2(1*H*)-pyridinethione (1 mmol) in absolute ethanol (30 mL) was refluxed for ~15 min. The IR and NMR spectra taken on small samples of the solution after evaporation to dryness showed that condensation of the reagents was practically complete. After the solution was cooled to room temperature, the metal perchlorate salt (1 mmol) was added with stirring and the mixture was again refluxed for a few minutes. After it was cooled, the resulting solution was concentrated to a small volume under vacuum. The copper(II) (dark green) and zinc(II) (yellow) complexes gave precipitates at this stage, whereas precipitation of the copper(I) complex (red-brown) occurred upon addition of degassed diethyl ether to the ethanolic solution. The complex [Cu(sal-N,S-im)][ClO_4] was prepared similarly from equimolar amounts of salicylaldehyde,free 4-{[(2-aminoethyl)thio]-methyl}-5-methylimidazole, and copper(II) perchlorate hexahydrate (1 mmol). Addition of slightly less than the stoichiometric amount of methanolic ~1 N sodium hydroxide to the reaction solution gave a brownish green precipitate. The complex [Cu(N,S-im)][ClO_4]$_2$ was prepared by mixing equimolar amounts of 4-{[(2-aminoethyl)-thio]methyl}-5-methylimidazole and copper(II) perchlorate hexahydrate (1 mmol) in absolute ethanol. Concentration almost to dryness of the solution and addition of dry diethyl ether to the residue yielded a green precipitate. All the products were dried under vacuum.

[Cu(pyt-N,S-im)][ClO_4]. Anal. Calcd for $C_{19}H_{20}ClCuN_4O_4S_2$: C, 42.93; H, 3.79; N, 10.54; Cu, 11.95. Found: C, 42.65; H, 3.90; N, 10.15; Cu, 12.4. IR (Nujol mull, cm^{-1}): 3270 w (broad), 3086 vw, 3055 vw, 1634 w, 1590 m, 1544 s, 1488 m, 1264 vw, 1236 w, 1144 m, 1090 vs (broad), 1009 vw, 973 vw, 922 vw, 790 vw, 763 m, 718 m, 694 m, 667 vw, 623 s. UV–vis (CH_3CN; λ_{max}, nm (ϵ)): 400 (4500), 315 (6200), 270 sh (9600), 225 sh (25 000).

[Cu(pyt-N,S-im)][ClO_4]$_2$. Anal. Calcd for $C_{19}H_{20}Cl_2CuN_4O_8S_2$: C, 36.17; H, 3.20; N, 8.88; Cu, 10.07. Found: C, 36.37; H, 3.22; N, 8.56; Cu, 10.5. IR (Nujol mull, cm^{-1}): 3250 w (broad), 3135 vw, 3086 vw, 3053 vw, 1643 m, 1622 w, 1589 w, 1557 s, 1505 vw, 1487 w, 1400 s, 1277 vw, 1240 m, 1221 vw, 1154 m, 1090 vs (broad), 981 m, 929 w, 843 vw, 803 w, 764 m, 741 m, 695 m, 622 s. UV–vis (CH_3CN; λ_{max}, nm (ϵ)): 578 (520), 382 (11 500), 323 (7300), 250 sh (14 000), 218 (32 000).

[Zn(pyt-N,S-im)][ClO_4]$_2$. Anal. Calcd for $C_{19}H_{20}Cl_2N_4O_8S_2Zn$: C, 36.06; H, 3.19; N, 8.86. Found: C, 36.38; H, 3.45; N, 9.01. IR (Nujol mull, cm^{-1}): 3226 w, 3200 m, 3146 vw, 3081 w, 3033 vw, 1642 s, 1614 w, 1598 w, 1587 m, 1561 s, 1510 w, 1486 m, 1427 m, 1399 s, 1350 vw, 1289 m, 1268 w, 1263 w, 1237 m, 1207 w, 1173 m, 1149 m, 1126 s, 1106 s, 1095 vs, 1073 s, 1052 s, 1044 s, 1005 vw, 972 vw, 985 w, 972 vw, 930 w, 921 vw, 796 m, 774 s, 761 m, 719 m, 700 m, 677 vw, 634 m, 623 s. UV–vis (CH_3CN; λ_{max}, nm (ϵ)): 368 (6100), 321 (9700), 245 sh (10 000), 214 (32 000).

[Cu(sal-N,S-im)][ClO_4]. Anal. Calcd for $C_{14}H_{15}ClCuN_3O_5S$: C, 38.53; H, 3.47; N, 9.63; Cu, 14.56. Found: C, 38.86; H, 3.80; N, 9.44; Cu, 14.9. IR (Nujol mull, cm^{-1}): 3255 m, 3223 w, 3129 w, 3060 vw, 1620 s, 1600 m, 1532 m, 1498 w, 1444 s, 1398 m, 1348 w, 1317 m, 1257 w, 1233 w, 1216 w, 1205 w, 1197 w, 1155 m, 1130 w, 1100 s (broad), 1012 vw, 985 w, 965 vw, 931 vw, 902 w, 867 w, 792 w, 767 m, 721 vw, 650 vw, 634 vw, 621 s, 609 vw. UV–vis (CH_3CN; λ_{max}, nm (ϵ)): 584 (350), 450 sh (380), 372 (4500), 324 (9000), 271 (13 800), 240 sh (20 000), 225 (30 000).

