

Complexes of Copper(II) with Substituted Benzylideneamines

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Abstract

The synthesis and identification of copper(II) complexes with *N*-phenyl- (PBI), *N*-(1-phenylmethyl)- (PMBI) and *N*-(1-phenylmethoxy)-benzoyl-benzylideneamine (PXBI) are described. These monoamine ligands present the possibility of coordinating to the metal atom either through the oxygen or through the nitrogen atom, or of acting as bidentate chelating agents. The compounds were assigned as CuL_2Cl_2 for the chloro complexes based upon analytical data and molar conductivity measurements. The preparation of Cu(II) complexes using $\text{Cu}(\text{ClO}_4)_2$ and $\text{Cu}(\text{NO}_3)_2$ was not possible.

Attempts have been made to assign their probable structure on the basis of absorption and reflectance spectra, IR spectra, magnetic data and electron paramagnetic resonance. In the resulting compounds two ligands that act as unidentate via their nitrogen atom, and two chlorines are bound to the Cu(II) centre. All compounds appear to be monomeric.

Introduction

The coordination behaviour of benzylideneamines has been the subject of great attention over the past years. Benzylideneamines afford many kinds of complexes with the five-membered ring structure. These organometallic intramolecular coordination compounds are, in a general sense, those which have at least one M—C bond and at least one group forming an intramolecular coordination bond [1–5].

On the other hand, these monoamine ligands present great interest because of their possibility of coordinating to the metal atom either through the oxygen atom or through the imine nitrogen atom, or of acting as bidentate chelating agents.

Following our current studies with coordination behaviour of *N*-substituted benzoyl-benzylideneamine derivatives [6], we now report the preparation and characterization of complexes with Cu(II). Complexes with Cu(II) chloride have been obtained and are assigned the formulae $\text{Cu}(\text{PBI})_2\text{Cl}_2$, Cu

$(\text{PMBI})_2\text{Cl}_2$ and $\text{Cu}(\text{PXBI})_2\text{Cl}_2$ (where PBI = *N*-phenyl-, PMBI = *N*-(1-phenylmethyl-, and PXBI = *N*-(1-phenylmethoxy-benzoyl-benzylideneamine).

However, the preparation of copper(II) complexes using $\text{Cu}(\text{ClO}_4)_2$ or $\text{Cu}(\text{NO}_3)_2$ as starting materials was not possible. This is probably due to the fact that these organic ligands act as monodentate ligands coordinating to the copper atom through the imine nitrogen atom (as indicated in the IR discussion) which makes the existence of four ligand molecules around the Cu(II) ion impossible because of steric hindrance.

Experimental

Solvents of commercial quality were purified and dried by standard methods. Copper(II) chloride (Probus) was dried by the standard method. The ligands PBI, PMBI and PXBI were kindly supplied by Drs J. Plumet and R. Alvarez-Osorio of the Universidad Complutense de Madrid.

All preparations and sampling were made in a dry-box, which was continuously flushed with dry nitrogen.

The complexes were prepared by dropwise addition of a solution of the appropriate ligand in the minimum volume of dry 1,2-dichloroethane to a suspension of the copper(II) chloride in dry 1,2-dichloroethane, under continuous stirring, using 2:1 ligand-to-copper(II) molar ratios. The mixture was stirred overnight, the precipitate was filtered off, washed several times with dry 1,2-dichloroethane and dried *in vacuo* at room temperature.

Chemical analyses were carried out using standard methods.

The IR spectra were recorded in Nujol mulls in the range 4000–200 cm^{-1} with a Perkin-Elmer 325 instrument. The solid reflectances of finely powdered complexes were recorded on a Beckman DK-2 spectrophotometer. The spectra of 10^{-3} M solutions of each of the complexes in acetonitrile were also recorded at room temperature on Carl Zeiss UV and Visible Specord. The conductivity measurements were carried out with a Metrohm Herisau, model E-512, at 20 °C for 10^{-3} M solutions in acetonitrile.

