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Copper(II)–N_2S_2 Complexes of the Imines of 1-Phenyl-3-formyl-2(1*H*)-pyridinethione

LUIGI CASELLA*, MICHELE GULLOTTI and ROBERTO VIGANÒ

Dipartimento di Chimica Inorganica e Metallorganica, Università di Milano, Via Venezian 21, 20133 Milan, Italy

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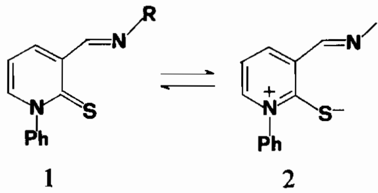
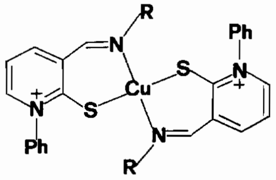
Abstract

Several copper(II) complexes of the imines formed by condensation of 1-phenyl-3-formyl-2(1*H*)-pyridinethione and a primary amine (pyt-R) or a diamine (pyt_2-R′) have been synthesized and characterized. The complexes have a CuN_2S_2 core and the sulfur donors exhibit thiolate character. The complexes of type [Cu(pyt_2-R′)] $[ClO_4]_2$ display optical and ESR spectral behavior that indicates a progressive distortion of the metal coordination geometry from square-planar toward flattened tetrahedral as the carbon chain length of the R′ bridge is varied from two to four atoms. The spectral properties of the complexes of type $[Cu(pyt\text{-}R)_2]$ $[ClO_4]_2$ are more similar to one another and indicate significant distortion of Cu(II) from the planar arrangement.

Introduction

Copper(II)–thiolate interactions have attracted considerable interest for some time because they are responsible for the peculiar spectroscopic properties of a variety of copper proteins containing ‘blue’ sites in their oxidized forms [1]. The synthetic problems that are met in the development of realistic models for these protein sites are associated with the inherent redox instability of the copper(II)–alkanethiolate bonding, with respect to copper(I) and disulfide, particularly for geometrical arrangements of the ligands that tend to favor the copper(I) state [1]. Although in a few instances a limited stability for copper(II)–alkanethiolate systems could be obtained [2–4], the more general approach to the synthesis of redox-stable copper(II)–thiolate complexes involves the use of ligands containing at least a partial double bond character at the donor sulfur [4–14], e.g. using aromatic or heterocyclic thiols. It has been shown recently [14–16] that the imines derived from 1-phenyl-3-formyl-2(1*H*)-pyridinethione (**1**) exist as pyridinium thiolate tautomers (**2**) in their complexes with metal ions and can provide copper(II)–thiolate systems with reasonable stability. In the present investigation we report several copper(II) complexes of type **3** and **4** in which the ligands result from the condensation of 1-phenyl-3-formyl-2(1*H*)-pyridinethione and simple amines, diamines or diamino esters*. One main purpose of this study is to relate





$[Cu(pyt\text{-}R)_2]^{2+}$

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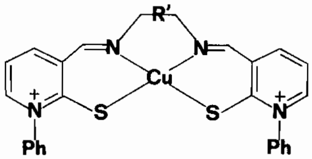

$[Cu(pyt_2\text{-}R')]^{2+}$

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*Author to whom correspondence should be addressed.

*Abbreviations. The symbol pyt-R indicates the Schiff base formed by 1-phenyl-3-formyl-2(1*H*)-pyridinethione and a primary amine. The amine residues R are abbreviated as follows: n-bn = n-butylamine; s-bn = s-butylamine; p-tol = p-toluidine; m-niph = m-nitroaniline. The symbol pyt_2-R′ indicates the ligand bis-imine derived from two molecules of formylpyridinethione and a diamine or a diaminoester. The diamine residues R′ are: en = ethylenediamine; 1,2-diab = phenylenediamine; 1,3-pn = 1,3-propylenediamine; 1,4-bn = 1,4-butanediamine; ornOMe = ornithine methyl ester; lysOEt = lysine ethyl ester.

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TABLE I. Elemental Analyses for the Copper(H) Complexes

