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Synthesis, Spectroscopic and Magnetic Properties of Copper Complexes with a Ligand containing the Pyridoxal Moiety

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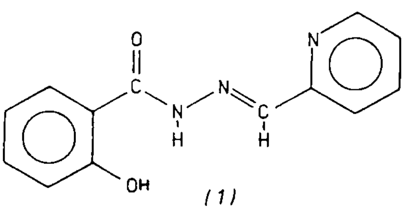
Summary

Seven new copper(II)pyridoxal salicyloylhydrazone complexes have been prepared and characterized by vibrational and electronic spectra and magnetic measurements. The u.v. absorption band maxima are compared with those of metal chelates of Schiff bases obtained from condensation of pyridoxal with amines or amino acids.

Introduction

The biological activity of the pyridoxal moiety in several enzymatic reactions is well known(1–4) and justifies the considerable interest in metal chelates of Schiff bases obtained from condensation of pyridoxal with amines or aminoacids(5–12).

Recently, we have been interested in the ligand behaviour of pyridoxal aroylhydrazones(13) in some tin(IV) and organotin(IV) compounds and, as part of an investigation of metal complexes containing such ligands, we report the synthesis and the characterization of a number of pyridoxal salicyloylhydrazone copper(II) derivatives. This study is a part of a more general research program on the chelating properties of aromatic aldehyde aroylhydrazones in which metal complexes of the organic ligands(14–17) HSIPOX, (*1*) and (*2*), have been prepared and characterized by spectroscopic and x-ray techniques. In HSIPOX, the pyridoxal moiety confers coordination properties upon the ligand similar to those of complexes investigated as models for several enzymatic processes.



(*1*)

A recent x-ray structural analysis, of Cu(SIPOX)Cl · H_2O, has shown that the deprotonated form of HSIPOX acts as a terdentate ligand(18) as illustrated in the (*3*).

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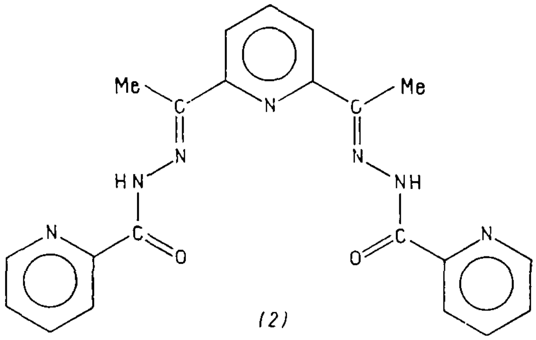

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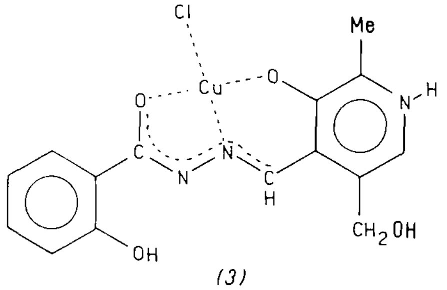

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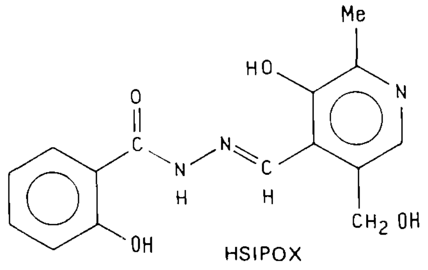


