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An FT-IR and XPS Study of Copper(II)–Diazine Polymers

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Abstract

Solid copper(II) complexes have been obtained following reaction of copper chloride with pyridazine (pdz) and pyrimidine (pym) ligands. Elemental analyses, diffuse reflectance Fourier-Transform and X-ray photoelectron spectral data recorded from these compounds are consistent with polymeric structures of the general formulae $Cu(pdz)Cl_2$ and $Cu(pym)Cl_2$. X-ray photoelectron data also indicates that the surface composition of each of these complexes closely resembles that of the bulk material.

Introduction

The nature of chemical bonding in metal complexes containing heterocyclic ligands is of fundamental scientific importance and relates to several industrial applications. For instance, azoles have been extensively used to model chemical bonding in peptides [1] and as corrosion inhibitors for metal and alloy surfaces [2–6]. Several experimental techniques, including infrared spectroscopy [3], X-ray photoelectron spectroscopy [5] and ellipsometry [6], have been employed to study the nature of the passivating film on copper.

Studies of copper–azole coordination chemistry, however, have been hampered by the fact that many of these complexes are insoluble and form powders that are not suitable for single-crystal X-ray diffraction analysis. Recently, we have been able to study the surface and bulk composition of a series of copper(II) complexes with imidazole and benzimidazole ligands using diffuse reflectance Fourier-Transform spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) [7]. In this paper we report the results of a related spectroscopic investigation of copper complexes formed with the diazine ligands pyrimidine (pym) and pyridazine (pdz).

Experimental

Materials

Anhydrous $CuCl_2$, pyrimidine (pym) and pyridazine (pdz) were all obtained in high grade purity from Aldrich Chemical Co. and used without further purification. Ethanol was dried and stored over potassium carbonate.

Preparation of Complexes

All compounds were synthesized in solution at ambient temperature. The solid products were purified by repeated ethanol washings and subsequently vacuum dried at 60 °C for a minimum of 12 h.

Cu(pdz)Cl₂

A solution of cupric chloride (0.460 g, 3.4 mmol) in ethanol (50 ml) was added to a solution of pyridazine (0.3043 g, 3.8 mmol) in ethanol (20 ml). A green complex precipitated immediately. Unreacted pyridazine and cupric chloride were removed by repeated ethanol washes. The compound was vacuum filtered and then dried *in vacuo* at 60 °C overnight. Yield 85%; melting point (m.p.) = 248–250 °C.

Cu(pym)Cl₂

A solution of cupric chloride (0.2541 g, 1.9 mmol) in ethanol (60 ml) was added to a solution of pyrimidine (0.3027 g, 3.8 mmol) in ethanol (20 ml). A green complex precipitated immediately. Unreacted pyrimidine and cupric chloride were removed by repeated ethanol washes. The compound was vacuum filtered and then dried *in vacuo* at 60 °C overnight. Yield 82%; m.p. = 200 °C (dec).

The compounds were analyzed for Cu by iodometric determination [8] and analyses for carbon, hydrogen, and nitrogen were determined via combustion techniques performed by Desert Analytics, Inc. of Tucson, Ariz.

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TABLE I. Elemental Analyses and Colors of Copper(II)–Diazine Compounds

Compound	Cu (%)		C (%)		H (%)		N (%)		Color
	calc.	found	calc.	found	calc.	found	calc.	found	
$Cu(pdz)Cl_2$	29.6	29.4	22.4	22.9	1.9	2.1	13.1	13.1	green
$Cu(pym)Cl_2$	29.6	29.3	22.4	22.2	1.9	1.7	13.1	13.3	green

Physical Measurements

All infrared spectra were recorded on a Nicolet 20SXC Fourier-Transform Infrared Spectrophotometer. The spectra from the free ligands were recorded from the neat liquids using a Spectra-Tech cylindrical internal reflectance accessory and the solid spectra were recorded from samples as finely ground powders with a Spectra-Tech diffuse-reflectance attachment. Although the instrumental resolution is specified as 0.05 cm^{-1}, in practice, spectral resolution was limited by the particle size of these solids and the reported band maxima are considered accurate to 1 cm^{-1}. Diffuse reflectance infrared spectra were analyzed using the Kubelka–Munk theory (see eqn. (1)).

$$f(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S} \qquad (1)$$

In eqn. (1) R is the measured reflectance, and K and S are the absorption and scattering constants, respectively [9]. The conversion to Kubelka–Munk units was carried out with the Nicolet SX FT-IR software system V4.0.