[Cu(N,S-im)][ClO_4]$_2$. Anal. Calcd for $C_7H_{13}Cl_2CuN_3O_8S \cdot C_2H_5OH$: C, 22.53; H, 3.99; N, 8.76; Cu, 13.24. Found: C, 22.25; H, 3.46; N, 8.25; Cu, 13.8. IR (Nujol mull, cm^{-1}): 3515 m, 3305 m, 3252 m, 3147 m, 3049 vw, 1669 w, 1616 m, 1585 sh, 1505 m, 1420 sh, 1288 vw, 1278 vw, 1235 w, 1100 vs (broad), 982 m, 929 m, 882 w, 839 vw, 816 vw, 760 w, 742 w, 721 w, 666 vw, 623 s. UV–vis (CH_3CN; λ_{max}, nm (ϵ)): 638 (75), 338 (2100), 260 sh (2200), 220 sh (9300), 200 (13 300).

The proton NMR data for [Cu(pyt-N,S-im)][ClO_4] and [Zn-(pyt-N,S-im)][ClO_4]$_2$ are reported in Table I.

Table II. Conductivity Data for the Complexes in Acetonitrile Solution

complex	Λ_M[a]	A[b]
[Cu(pyt-N,S-im)][ClO_4]	140	420
[Cu(sal-N,S-im)][ClO_4]	141	380
[Cu(pyt-N,S-im)][ClO_4]$_2$	270	780
[Zn(pyt-N,S-im)][ClO_4]$_2$	234	750
[Cu(N,S-im)][ClO_4]$_2$	244	800

[a] Values interpolated at 10^{-3} M are in S cm^2 mol^{-1}. [b] Slope of the Onsager plot ($\Lambda_0 - \Lambda_e$) vs. $c^{1/2}$.

Results and Discussion

The condensation of I with primary amines readily gives rise to the corresponding imines.[32,40] These products are easily identified by their IR and ^1H NMR spectra, where replacement of the formyl by the imine group gives rise to the expected changes: (i) lowering of the energy of the ν(C=X) stretch in the IR spectrum and (ii) shift to higher field of the CH=X proton signal in the ^1H NMR spectrum. The assignment of the other proton NMR resonances of pyt-N,S-im (III) is based on the data related to I,[37,38] and the assumption that the methylene group (δ) attached to the amine nitrogen atom of N,S-im is shifted downfield on Schiff base formation (Table I). Metal complexes of the imines derived from I, or salicylaldehyde, and N,S-im are readily formed on mixing of the reagents. The metal perchlorate salts were routinely used in the preparations because of the very weak coordination properties of this anion, especially in solution. The solid-state IR spectra of all the complexes show, in fact, broad bands near 1100 cm^{-1} that indicate the perchlorate ions are not coordinate to the metal.[41] Solution conductivity measurements were performed to establish the electrolyte type of the complexes and to determine whether these are monomers in solution. Although molar conductivities at 10^{-3} M concentration for the complexes are in the range expected for their formulation as 1:1 or 1:2 electrolytes (Table II),[42] measurements over a concentration range give a more correct indication of the ion type in solution.[43] The slopes A, obtained from plots of $\Lambda_0 - \Lambda_e$ vs. $c^{1/2}$, clearly establish that [Cu(pyt-N,S-im)][ClO_4] and [Cu(sal-N,S-im)][ClO_4] behave as 1:1 electrolytes and [Cu(pyt-N,S-im)][ClO_4]$_2$, [Zn(pyt-N,S-im)][ClO_4]$_2$, and [Cu(N,S-im)][ClO_4]$_2$ as 1:2 electrolytes (Table II).[44] These data exclude that molecular association can occur in solution for all the complexes, since it would give rise to ion types higher than 1:1 or 1:2 and could be easily recognized by larger magnitudes of the A slopes.[42-44]

(40) Casella, L.; Gullotti, M.; Viganò, R., to be submitted for publication.
(41) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; Chapter 3.
(42) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.
(43) Boggess, R. K.; Zatko, D. A. *J. Chem. Educ.* **1975**, *52*, 649–651.
(44) See for instance: Davidson, A.; Howe, D. V.; Shawl, E. T. Inorg. Chem. **1967**, *6*, 458–463.

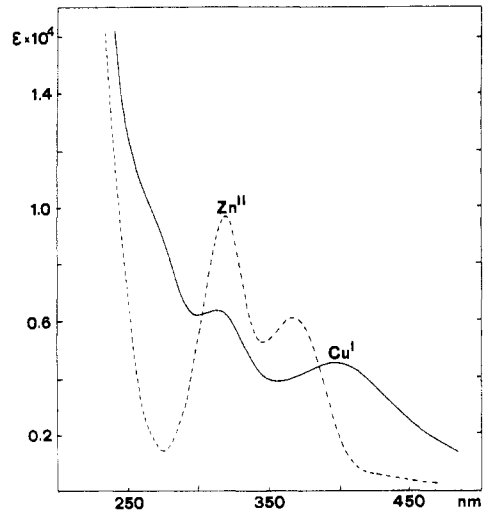

Figure 1. Electronic spectra of [Cu(pyt-N,S-im)][ClO_4] (—) and [Zn(pyt-N,S-im)][ClO_4]$_2$ (---) in acetonitrile solution.