Compound	% Calculated			% Found		
	C	H	N	C	H	N
$[\mathrm{Cu(pyt\text{-}n\text{-}bn)_2}][\mathrm{ClO_4}]_2\cdot\mathrm{H_2O}$	46.79	4.42	6.82	46.85	4.42	6.83
$[\mathrm{Cu(pyt\text{-}s\text{-}bn)_2}][\mathrm{ClO_4}]_2$	47.84	4.52	6.97	48.03	4.56	7.09
$[\mathrm{Cu(pyt\text{-}p\text{-}tol)_2}][\mathrm{ClO_4}]_2$	52.38	3.70	6.43	52.11	3.78	6.40
$[\mathrm{Cu(pyt\text{-}m\text{-}niph)_2}][\mathrm{ClO_4}]_2$	46.33	2.80	9.00	45.76	2.77	8.96
$[\mathrm{Cu(pyt_2\text{-}en)}][\mathrm{ClO_4}]_2$	a					
$[\mathrm{Cu(pyt_2\text{-}1,2\text{-}diab)}][\mathrm{ClO_4}]_2\cdot 2\mathrm{H_2O}$	44.97	3.27	6.99	45.33	3.74	6.71
$[\mathrm{Cu(pyt_2\text{-}1,3\text{-}pn)}][\mathrm{ClO_4}]_2$	44.35	3.31	7.66	45.18	3.79	8.03
$[\mathrm{Cu(pyt_2\text{-}1,4\text{-}bn)}][\mathrm{ClO_4}]_2$	45.13	3.51	7.52	45.88	3.67	7.66
$[\mathrm{Cu(pyt_2\text{-}ornOMe)}][\mathrm{ClO_4}]_2$	44.80	3.63	6.97	44.45	3.82	6.65
$[\mathrm{Cu(pyt_2\text{-}lysOEt)}][\mathrm{ClO_4}]_2\cdot 0.5\mathrm{H_2O}$	45.68	3.95	6.66	45.42	4.17	6 55

[a] Ref. 14.

the spectral features of the complexes to the effect of tetrahedral distortion occurring in **3** on increasing the steric bulk of the R groups and in **4** on extending the carbon chain length of the R′ residues.

Experimental

Elemental analyses were performed at the microanalytical laboratory of the University of Milan. Proton NMR spectra were recorded at 80 MHz on a Bruker WP-80 FT-spectrometer. Infrared spectra were recorded on a Nicolet MX-1E FT-IR instrument. Electronic spectra were recorded on Perkin-Elmer Lambda-5 and Beckman DK-2A spectrophotometers. Electron spin resonance spectra were obtained at X-band frequencies on a Varian E-109 instrument. 1-Phenyl-3-formyl-2(1*H*)-pyridinethione [17] and ornithine methyl ester dihydrochloride [18] were prepared according to published procedures. The complex $[\mathrm{Cu(pyt_2\text{-}en)}][\mathrm{ClO_4}]_2$ has already been reported recently [14].

Preparation of the Complexes

Since the Schiff bases pyt-R or pyt$_2$-R′ are formed readily on simply warming ethanol solutions of 1-phenyl-3-formyl-2(1*H*)-pyridinethione and the amine or the diamine, in the appropriate stoichiometric ratio, the ligands were not routinely isolated. The copper(II) complexes were prepared on a millimolar scale by adding an alcoholic solution of copper(II) perchlorate hexahydrate to the ethanol solution of the ligand at room temperature. The precipitate thus formed was collected by filtration, washed with small amounts of ethanol and dried under vacuum. To obtain the complexes $[\mathrm{Cu(pyt_2\text{-}ornOMe)}][\mathrm{ClO_4}]_2$ and $[\mathrm{Cu(pyt_2\text{-}lysOEt)}][\mathrm{ClO_4}]_2$ the diamino ester was previously freed from its dihydrochloride salt by treatment with the stoichiometric amount of methanolic ~1 N sodium hydroxide in ethanol–dichloromethane (1:2), and filtration of the precipitate of sodium chloride. The elemental analyses of the complexes are reported in Table I.

Results and Discussion

The condensation of 1-phenyl-3-formyl-2(1*H*)-pyridinethione with primary amines occurs easily and leads to the corresponding imines. We have isolated a few of these compounds and all show typical ν(C=N) absorptions in the IR spectra at 1630–1640 cm^{-1}, imine proton signals at $\delta \sim 9$ in the ^{1}H NMR spectra and low-energy absorption bands near 320 ($\epsilon \sim 12\,000$ M^{-1} cm^{-1}) and 405 nm ($\epsilon \sim 4000$) in the UV–Vis spectra. The electronic band near 405 nm is associated with the pyridinethione tautomer **1** and is replaced by a band at higher energy when the imines bind to a metal ion, since binding of these ligands occurs through the pyridinium thiolate tautomeric form **2** [15]. This was confirmed here by preparing *in situ* the zinc(II) complex of the ligand pyt-n-bn; its electronic spectrum shows two low-energy bands near 320 and 360 nm.