Samples for XPS analysis were prepared as powders that were spread over indium foil and the specta were obtained on a XSAM-800 Kratos system. Photoelectrons from the Cu(2p), C(1s), N(1s) and Cl(2p) core levels were excited using Al Kα (1486.6 eV) or Mg Kα (1253.6 eV) radiation and collected using a hemispherical analyzer equipped with a multichannel detector. The overall energy resolution was estimated to be 0.9 eV from the Ag ($3d_{5/2}$) emission line. Effects of sample charging were determined from shifts in the C–H contribution to the C(1s) XPS band; these shifts were typically 2–4 eV and did not significantly affect the Cu(2p) lineshape. The XPS lineshapes were deconvoluted using a least-squares fitting technique that employs Gaussian functions; the fitting parameters were kept free for each of the core levels, except for the Cl(2p) lineshape where the branching ratio was fixed at $2p_{3/2}/2p_{1/2} = 2$. The probe depth of XPS measurement in these experiments is of the order of 10–50 Å. .

Results and Discussion

Synthesis

Identical copper–diazine products were obtained with the general formula $CuLCl_2$ (L = pdz and pym) following synthesis of metal:ligand ratios in the 1:1 to 1:6 range. Synthesis with less than a 1:1 metal: ligand ratio resulted in unreacted $CuCl_2$ remaining in the reaction vessel. The synthesized compounds and their elemental analyses (Cu, C, H, N) are presented in Table I.

FT-IR Spectra

Fourier-Transform infrared (FT-IR) spectra were obtained in the absorbance mode for the free pdz and pym ligands, and in the diffuse reflectance mode for the $Cu(pdz)Cl_2$ and $Cu(pym)Cl_2$ product compounds. These spectra were each recorded between 4000–550 cm^{-1} and are depicted in Figs. 1 and 2. A summary of FT-IR data obtained from both the free ligands and the metal complexes is listed in Table II. For each Cu–diazine compound the reported infrared bands correspond to the vibrational modes of the complexed ligand; the spectral assignments are based on a force constant analysis performed on the free ligands [10].

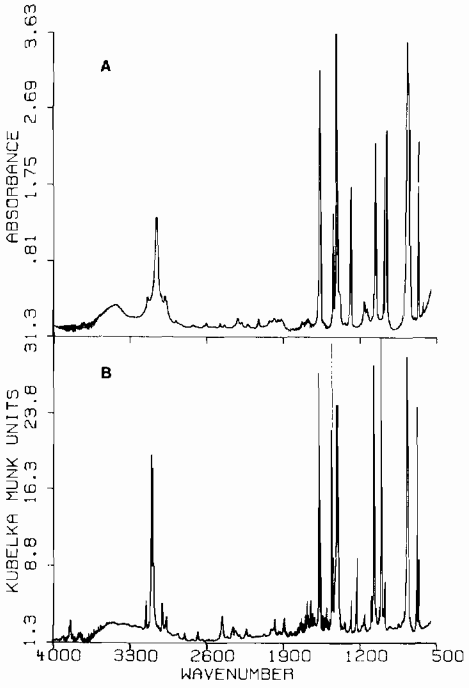


Fig. 1. Fourier-Transform infrared spectra in the 4000–550 cm^{-1} region of (A) free pyridazine (pdz) ligand (absorbance spectrum) and (B) $Cu(pdz)Cl_2$ complex (diffuse reflectance spectrum).