In the case of pyt-N,S-im and of its metal complexes it is particularly important to establish whether the molecule retains the thione character of its formyl precursor, I. The most useful techniques to investigate the tautomeric forms VIIa and VIIb of these pyridine derivatives are UV and NMR spectroscopy, while IR seems of limited value here because location of the ν(C=S) and ν(C—S) stretches in the spectra is made difficult by the abundance of aromatic skeletal modes. In general, a largely prevalent thione character is attributed to simple mercaptopyridines and their N-substituted derivatives on the basis of their electronic[45] and ^{1}H NMR spectra.[46] The lowest energy $\pi \rightarrow \pi^*$ electronic transition of these compounds, in fact, occurs at longer wavelength than for the corresponding S-substituted derivatives, e.g. VIII, and thiolate anions, e.g. IX, while the NMR argument is based on chemical shifts and coupling constants for the ring protons. The electronic spectrum and the aromatic portion of the proton NMR spectrum of pyt-N,S-im are very similar to the corresponding spectra of I, indicating that, as expected, imine formation does not change the prevalent thione character, VIIa, of the molecule. Considering the electronic spectra of the copper(I) and zinc(II) complexes of pyt-N,S-im, it can be seen that the former contains a long-wavelength absorption (400 nm) not far from the position observed for the free ligand (408 nm), while for the latter the absorption bands occur at significantly higher energy (Figure 1). In spite of the apparent contradiction, the ligand displays thiolate character in both complexes, since the 400-nm band of [Cu(pyt-N,S-im)][ClO_4] and also the shoulder near 270 nm that is absent in the spectra of either pyt-N,S-im or [Zn(pyt-N,S-im)][ClO_4]$_2$ are assigned to charge-transfer transitions from the filled copper(I) d orbitals to low-energy π^* orbitals of the ligand.[47] The different nature of pyt-N,S-im when it is free and when it is bound to a metal ion can be best appreciated by examining the pattern of NMR signals for the protons on the pyridine ring. Inspection of Figure 2 shows an ABX pattern ($J_{AX} \approx J_{BX}$) for the protons at positions 6 (δ 8.00), 4 (δ 7.92), and 5 (δ, 6.83) of the pyridine ring of pyt-N,S-im, respectively, while the azomethine proton signal (δ 9.04) occurs at unusually low field.[52] On complex formation the signals for the pyridine

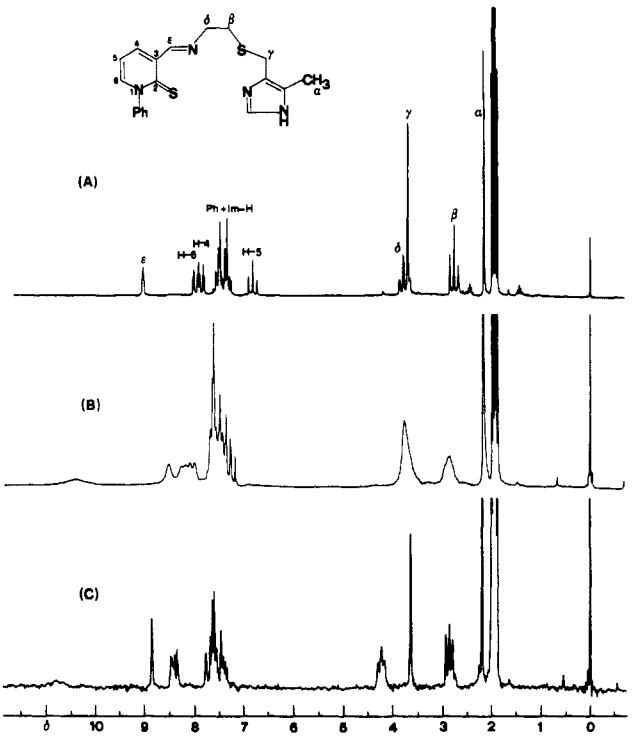

Figure 2. Proton NMR spectra in CD_3CN solution of (A) the pyt-N,S-im ligand, (B) [Cu(pyt-N,S-im)][ClO_4], and (C) [Zn(pyt-N,S-im)][ClO_4]$_2$.

(45) (a) Albert, A.; Barlin, G. B. *J. Chem. Soc.* **1959**, 2384–2396. (b) Mason, S. F. *Ibid.* **1960**, 219–224. (c) Katritzky, A. R.; Lagowski, J. M. *Adv. Heterocycl. Chem.* **1963**, *1*, 312–338. (d) Beak, P.; Fry, F. S., Jr.; Lee, J.; Steele, F. *J. Am. Chem. Soc.* **1976**, *98*, 171–179.

(46) Stewart, W. E.; Siddal, T. H., III. *J. Phys. Chem.* **1970**, *74*, 2027–2029.

(47) For copper(I) complexes MLCT transitions of low energy are observed, usually in the visible region, when the ligand donors are part of or are conjugated to aromatic π systems (see for instance ref 48–50). For zinc(II) complexes with related ligands only intraligand transitions can be observed, since the CT bands occur at much higher energy (see for instance ref 51).