The copper(II) complexes that we were able to isolate in reasonably pure form are given in Table I. Actually we carried out preparations of complexes of type **3** and **4** with many other amines containing bulky R groups and diamines with longer R′ carbon chains but obtained impure materials. Often the dark green or blue solutions resulting from the addition of the Cu(II) salt to the ligand solutions turned rapidly brown, even at low temperature or operating under inert atmosphere, before we were able to isolate the complexes. Using the ligand pyt-t-bn, derived from t-butylamine, an instantaneous reduction of Cu(II) occurred, with no transient green or blue color, and a brown diamagnetic material was obtained. Although we were unable to obtain

TABLE II. Electronic Spectra of the Copper(II) Complexes in Acetonitrile Solution

Compound	λ_{max} (nm) (ϵ(M^{-1} cm^{-1}))^a				
[Cu(pyt-n-bn)$_2$][ClO$_4$]$_2$	323	380sh		600sh	
[Cu(pyt-s-bn)$_2$][ClO$_4$]$_2$	328	380sh		620sh	
[Cu(pyt-p-tol)$_2$][ClO$_4$]$_2$	323	375	450sh	625	750sh
	(22000)	(15700)	(3500)	(1500)	(300)
[Cu(pyt-m-niph)$_2$][ClO$_4$]$_2$	325	375	465sh	645	800sh
	(21000)	(12500)	(5000)	(1000)	(200)
[Cu(pyt$_2$-en)][ClO$_4$]$_2$	315	364	400sh	510	670sh
	(11000)	(15000)	(8500)	(550	(100)
	320sh				
	(10500)				
[Cu(pyt$_2$-1,2-diab)][ClO$_4$]$_2$	292	372	440sh	550sh	700sh
	(17000)	(12000)	(1500)	(350)	(130)
	319				
	(15000)				
[Cu(pyt$_2$-1,3-pn)][ClO$_4$]$_2$	320	375br^b		540	750sh
	(12000)	(11500)		(650)	(80)
[Cu(pyt$_2$-1,4-bn)][ClO$_4$]$_2$	328	370	450sh	575	800sh
	(15200)	(17500)	(4200)	(1500)	(120)
[Cu(pyt$_2$-ornOMe)][ClO$_4$]$_2$	325	380	440sh	600sh	800sh
[Cu(pyt$_2$-lysOEt)][ClO$_4$]$_2$	323	375		650sh	

^{a}Shoulder = sh. ^{b}Broad maximum = br.

pure complexes of the type [Cu(pyt$_2$-R')]$^{2+}$ with aliphatic diamines with carbon chains longer than four atoms, we succeeded in isolating the complex [Cu(pyt$_2$-lysOEt)]$^{2+}$, where the chain between the two nitrogen atoms is of five atoms, probably because of its lower solubility in the reaction medium. Interestingly repeated preparations of both the complexes derived from the chiral diamino esters gave analytically pure but completely optically inactive materials. This facile racemization of imines of amino acid esters coordinated to metal ions has already been found to occur in several systems and results from a ready proton exchange at the α-carbon atom of the amino acid residue [19].

The electronic spectral data of the complexes are summarized in Table II. In general, solutions of these copper(II) complexes exhibit redox instability with respect to copper(I), as indicated for instance by the progressive decrease in intensity of the Cu(II) visible bands on aging of the solutions. This effect is very pronounced for the complexes of type [Cu(pyt-R)$_2$]$^{2+}$ derived from aliphatic amines and for those of type [Cu(pyt$_2$-R')]$^{2+}$ derived from the diamino esters. In all these cases nearly complete Cu(II) reduction in solution occurs within times of the order of a few minutes and it has been impossible to record accurate spectra for these systems at room temperature.

The near-UV portions of the electronic spectra of the complexes display an intraligand band near 320 nm that remains completely unaffected by reduction of Cu(II) on aging of the solutions. At lower energies the spectra are dominated by intense bands in the range 360–380 nm, with more or less defined shoulders at 400–465 nm. Weaker bands or shoulders occur at 510–650 and 670–800 nm. The latter bands are quite certainly associated with d–d transitions, since their intensity is very low. The bands at 360–380 nm contain contributions by various transitions: low-energy $\pi \rightarrow \pi^*$ transitions of the conjugated imine chromophores and possibly, other intraligand transitions [15], and charge transfer transitions from the sulfur donors [15] and the imine nitrogen donors to Cu(II) [20]. The bands at 400–465 and 510–650 nm may also be due to S → Cu(II) LMCT but, as for the component at 360–380 nm, their exact assignment is uncertain, since they are likely to originate from different combinations of σ- and π-type sulfur orbitals [21–23]. The positions of all the visible bands shift to lower energy on increasing the extent of distortion of the copper(II) chromophore from the square-planar arrangement to a flattened tetrahedral stereochemistry. This effect can be followed clearly in the series of complexes [Cu(pyt$_2$-R')]$^{2+}$ with R' = en, 1,3-pn and 1,4-bn, where the increase of tetrahedral distortion follows the length of the carbon chain of the diamine residue. For the complexes of type [Cu(pyt-R)$_2$]$^{2+}$ the extent of such distortion must be significant even with R = n-alkyl, apparently because of some severe steric interactions between adjacent R and phenyl groups in 3 when the Cu(II) site is planar. The intense bands at 360–380 nm appear very little affected by changes in Cu(II) geometry, even though