HSIPOX

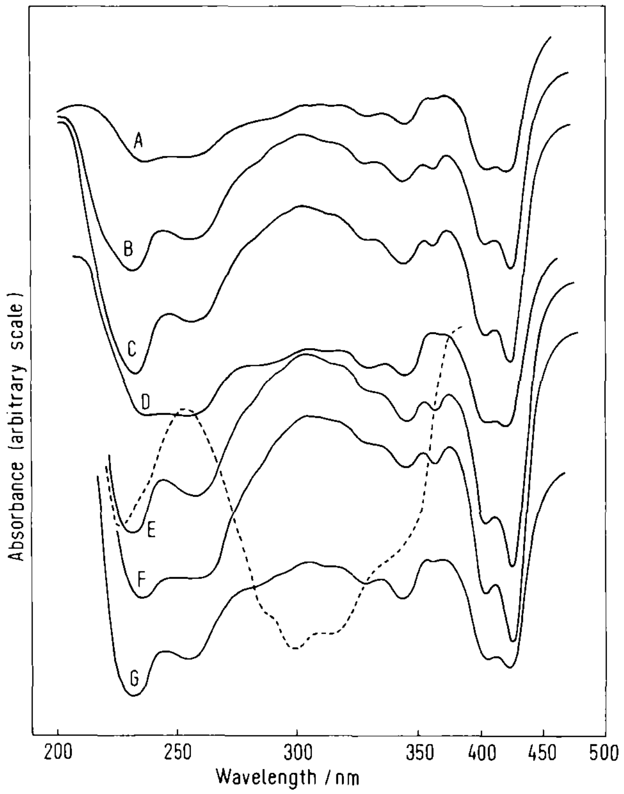
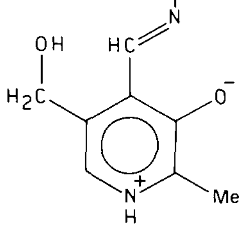


Figure 1. Electronic spectra of HSIPOX (– – – – – – –); A, Cu(SIPOX)Cl · H_2O; B, Cu(SIPOX)Br · H_2O; C, Cu(SIPOX)I · H_2O; D, Cu(SIPOX)ClO_4 · 3 H_2O; E, Cu(SIPOX)NO_3 · H_2O; F, $Cu_2(SIPOX)_2SO_4$ · 2 H_2O and G, Cu(SIPOX)SCN · 3 H_2O.

Results and Discussion

The stoichiometric formulae of the complexes isolated are listed in Table 1 together with the corresponding analytical data, colours, magnetic properties and visible absorption band maxima. In all the compounds the metal : ligand ratio is 1 : 1. The HSIPOX molecule is in its deprotonated form and one or more water molecules are present.

Figure 1 shows the electronic absorption bands of the complexes and the free ligand in the 190–450 nm region (methanol or ethanol solution). The free ligand spectrum is well characterized by two multiple bands, the first of which shows an absorption maximum at 227 nm with a shoulder at 235 nm, the second is maximal at 298 nm with shoulders at 288, 313 and 338 nm. In both bands the two absorptions, characteristic of the *ortho*-disubstituted benzene ring, are present. The other four absorptions are assignable to the system formed by the pyridoxal moiety and the hydrazidic nitrogen chain which can exist in two tautomeric forms, (*4*) and (*5*):



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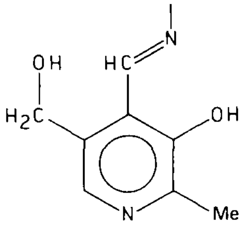


(5)

Table 1. Analytical data, colours, magnetic data and visible absorption maxima of the copper complexes

Formula	Found (Calcd.)% C	H	N	Cu	Colour	$10^6\chi'_m$ (c.g.s.u.)	μ_{eff} (B.M.)	λ_{max} (nm)
Cu(SIPOX)Cl · H_2O	43.35 (43.2)	3.7 (3.9)	10.1 (10.1)	15.1 (15.2)	brown	1.231	1.72	720[a]
Cu(SIPOX)Br · H_2O	38.8 (39.0)	3.3 (3.5)	9.4 (9.1)	14.0 (13.8)	brown green	1.393	1.83	650[b]
Cu(SIPOX)I · H_2O	35.05 (35.4)	3.3 (3.2)	8.6 (8.3)	12.6 (12.5)	brown green	1.424	1.85	645[b]
Cu(SIPOX)ClO_4 · 3 H_2O	35.2 (34.8)	3.7 (3.9)	8.5 (8.1)	12.2 (12.3)	brown green	1.470	1.88	650[a]
Cu(SIPOX)NO_3 · H_2O	40.8 (40.6)	4.0 (3.6)	12.6 (12.6)	14.6 (14.3)	green	1.852	2.11	655[a]
$Cu_2(SIPOX)_2SO_4$ · 2 H_2O	41.65 (41.9)	4.1 (3.75)	9.7 (9.8)	15.1 (14.8)	green	2.106	2.25	640[a]
Cu(SIPOX)SCN · 3 H_2O	40.6 (40.4)	4.4 (4.2)	12.0 (11.8)	13.7 (13.7)	pale green	1.232	1.72	650[b]