(48) (a) Kitagawa, S.; Munakata, M.; Higashie, A. *Inorg. Chim. Acta* **1982**, *59*, 219–223. (b) Ponganis, K. V.; De Araujo, M. A.; Hodges, H. L. *Inorg. Chem.* **1980**, *19*, 2704–2709. (c) Al-Shatti, N.; Lappin, A. G.; Sykes, A. G. *Ibid.* **1981**, *20*, 1466–1469. (d) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1981**, *103*, 5906–5912.

(49) Nelson, S. M.; Esho, F. S.; Drew, M. G. B. *J. Chem. Soc., Chem. Commun.* **1981**, 388–389.

(50) Casella, L.; Ghelli, S. *Inorg. Chem.* **1983**, *22*, 2458–2463. The electronic spectra of the copper(I) complexes reported in this paper, besides the intense absorptions due to intraligand transitions below ~300 nm, show moderately intense bands at 350–400 nm ($\epsilon \approx 4000$) that are absent in the spectra of the ligands.

(51) (a) Simmons, M. G.; Merrill, C. L.; Wilson, L. J.; Bottomley, L. A.; Kadish, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1827–1837. (b) Casella, L.; Gullotti, M. *Inorg. Chem.* **1983**, *22*, 2259–2266. (c) Casella, L.; Silver, M. E.; Ibers, J. A. *Ibid.* **1984**, *23*, 1409–1418.

(52) The NMR signal for the imine proton of pyt-N,S-im occurs at significantly lower field than for pyridine aldimines.[53,54] This behavior parallels that observed for the aldehydic proton of I with respect to the corresponding protons of pyridine aldehydes.[55] Upon binding of pyridine aldimines to metal ions, downfield shifts for the imine proton NMR signals are systematically observed.[54,56] These signals occur near the positions observed here for [Cu(pyt-N,S-im)][ClO_4] and [Zn(pyt-N,S-im)][ClO_4]$_2$. Therefore, the NMR signals for the aldimine protons of these complexes are only virtually upfield shifted compared to those for the free ligand, due to different electronic effects in the latter compound.

(53) See for instance: Abbott, E. H.; Martell, A. E. *J. Am. Chem. Soc.* **1970**, *92*, 1754–1759.

ring protons undergo significant downfield shifts (Figure 2). The amount of this shift appears rather large particularly for the proton at ring position 5, which is far from the site of metal binding, and cannot be accounted for only by the influence of the positively charged metal ions. Shifts of this kind can only be explained in terms of the occurrence of an extensive ring π-electron delocalization and a positively charged pyridine nitrogen upon coordination of pyt-N,S-im to copper(I) or zinc(II). Therefore, these complexes are both correctly formulated according to the tautomeric structure IV containing the thiolate sulfur donor. The aldimine proton signals of [Cu(pyt-N,S-im)][ClO_4] and [Zn(pyt-N,S-im)][ClO_4]$_2$ occur in the range δ 8.5–8.9 and appear upfield shifted relative to those of the free ligand. This is only due to different electronic effects in the thione form of the ligand,[52] while the positions observed here for these aldimine protons are quite normal for pyridine aldimine complexes.[51b,54,56] The NMR spectra in Figure 2 reveal other interesting features. Metal chelation by pyt-N,S-im prevents tautomeric exchange of the imidazole NH between the two nitrogen sites of the ring, and as a result, the NMR signal for this proton (broad, by ^{14}N nuclear quadrupole relaxation) can be observed above δ 10 in the spectra of [Cu(pyt-N,S-im)][ClO_4] and [Zn(pyt-N,S-im)]-[ClO_4]$_2$. Moreover, it can be seen that the signals for the protons on methylene carbons attached to the donor atoms of these complexes undergo relatively small, but different, downfield shifts upon binding to copper(I) or zinc(II). For the zinc(II) complex the largest shift is that undergone by the methylene protons on the imine nitrogen donor. For the copper(I) complex the signals of both methylene groups attached to the thioether sulfur appear slightly downfield shifted, while the methylene group on the imine seems very little affected. These differences in chemical shifts probably reflect different interactions between the central ion and the donor atoms in the two complexes: the softer acid Cu(I) interacts more strongly with the softer sulfur base R–S–R′, while the harder acid Zn(II) is more strongly bound to the harder nitrogen base –CH=N–.[57]

The electronic spectrum of [Cu(pyt-N,S-im)][ClO_4]$_2$ shows that the low-energy band attributable to the thione chromophore (above 400 nm, eventually red shifted by metal chelation) is absent (Figure 3). As for the zinc(II) derivative, this indicates that the ligand is in its thiolate structure. The stability of this copper(II)–thiolate system is high: solutions of [Cu(pyt-N,S-im)][ClO_4]$_2$ gave completely identical spectra after having being stored for 1 week. The UV portion of the electronic spectrum of [Cu(pyt-N,S-im)][ClO_4]$_2$ displays bands at 323 and 218 nm, with a shoulder near 250 nm. At lower energy the spectrum is dominated by an intense, broad absorption band centered at 382 nm, while a weaker band at 578 nm comprises the ligand field transitions. The bands in the UV region are mainly contributed by $\pi \rightarrow \pi^*$ transitions of the aromatic chromophore, but also LMCT transitions originating from the imidazole nucleus (Im(σ) →, Im(π_2) →, and Im(π_1) → Cu(II)) occur in this region (near 220, 260–300, and 300–350 nm, respectively).[58-60] The intense 382-nm band