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TABLE I. Analytical and Other Data of the Prepared Compounds

Compound	Colour	C (%)	N (%)	H (%)	Ω (cm ² mol ⁻¹) ^b
Cu(PBI) ₂ Cl ₂	pale brown	66.64(68.18) ^a	3.80(3.98)	4.31(4.26)	28
Cu(PMBI) ₂ Cl ₂	yellow	69.02(68.74)	3.98(3.81)	4.68(4.63)	25
Cu(BXBI) ₂ Cl ₂	orange	66.34(65.86)	3.01(3.65)	4.45(4.44)	26

^aTheoretical percentage is given in brackets.^bMolar conductivity in 10⁻³ M solution of acetonitrile at 25 °C.

The EPR spectra were recorded on a Varian E12 spectrometer provided with a 100 KHz field modulation. The g factor was obtained by means of eqn. (1) where the magnetic field H (in gauss) at the sample was obtained with a gaussmeter. The microwave frequency ν (in MHz) was measured with a high precision frequency meter.

$$g = 0.714484\nu/H \quad (1)$$

All spectra were recorded on very finely ground powders enclosed in commercially available quartz sample tubes. The magnetic measurements of finely powdered complexes were carried out with a BE-15 Bruker balance.

Results and Discussion

The solids prepared in this study along with their colours, partial elemental analyses, and molar conductivities of solutions in acetonitrile are shown in Table I.

The conductivity measurements in 10⁻³ M acetonitrile solution indicate that the complexes are nonelectrolytes. The molar conductivity values are higher than expected for nonelectrolytes but lower than expected for univalent electrolytes. Although the compounds are nonionic, due to solvation there is some increase in the conductivity values [7].

The temperature dependence of the magnetic susceptibility was studied in the temperature range 77–300 K. It was found that the magnetic moments of the complexes are in the range 1.80–2.00 BM (1.83, 1.91, 1.87 BM) corresponding to one unpaired electron and are in agreement with the general range for Cu(II) complexes [8].

Assignments of the important IR bands which aid in the understanding of the bonding of the complexes are presented in Table II. Only those bands which are diagnostic for the nature of the Cu(II) ligand bonding are included. The IR spectra of the free ligands exhibit bands in the region *ca.* 1675–1660, 1625–1615 cm⁻¹, which are assigned to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$, respectively [9, 10].

These ligands are capable of acting as O,N-bidentate, O-monodentate or N-monodentate.

The results of our IR study show that the bands assigned to the $\nu(\text{C}=\text{O})$ stretching frequencies remain

TABLE II. IR Spectral Assignments (cm⁻¹) of Cu(II) Complexes

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{Cu}-\text{Cl})$	$\nu(\text{Cu}-\text{N})$
PBI	1664vs	1620s		
Cu(PBI) ₂ Cl ₂	1670vs	1613s	290vs	328s
PMBI	1660vs	1615s		
Cu(PMBI) ₂ Cl ₂	1672vs	1610s	292vs	328s
PXBI	1669vs	1624s		
Cu(PXBI) ₂ Cl ₂	1669vs	1615s	292vs	328s

almost unchanged or are shifted to slightly higher frequencies in the metal ion complexes compared to the free ligand. On the other hand there are negative shifts in the $\nu(\text{C}=\text{N})$ stretching frequency, strongly suggesting coordination through the amine nitrogen to the Cu(II) ion, and that there is no coordination through the oxygen of the C=O group.

In the 200–400 cm⁻¹ region of the spectrum there are two bands present for all the complexes. We have assigned the lower energy band, in the region 290–292 cm⁻¹, as terminal coordinated chloride ions [11, 12]. This also is in good agreement with the ranges 285–310 cm⁻¹ reported by Sharpe *et al.* [13].

The absence of one band in the 225–215 cm⁻¹ region suggests that the complexes are monomeric, in agreement with the magnetic moments.

The higher energy band in the 200–400 cm⁻¹ region of the spectrum of each of the compounds is assigned as having substantial $\nu(\text{Cu}-\text{N})$ character. This band is observed at *ca.* 328 cm⁻¹ in the spectra of the compounds. This assignment of $\nu(\text{Cu}-\text{N})$ in Table II is consistent with the values assigned for the analogous bands in the Cu(II) complexes [14], while other authors have reported $\nu(\text{Cu}-\text{N})$ for amines at 324 and 361 cm⁻¹ [15, 16].