TABLE III. ESR Parameters Obtained from Frozen-solution Spectra at −140 °C

Compound	Solvent[a]	$g_{\parallel}$	$\lvert A_{\parallel}\rvert \times 10^{-4}$ (cm^{-1})
[Cu(pyt-n-bn)$_2$] [ClO$_4$]$_2$	AC	2.158	162
[Cu(pyt-s-bn)$_2$] [ClO$_4$]$_2$	DM	2.168	160
[Cu(pyt-p-tol)$_2$] [ClO$_4$]$_2$	AC	2.147	150
[Cu(pyt-m-niph)$_2$] [ClO$_4$]$_2$	AC	2.151	145
[Cu(pyt$_2$-en)] [ClO$_4$]$_2$	AC	2.136	182
[Cu(pyt$_2$-1,2-diab)] [ClO$_4$]$_2$	AN/T	2.165	169
[Cu(pyt$_2$-1,3-pn)] [ClO$_4$]$_2$	AN/T	2.149	176
[Cu(pyt$_2$-1,4-bn)] [ClO$_4$]$_2$	AC	2.154	160
[Cu(pyt$_2$-ornOMe)] [ClO$_4$]$_2$	AN/T	2.215[b]	150[b]
[Cu(pyt$_2$-lysOEt)] [ClO$_4$]$_2$		[c]	[c]

[a]Acetone = AC, dichloromethane = DM, acetonitrile = AN, toluene = T. [b]Major species. [c]Mixture of species.

they contain contributions from S → Cu(II) LMCT. However it is difficult to predict to what extent and in which direction the intraligand transitions occurring at these energies are affected by the changes in metal geometry.

The ESR parameters obtained from frozen-solution spectra are given in Table III. The data refer to the solvent mixtures that gave better revolved spectra but, in general, we found little solvent dependence for the ESR parameters. The anisotropic spectra display the usual shape for copper(II) complexes with $d_{x^2-y^2}$ ground state; the rather low $g_{\parallel}$ values are typical for Cu(II) chromophores containing sulfur ligands [5–12, 24]. Although the metal coordination geometry in the frozen-solution phase may not be strictly related to that present in fluid solution at room temperature, the trends in the $g_{\parallel}$ and $A_{\parallel}$ values parallel the variation observed in the optical spectra. Thus, for instance, $g_{\parallel}$ increases and $A_{\parallel}$ decreases with increasing carbon chain length in the series [Cu(pyt$_2$-R')]$^{2+}$ with R' = en, 1,3-pn and 1,4-bn. The ESR spectra confirm that for the copper(II) centers of the complexes [Cu(pyt-R)$_2$]$^{2+}$ the degree of tetrahedral distortion must be significant. Therefore the higher redox stability of these complexes when R is an aromatic residue than for R = alkyl is apparently due to the extended conjugation occurring in the ligands. For the complexes derived from the diamino esters we observed ESR features related to different species; in the case of the derivative of lysine it was impossible to detect a single major species.

In conclusion we have synthesized and characterized members of two series of CuN$_2$S$_2$ complexes containing copper(II)–thiolate ligation. While the spectroscopic properties of the complexes of type [Cu(pyt-R)$_2$]$^{2+}$ display modest variation on changing the nature of the R substituents, implying rather similar structures for the copper(II) centers, the trends observed in the optical and ESR spectra of the complexes of type [Cu(pyt$_2$-R')]$^{2+}$ are consistent with progressive tetrahedral distortion at the Cu(II) sites on extending the carbon chain length of the R' bridge. Similar trends have been established, on a wider basis, for different series of CuN$_2$O$_2$ and CuN$_4$ chromophores [24–27], but so far only a single homologous series of copper(II)–thiolate complexes where distortion of a CuN$_2$S$_2$ core was systematically varied has appeared [7]. In the complexes investigated by Bereman [7] the source of thiolate sulfur was a dithiocarboxylate group and increasing tetrahedral distortion at Cu(II) was achieved, as it was done here, by extending the carbon chain length of a diamine residue from en to 1,4-bn. A comparison of the spectral data for complexes containing the same diamine residue indicates that the ligands employed by Bereman can induce a slightly higher degree of tetrahedral distortion at Cu(II) than the present bis(imines) of pyridinethione. This can be inferred, for instance, from the values of the empirical index $g_{\parallel}/A_{\parallel}$ [28]. For the complexes of type [Cu(pyt-R)$_2$]$^{2+}$ with R = aryl such distortion at Cu(II) becomes comparable with that of the dithiocarboxylato complex containing a tetramethylene bridge. However, in general the spectroscopic properties of both series of complexes are still rather far from those of the protein 'blue' sites.

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