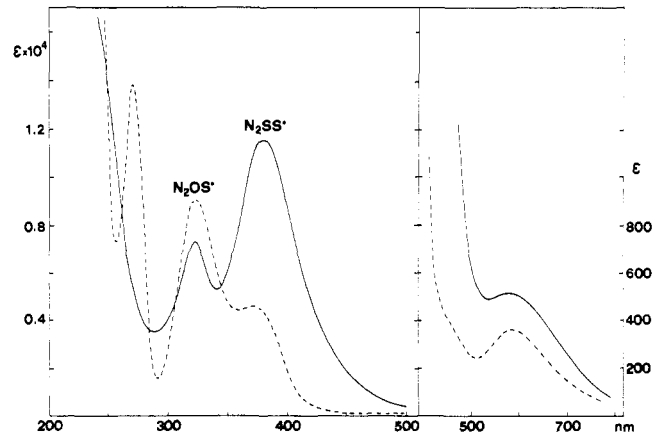

Figure 3. Electronic spectra of [Cu(pyt-N,S-im)][ClO_4]$_2$ (—, N_2SS^* ligand donor set) and [Cu(sal-N,S-im)][ClO_4] (---, N_2OS^* ligand donor set) in acetonitrile solution.

results from the overlap of a low-energy $\pi \rightarrow \pi^*$ transition mainly localized within the imine chromophore[61] and a LMCT transition from the lone pairs of the thiolate sulfur donor, S(σ) → Cu(II),[14,15,32] though also the corresponding LMCT transition from the thioether sulfur, S*(σ) → Cu(II), is expected to occur somewhere between 320 and 400 nm.[15-19,59] There is no apparent spectral feature that can be associated with the thiolate S(π) → Cu(II) LMCT transition.[62] This fact deserves comment, since absorption bands that can be attributed to S(π) → Cu(II) LMCT (not always explicitly assigned, though) are often observed in the spectra of copper(II)–thiolate systems, especially those containing aromatic thiolates.[10,12,13,59] It is likely that in thiolate ligands of type VIIb conjugation with the pyridinium ring stabilizes the sulfur π-symmetry lone pairs more than in simple aromatic thiolates. This stabilization is expected to lead to a blue shift for the S(π) → Cu(II) LMCT in the copper(II) systems derived from VIIb compared to those derived from aromatic thiolates. In the case of [Cu(pyt-N,-S-im)][ClO_4]$_2$ the S(π) → Cu(II) LMCT probably occurs unresolved under the intense band at 382 nm. Support for the above assignments comes from the examination of the electronic spectra of [Cu(sal-N,S-im)][ClO_4] (Figure 3) and [Cu(N,S-im)][ClO_4]$_2$. The spectrum of the latter compound is much simpler for the absence of a conjugated aromatic chromophore in the ligand, and the assignment of the absorption maxima is straightforward: the band at 220 nm is associated with the Im(σ) → Cu(II) LMCT transition and the band near 260 nm is contributed by the Im(π_2) → Cu(II) and NH_2(σ) → Cu(II)[17,60,64] LMCT transitions, while the band at 338 nm results from the overlap of the Im(π_1) → Cu(II) and S*(σ) → Cu(II) LMCT transitions. Although the last contribution may be questioned, it should be noted that the

(54) Casella, L.; Gullotti, M. *J. Am. Chem. Soc.* **1981**, *103*, 6338–6347.
(55) (a) Gansow, O. A.; Holm, R. H. *Tetrahedron*, **1968**, *24*, 4477–4487 and references therein. (b) Pocker, Y.; Meany, J. E.; Nist, B. J. *J. Phys. Chem.* **1967**, *71*, 4509–4513.
(56) (a) Gansow, O. A.; Holm, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 573–581. (b) Abbott, E. H.; Martell, A. E. *Ibid.* **1970**, *92*, 5845–5851; **1973**, *95*, 5014–5019. (c) Fischer, J. R.; Abbott, E. H. *Ibid.* **1979**, *101*, 2781–2782.
(57) Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; pp 276–288.
(58) (a) Fawcett, T. G.; Bernaducci, E. E.; Krogh-Jespersen, K.; Schugar, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 2598–2604. (b) Bernaducci, E.; Schwindinger, W. F.; Hughey, J. L.; IV; Krogh-Jespersen, K.; Schugar, H. J. *Ibid.* **1981**, *103*, 1686–1691.
(59) Schugar, H. J. In "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, **1982**; pp 43–74.
(60) Casella, L.; Gullotti, M.: (a) *J. Inorg. Biochem.* **1983**, *18*, 19–31. (b) *Inorg. Chem.* **1983**, *22*, 242–249.
(61) (a) Bosnich, B. *J. Am. Chem. Soc.* **1968**, *90*, 627–632. (b) Downing, R. S.; Urbach, F. L. *Ibid.* **1969**, *91*, 5977–5983. (c) Casella, L.; Gullotti, M. *Ibid.* **1983**, *105*, 803–809. (d) Casella, L.; Gullotti, M.; Pacchioni, G. *Ibid.* **1982**, *104*, 2386–2396.
(62) It is generally agreed that the S*(π) → Cu(II) LMCT transition is very weak or absent in the spectra of simple copper–thioether complexes.[59] A recent report[63] shows that also the two intense visible bands observed in the spectra of copper(II)–polythioether complexes,[25a,d] previously assigned to S*(σ) → and S*(π) → Cu(II) LMCT, in fact originate from different combinations of σ-type lone-pair orbitals of the ligand S_4 donor set.
(63) Yamabe, T.; Hori, K.; Minato, T.; Fukui, K.; Sugiura, Y. *Inorg. Chem.* **1982**, *21*, 2040–2046.
(64) Kennedy, B. P.; Lever, A. B. P. *J. Am. Chem. Soc.* **1973**, *95*, 6907–6913.