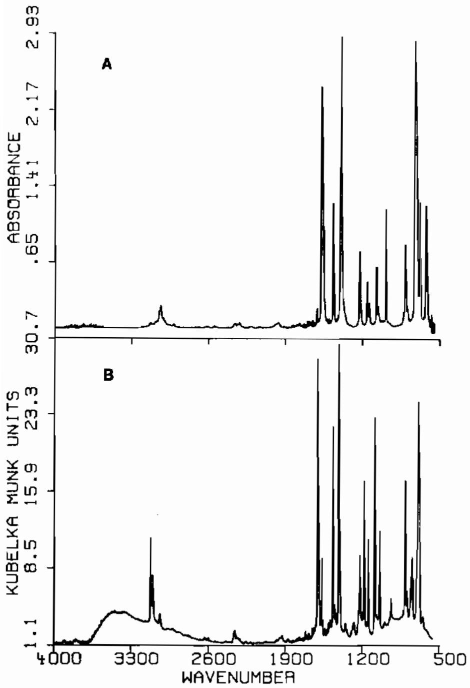


Fig. 2. Fourier-Transform infrared spectra in the 4000–550 cm^{-1} region of (A) free pyrimidine (pym) ligand (absorbance spectrum) and (B) Cu(pym)Cl$_2$ complex (diffuse reflectance spectrum).

XPS Spectra

The XPS binding energies obtained from the Cu(2p), C(1s), N(1s) and Cl(2p$_{3/2}$) core levels of the diazine complexes are listed in Table III. Also included are the determined Cl/Cu, N/Cu and C/N relative atomic ratios. The errors associated with these ratios are dependent on several parameters and are estimated here to be ±20% [11]. Nonetheless, within these errors the XPS data indicates that the surface composition is identical to that of the bulk material.

The Cl(2p) lineshapes were fitted to two Gaussian functions separated by 0.5 eV, with a peak ratio of 1:2, indicating that the Cl atoms in each complex are in only one bonding configuration. Moreover, the Cu(2p) lineshapes exhibit shakeup satellites (see Fig. 3) characteristic of Cu(+2) emission lines and the XPS data indicates that only paramagnetic Cu(+2) ions are present in these compounds.

The binding energy of Cu(2p$_{3/2}$) in the Cu(pym)Cl$_2$ complex is higher than that in the Cu(pdz)Cl$_2$ complex. This increase in binding energy indicates that the ionicity of the Cu atom is increased in Cu(pym)Cl$_2$ compared to the Cu(pdz)Cl$_2$ complex. This observation can be attributed to the electronic differences between the two ligands. In addition, the C(1s) and N(1s) XPS signals obtained from Cu(pym)-

TABLE II. FT-IR Spectra of Pyridazine (pdz) and Pyrimidine (pym) Ligands and the Copper(II)–Diazine Complexes[a]

pdz	Cu(pdz)Cl$_2$	Assignments	pym	Cu(pym)Cl$_2$	Assignments
	3155(w)		3129(w)	3123(s)	$A_1 \times A_1 = A_1$
3138(w)		$A_1 \times A_1 = A_1$		3110(w, sh)	
	3107(s)			3102(m)	
	3092(s)		3048(m)		A_1
3058(s)		A_1, B_1	3037(m)	3036(w)	
	3008(w)		3017(w)		
2980(w)	2968(w)	$A_1 \times A_1 = A_1$	3005(w)		A_1
2877(w)			2918(w)		A_1
	2801(w)		1967(w)		$B_2 \times B_2 = A_1$
2722(w)		$A_1 \times A_1 = A_1$	1712(m)		
	2680(w)			1604(s)	
2600(w)		$A_1 \times B_1 = B_1$		1576(w)	
2473(w)	2460(w)		1564(s)	1569(s)	A_1
	2452(w, sh)			1559(w)	
2312(w)		$B_1 \times B_1 = A_1$	1465(s)		B_1
2275(w)				1447(w)	
	2237(w)			1410(s)	
2218(w)		$A_1 \times A_1 = A_1$	1397(s)		A_1
2124(w)		$A_1 \times A_1 = A_1$		1351(w)	
	1978(w)			1274(w)	
	1890(w)			1220(s)	
1725(w)		$A_1 \times B_2 = B_2$	1225(s)		A_1
1667(w)	1684(w)			1184(s)	
	1653(w)		1158(m)		B_2
	1576(s)		1145(s)		
1566(s)	1560(m)	A_1, B_1	1138(m)		A_1

(continued)