[a] EtOH; [b] MeOH.

A similar situation has been found in several pyridoxal-aminoacid systems for which the four electronic absorptions are attributed to π–π^* transitions(4, 7).

The electronic spectra of all the complexes in the u.v. region are quite similar and, from the comparison with the free ligand spectrum, the following observations can be made: *a.* the two multiple bands are red shifted with corresponding absorption values at *ca.* 233, 256 nm and 312, 338, 343 and 365 nm respectively; *b.* the intensity of the second band is considerably decreased with respect to that of the first; *c.* at 405 and 425 nm two new intense absorptions appear which can be attributed to a M → L charge-transfer as well as to electronic transitions in the pyridoxal system containing the pyridine nitrogen, protonated at the expense of the phenolic oxygen atom. This dipolar form, which is frequently found in solution for similar systems(6, 8), has been confirmed also in the solid state for Cu(SIPOX)Cl · H_2O by a recent x-ray structural analysis(18). Both *a* and *b* are a consequence of the deprotonation of the CONH group and of the metal coordination effect.

With the exception only of Cu(SIPOX)Cl · H_2O, the complexes exhibit in the visible region a large absorption maximum at *ca.* 650 nm (Table 1), whose position suggests probable pentacoordination for copper(19, 20). The 720 nm band for Cu(SIPOX)Cl · H_2O is consistent with a distorted square planar coordination previously established by x-ray analysis.

Like the electronic spectra, the vibrational spectra of all the complexes are very similar, the only differences concerning the absorptions of the anionic groups (Table 2). In these spectra, the disappearance of ν(NH), as a consequence of the ligand deprotonation, is not well evident since the stretching vibrations of the OH groups fall in the same region. The vibrational absorptions of the phenolic and alcoholic hydroxyl groups are difficult to assign, even if it seems more correct to assign the broad band at *ca.* 2600 cm^{-1} to the OH stretching of the salicyloyl moiety, which is probably involved in an intramolecular hydrogen bond, as already found in Cu(SIPOX)Cl · H_2O(18) and in similar systems(15,21). The contribution of the stretching vibration of the NH bond of the pyridine nitrogen is probably present in the same band.

The negative shift of the 'amide I' band [mainly due to ν(CO)] and the positive shift of the 'amide II' and 'amide III' bands [mainly due to ν(CN) and to δ(NH)] commonly indicate that –C(O)NH-group coordinates to metals through oxygen(22, 23). In the present copper complexes, both 'amide I' and 'amide II' bands shift to lower frequencies (the 'amide III' band assignment is difficult owing to the complicated nature of the ligand). The decrease of the 'amide II' band, in apparent contrast with the coordination through the oxygen, is a consequence of the coupling of the amide bands with those of the azomethine groups, whose N-atom seems to be coordinating, as has already found for other similar systems(13, 24).

Nitrate, perchlorate and sulphate groups are ionic in the corresponding complexes, while ν_1 (2105s cm^{-1}) and ν_3(775w cm^{-1}) values of the thiocyanate group suggest a probable bridging behaviour for this anion in Cu(SIPOX)SCN(14, 25).

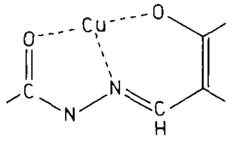
The magnetic measurements, carried out at 25° using the Gouy balance method, corrected by Pascal's constants(26) reveal the complexes to be paramagnetic with μ_{BM} values (Table 1) in agreement with those usually reported for magnetically dilute copper(II) chelates.