Table III. ESR Parameters for the Copper(II) Complexes[a,b]

complex	$g_\parallel$	$g_\perp$	$\lvert A_\parallel \rvert$
$[Cu(pyt\text{-}N,S\text{-}im)][ClO_4]_2$	2.163	~2.04	176
$[Cu(sal\text{-}N,S\text{-}im)][ClO_4]$	2.206	~2.05	170
$[Cu(N,S\text{-}im)][ClO_4]_2$	2.287	2.055[c]	176

[a] Recorded in frozen acetonitrile–chloroform (1:1) solution at −150 °C. [b] $\lvert A_\parallel \rvert$ values are in $cm^{-1} \times 10^{-4}$. [c] $\lvert A^N \rvert = 13 \times 10^{-4}$ cm^{-1}.

intensity of the band at 338 nm is much higher than those resulting from coordination of single imidazole nuclei to copper(II).[58-60] Since the ligand field strength in $[Cu(N,S\text{-}im)][ClO_4]_2$ is lower than in either $[Cu(pyt\text{-}N,S\text{-}im)][ClO_4]_2$ or $[Cu(sal\text{-}N,S\text{-}im)][ClO_4]$, the $S^*(\sigma) \rightarrow Cu(II)$ LMCT transition cannot be located at lower energy in the latter complexes. In these systems, therefore, the $S^*(\sigma) \rightarrow Cu(II)$ LMCT is probably hidden under the absorption bands near 325 nm. The electronic spectrum of $[Cu(sal\text{-}N,S\text{-}im)][ClO_4]$ exhibits two important features attributable to the change in ligand donor set: a marked reduction in intensity (to less than half), with a slight blue shift, of the band near 380 nm and the appearance of a weak band near 450 nm. The reduction in intensity of the absorption near 380 nm must be related to the absence of transitions originating from the thiolate sulfur: the absorption of $[Cu(sal\text{-}N,S\text{-}im)][ClO_4]$ in this region is similar, in both position and intensity, to that of $[Zn(pyt\text{-}N,S\text{-}im)][ClO_4]_2$. Though, it is interesting to note that while a molar extinction coefficient of 3000–5000 M^{-1} cm^{-1} is normally associated with the $S(\sigma) \rightarrow Cu(II)$ LMCT transition in the blue proteins[1-3] and in model copper–thiolate systems,[10-15] here the reduction in ϵ near 380 nm, from $[Cu(pyt\text{-}N,S\text{-}im)][ClO_4]_2$ to $[Cu(sal\text{-}N,S\text{-}im)][ClO_4]$ or $[Zn(pyt\text{-}N,S\text{-}im)][ClO_4]_2$, is well above 6000 M^{-1} cm^{-1}. This seems to confirm that, besides the imine $\pi \rightarrow \pi^*$ and the $S(\sigma) \rightarrow Cu(II)$ LMCT, another transition, the $S(\pi) \rightarrow Cu(II)$ LMCT, can be contained under the envelope of the 382-nm band of $[Cu(pyt\text{-}N,S\text{-}im)][ClO_4]_2$. The weak band at 450 nm appearing in the spectrum of $[Cu(sal\text{-}N,S\text{-}im)][ClO_4]$ corresponds to a charge-transfer transition involving the phenolate group. Although the precise nature of this transition is under dispute (it has been considered as an O(phenolate) → Cu(II) LMCT[65] or as a Cu(II) → π^*(phenolate) MLCT[15] transition), it is agreed that a higher energy component should exist near 330 nm.[15,65] In the case of $[Cu(sal\text{-}N,S\text{-}im)][ClO_4]$ this component is likely to contribute to the absorption maximum at 324 nm, which is more intense than the corresponding band of $[Cu(pyt\text{-}N,S\text{-}im)][ClO_4]_2$. An additional band that is observed at 271 nm in the spectrum of $[Cu(sal\text{-}N,S\text{-}im)][ClO_4]$ but is absent in that of $[Cu(pyt\text{-}N,S\text{-}im)][ClO_4]_2$ corresponds to a transition typical for the salicylaldimine chromophore.[61]

The assignments of the absorption bands observed in the electronic spectra of the copper(II) complexes were made with the assumption that the change from N_2SS^* ($[Cu(pyt\text{-}N,S\text{-}im)]^{2+}$) to N_2OS^* ($[Cu(sal\text{-}N,S\text{-}im)]^+$) in the copper donor set does not involve any significant stereochemical change in the copper chromophore. This point can be assessed by examining the ESR spectra of the complexes; the relevant data are collected in Table III. The ESR spectra were recorded in frozen acetonitrile–chloroform (1:1) solution because this mixture gave the best resolution (note that the UV–vis spectra of the complexes recorded in acetonitrile–chloroform solution were identical with those in pure acetonitrile). A typical axial spectrum ($g_\parallel > g_\perp$), indicative of nearly tetragonal stereochemistry, was observed only for $[Cu(N,S\text{-}im)][ClO_4]_2$; this