The results of the electronic spectral measurements recorded in the solid state and 10⁻³ M acetonitrile solutions are presented in Table III.

The solution spectra are different from the solid state spectra, suggesting that the solution spectra do not represent the isolated complexes. The d–d transitions are shifted significantly in acetonitrile solution, indicating changes may be occurring in the coordination sphere of the complexes. However,

TABLE III. Charge-transfer Bands (CT) and d-d Electronic Transitions (cm^{-1}) for the Copper(II) Complexes

Compound	Solid state		10^{-3} M CH_3CN	
	CT	d-d	CT	d-d
$\text{Cu}(\text{PBI})_2\text{Cl}_2$	20000sh	15300b	30300m 20730sh	16700m
$\text{Cu}(\text{PMBI})_2\text{Cl}_2$		15870m 12500sh 11360w	29000m 22200sh	11900b
$\text{Cu}(\text{PXBI})_2\text{Cl}_2$		15620m 12260sh 10900sh	28990m 20050sh	12190b

there is little change in the position of the charge transfer bands.

All of the complexes possess a band at *ca.* 37 000 cm^{-1} ; this band is always observable in the ligand, assignable to the $\pi \rightarrow \pi^*$ transition. We have omitted the intraligand bands from Table III since they do not provide much information about the bonding in metal ion complexes. There are also bands between 30 000–28 000 cm^{-1} in the spectra of each of the complexes which are assignable to ligand-to-Cu(II) charge-transfer bands. An additional band lower in energy than *ca.* 25 000 cm^{-1} is assignable to chloro-to-copper(II) charge-transfer bands and helps to confirm coordination to the Cu(II) centre. The yellow and orange colours are due to these charge-transfer bands at 20 000, 22 200 and 25 050 cm^{-1} for the $\text{Cu}(\text{PBI})_2\text{Cl}_2$, $\text{Cu}(\text{PMBI})_2\text{Cl}_2$ and $\text{Cu}(\text{PXBI})_2\text{Cl}_2$ complexes, respectively.

All the complexes contain the copper(II) ion in an essentially tetragonal environment with the ligands coordinating to form an approximately square-planar structure. The electronic spectra in the visible region show bands in the region around 15 000 cm^{-1} . These absorption maxima are consistent with other Cu(II) complexes with diamine ligands with approximately planar structure [17]. The energy level diagram for ligand fields of D_{4h} symmetry would predict three transitions from the ground state: ${}^2\text{A}_{1g} \leftarrow {}^2\text{B}_{1g}(\nu_1)$, ${}^2\text{B}_{2g} \leftarrow {}^2\text{B}_{1g}(\nu_2)$ and ${}^2\text{E}_g \leftarrow {}^2\text{B}_{1g}(\nu_3)$ [18]. The complexes with a single broad band at *ca.* 15 300 cm^{-1} , probably contain more than one transition under their envelope. The electronic spectra of the $\text{Cu}(\text{PMBI})_2\text{Cl}_2$ and $\text{Cu}(\text{PXBI})_2\text{Cl}_2$ complexes with d-d bands at 12 000 and 10 900 cm^{-1} indicate considerable deviation from planarity for these complexes.

To obtain further information about the structure of the present compounds we recorded the paramagnetic resonance spectra of the solid powdered compounds. The spectrum of $\text{Cu}(\text{PBI})_2\text{Cl}_2$ consists of a rather asymmetrical band, characteristic for large

line widths with respect to the value of A and the difference between g_{\perp} and g_{\parallel} . The only parameter that can be calculated from these spectra is g_{max} measured at the point with a derivative value of zero ($g_{\perp} = 2.033$). The spectrum of $\text{Cu}(\text{PXBI})_2\text{Cl}_2$ is characteristic of compounds having axial symmetry and consists of a two g -value signal, with g_{\parallel} not split into hyperfine components ($g_{\perp} = 2.048$ and $g_{\parallel} = 2.101$) [19, 20]. The spectrum of $\text{Cu}(\text{PMBI})_2\text{Cl}_2$ presents three weak rhombic components and probably arises from distortion in the xy plane [21].

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