The i.r. spectral data together with the stoichiometry of these chelates are in agreement with structure (*6*) for all the

Table 2. Selected i.r. bands (cm^{-1}) and relative assignments

Group	HSIPOX	A	B	C	D	E	F	G
OH		3440m	3435m	3420br	3440br	3420br	3480br	3440br
NH	3350s							
OH	3130w		3240m 3120sh	3240m 3120sh	3280sh	3260m	3280br	
CH	3050w	3050w	3080m	3080m	3080sh	3080w	3060w	3080w
CH	2930w	2920w	2920w	2920m	2920w	2920w	2920w	2920m
OH + NH⁺	2800br	2600br	2600br	2700br	2600br	2700br	2700br	
amide I	1650vs	1660s						
ring	1600m	1625vs	1613s	1610s	1620s,br	1618s,br	1620s,br	1620s,br
ring	1580sh	1590s	1585s	1580s	1593vs	1585s	1593vs	1590s
ring	1570sh	1575sh	1560sh	1575sh	1575sh	1575sh	1575sh	
ring	1560sh	1560sh	1550sh		1570sh	1567sh	1565sh	1530sh
amide II	1550vs							
CN		1510s	1500vs	1500vs	1510vs	1505s	1505vs	1505vs
ring	1480w	1490sh	1475sh	1475sh	1495sh	1480m	1490sh	1485sh
ring	1468sh	1470sh	1450w	1470sh	1465w	1440sh	1455sh	1455w
ring	1452m	1430m	1435w	1450sh	1445w			1440w
ring	1420w	1415vs	1410w	1435w	1425w		1410w	1430w
OH	1380m	1385vs	1370vs	1370vs	1380vs		1380vs	1380vs
NN	1040m							
anion					1140sh 1120sh 1105sh 1085vs 623s	1380vs 823m	1145sh 1110vs 1090sh 615s	2105s 775w

A = Cu(SIPOX)Cl.H_2O; B = Cu(SIPOX)Br · H_2O; C = Cu(SIPOX)I · H_2O; D = Cu(SIPOX)ClO_4 · 3 H_2O; E = Cu(SIPOX)NO_3 · H_2O; F = $Cu_2(SIPOX)_2SO_4$ · 2 H_2O; G = Cu(SIPOX)SCN · 3 H_2O.



(6)

compounds, where the hydrazone molecule acts as a deprotonated terdentate ligand. These results are confirmed by the spectral similarities all complexes show with Cu(SIPOX)Cl · H_2O for which the x-ray analysis has established a terdentate chelating behaviour.

Experimental

The total copper was determined by atomic absorption spectrometry using a Perkin-Elmer Model 303 spectrophotometer.

The C, H and N analyses were made with Perkin-Elmer Model 240 automated equipment The magnetic susceptibilities, at 25°, were measured with a Gouy balance (Newport Instruments). The i.r. spectra were recorded on a Perkin-Elmer spectrophotometer model 457 using the KBr disc technique. Electronic spectra were recorded in solution on a Perkin-Elmer spectrophotometer Mod. 402.

Preparation of the ligand

Salicyloylhydrazide (1 mol) and neutral pyridoxal (1 mol) were dissolved in absolute EtOH and heated to reflux with stirring for *ca.* 30 min. After cooling, a yellow microcrystalline product was obtained, which was filtered and washed with small portions of cold ether. The product melts at *ca.* 250° (dec.).

Preparation of the complexes

The complexes were, in general, prepared by mixing the required amounts of the inorganic salt and HSIPOX in boiling EtOH and, when possible, the products were allowed to crystallize. The iodide and thiocyanate complexes were precipitated by adding, at room temperature, KI and KSCN to the EtOH solutions of the copper chloride complex. In some cases, the reaction of the copper salt with the ligand gives also small amounts of a not-well-defined powder as a byproduct which probably differs from the main product containing the 1 : 1 copper : ligand ratio.

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