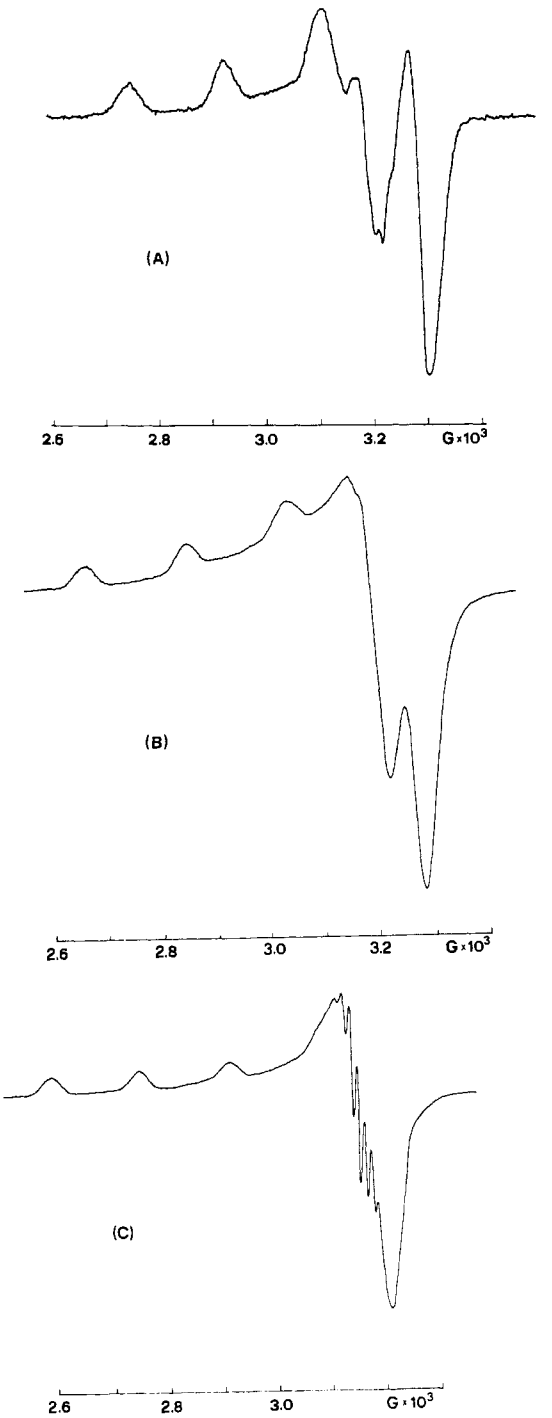

Figure 4. ESR spectra in frozen acetonitrile–chloroform (1:1) solution at −150 °C of (a) $[Cu(pyt\text{-}N,S\text{-}im)][ClO_4]_2$ (ν = 9.080 GHz), (B) $[Cu(sal\text{-}N,S\text{-}im)][ClO_4]$ (ν = 9.069 GHz), and (C) $[Cu(N,S\text{-}im)][ClO_4]_2$ (ν = 9.076 GHz).

spectrum also exhibited a well-resolved superhyperfine splitting pattern on the perpendicular component accounting for coupling to two ligand nitrogen atoms. The ESR spectra of $[Cu(pyt\text{-}N,S\text{-}im)][ClO_4]_2$ and $[Cu(sal\text{-}N,S\text{-}im)][ClO_4]$ have a similar appearance and may actually be rhombic in character (Figure 4). Accurate g values in the perpendicular region can only be obtained with appropriate simulation, though it can be seen by inspection and by comparison with systems that gave similar ESR spectra[8,32] that the eventual distortion from axial symmetry must be relatively small ($g_z > g_x \approx g_y$). Therefore, it is possible to consider an approximate tetragonal site symmetry ($g_z = g_\parallel$, $g_x \approx g_y = g_\perp$)[2c] also for these complexes. The data in Table III show that the $g_\parallel$ values are markedly influenced by the ligand type, while the $A_\parallel$ values

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and their almost identity in the three complexes indicate that a comparable but not strong apical interaction by solvent molecules occurs to these copper(II) centers. The $g_{\parallel}$ value increases significantly on replacement of the thiolate sulfur (CuN_2SS^* core of $[Cu(pyt\text{-}N,S\text{-}im)]^{2+}$) by an oxygen donor ($CuN_2OS^*$ core of $[Cu(sal\text{-}N,S\text{-}im)]^{+}$) in the copper coordination sphere, in spite of a reduction in the formal positive charge of the complex.[66] Moreover, the $g_{\parallel}$ and $A_{\parallel}$ values found here for CuN_2SS^* compare well with the corresponding values reported for the CuN_2S_2 cores of the copper(II) complexes of II ($g_{\parallel} = 2.140$, $A_{\parallel} = 184 \times 10^{-4}$ cm^{-1}; formal charge of the complex 2+)[32] and of the ligands derived from the condensation of ethylenediamine and two molecules of thiosalicylaldehyde ($g_{\parallel} = 2.121$, $A_{\parallel} = 186 \times 10^{-4}$ cm^{-1}; formal charge of the complex 0)[8] or related thiocarbonyl compounds.[9] The decrease in $g_{\parallel}$ and increase in $A_{\parallel}$ values in this series of complexes is in accord with the established trends of covalency.[20,66]

In conclusion, the present investigation has shown that I can provide an useful source of thiolate ligands to form stable copper(II)–thiolate complexes and that, by proper choice of the residue to be conjugated with I, it is possible to obtain ligand systems with donor sets that mimic those found in the blue proteins. The metal complexes of pyt-N,S-im reported here are apparently the first systems containing a N_2SS^* ligand donor set. The spectroscopic properties of the copper(II) complex are substantially determined by the presence of the thiolate sulfur donor, while binding by the other donor atoms can only be inferred by appropriate substitution analogues. Although this pyt-N,S-im ligand cannot provide to the metal a low-symmetry environment such as that of the protein blue sites, it is known from model studies[31,67] that an increase in the size of the fused chelate rings can lead to a significant distortion of the metal geometry. Thus, it is expected that ligand homologues of pyt-N,S-im containing longer carbon chains between the donor atoms will give rise to copper(II) complexes that progressively approach the spectral behavior of the blue sites. The synthesis of such ligand systems is currently under way in this laboratory. Finally, while the attention is usually focused only on the spectral properties of copper(II) model systems, it is important to give parallel development to the characterization of the corresponding copper(I) systems, even though they generally exhibit poor spectral properties. We have shown in this and in previous studies[50,51c] that careful examination of the solution behavior of copper(I) complexes can give useful information about the groups involved in metal binding.

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Registry No. I, 61856-49-3; III, 91002-69-6; [IV][ClO_4] (M = Cu(I)), 91002-60-7; [IV][ClO_4]$_2$ (M = Cu(II)), 91002-62-9; [IV][ClO_4]$_2$ (M = Zn(II)), 91002-64-1; [V][ClO_4], 91002-66-3; [VI][ClO_4]$_2$, 91002-68-5; 4-{[(2-aminoethyl)thio]methyl}-5-methylimidazole, 38585-67-0.

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Contribution from the Departments of Chemistry, The Chung-Cheng Institute of Technology, Taiwan, Republic of China, and The University of Mississippi, University, Mississippi 38677

Lower Valence Fluorides of Chromium. 1. The Hexagonal Bronze Type Phase Rb_xCrF_3

Y. S. HONG,[†] K. N. BAKER,[‡] R. F. WILLIAMSON,[‡] and W. O. J. BOO*[‡]

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Samples of Rb_xCrF_3 having compositions $x = 0.18$, 0.20, 0.225, 0.25, 0.275, and 0.30 were prepared and studied. The hexagonal bronze-like system spans the range $x = 0.18$–0.29. An orthorhombic sublattice ($a \approx 12.7$ Å, $b \approx 7.4$ Å, and $c \approx 7.4$ Å) was identified in every sample. Modulated structures resulting from $^1/_2$-, $^2/_3$-, and $^3/_4$-filled Rb^+ sites have compositions $x = 0.167$, 0.222, and 0.250 and are designated $\alpha(0.167)$, $\alpha(0.222)$, and $\alpha(0.250)$, respectively. The $\alpha(0.167)$ unit cell has the same dimensions as the orthorhombic sublattice, but unlike the sublattice, which is primitive, the superstructure is body centered. The $\alpha(0.222)$ unit cell has the same a and b dimensions as the sublattice, but it is base centered with c(super) = $^3/_2c$(sub). The $\alpha(0.250)$ phase has a primitive unit cell with dimensions a(super) = $2a$(sub), b(super) = $3b$(sub), and c(super) = $2c$(sub). Cooperative Jahn–Teller ordering is associated with $\alpha(0.222)$ and $\alpha(0.250)$, indicating Cr^{2+}–Cr^{3+} ordering (electronic ordering) in those phases. In samples where $x = 0.20$, 0.225, 0.25, and 0.275, $|a|/(3^{1/2}|b|)$ (the distortion ratio) is 0.98, but this ratio approaches unity at the limiting compositions $x = 0.18$ and 0.29. An undistorted hexagonal bronze phase was also observed in samples where $x = 0.20$, 0.225, 0.25, and 0.275. Magnetic interactions in Rb_xCrF_3 are predominantly antiferromagnetic, but Cr^{2+}–Cr^{3+} nearest-neighbor interactions appear to be ferromagnetic. In samples where $x = 0.18$, 0.20, and 0.225, short-range ordering sets in near 125 K. Long-range ordering at all compositions occurs between 35 and 25 K.

Introduction

The fluoride systems A_xVF_3,[1] A_xCrF_3,[2] and A_xFeF_3[3] (where A = K, Rb, or Cs and $x \approx 0.20$–0.30) were originally reported to crystallize in the hexagonal tungsten bronze structure, space group $P6_3/mcm$.[4] The vanadium fluorides (A = K, Rb, Tl, or Cs) were carefully prepared and intensively characterized in our laboratory[5–9] by polarized microscopy, high-precision

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