TABLE II. *(continued)*

pdz	$Cu(pdz)Cl_2$	Assignments	pym	$Cu(pym)Cl_2$	Assignments
	1506(w)		1085(s)		
	1458(s)			1078(w, sh)	
1443(s)	1430(m, sh)	B_1	1070(s)		B_1
	1424(s, sh)		1054(w)		A_1, $B_2 \times B_2 = A_1$
1412(s)	1419(s, sh)	A_1		1042(s)	
	1408(s)		990(s)		A_1
1386(sh)		$A_1 \times B_2 = B_2$		936(w)	
	1339(w)		810(s)	807(s)	B_2
1281(s)	1280(m)	B_1	793(w)	792(w)	$A_1 \times B_2 = B_2$
	1231(s)			745(m)	
1159(w)	1155(w)	A_1	717(s)	719(s)	B_2
1131(w)		B_1		687(s)	
	1096(w)		677(s)	678(s)	A_1
	1074(s)			668(w, sh)	
1062(s)	1066(s)	A_1			
1049(w, sh)		$A_1 \times B_2 = B_2$			
	1010(s)				
986(w)					
962(s)	974(m)	A_1			
760(s)	772(s)	B_2			
	743(w, sh)				
696(w)	680(s)	$A_1 \times B_2 = B_2$			
	668(w)				
665(s)	662(m)	B_1			
623(w)		$B_1 \times A_2 = B_2$			

[a] All data are in cm^{-1}; FT-IR absorption data were recorded from the free ligands as neat liquids; diffuse reflectance FT-IR data were recorded from the $CuLCl_2$ complexes as powders. Band intensities: s = strong, m = medium, w = weak, sh = shoulder.

TABLE III. Binding Energies and Relative Atomic Ratios for Cu(2p), Cl(2p), C(1s) and N(1s) Core Levels of the Copper(II)–Diazine Complexes[a]

Complex	Binding energy (eV)				Atomic ratio		
	Cu(2p)	C(1s)	N(1s)	Cl(2p)	Cl/Cu	N/Cu	C/N
$Cu(pdz)Cl_2$	935.0	285.0	400.2	197.9	2.1	2.1	2.1
$Cu(pym)Cl_2$	935.4	285.0	400.7	197.5	2.2	2.2	1.9

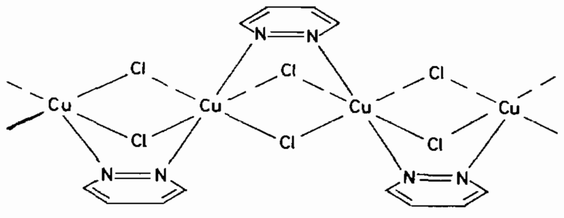
[a] Experimental uncertainties are ±0.1 eV and ±20%, respectively.

Cl_2 exhibit broader lineshapes than those obtained from $Cu(pdz)Cl_2$. This broadening could be related to differences either in the electronic characteristics of the ligands or the coordination geometries of the two complexes. Unfortunately, we were not able to obtain XPS spectra from the pure ligands to further explore this question as the diazine ligands were unstable at room temperature under ultra high vacuum conditions.

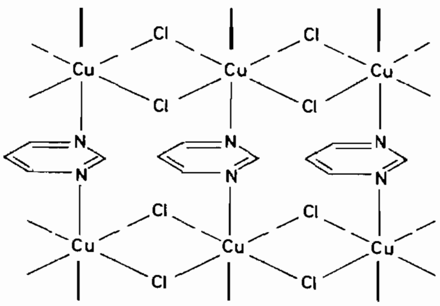
Bonding Models

The elemental analysis, FT-IR and XPS data obtained from these complexes indicate that the Cu(II)–diazine compounds are formed as polymeric materials. The following intra-chain and inter-chain polymeric models are proposed for these complexes.

Related structures have been proposed in our earlier study of a series of Cu(II)–azole (azole = imidazole and benzimidazole) polymers [7]. Although there are some similarities in bonding characteristics, the XPS data obtained for these $Cu(pdz)Cl_2$ and $Cu(pym)Cl_2$ complexes indicate that there is significantly higher covalency in the Cu–N linkages of the diazine polymers compared to the azole compounds, as evidenced by their pronounced Cu(2p) shakeup components. Additionally, the XPS data illustrate the absence of any surface fragmentation or reconstruction in these $Cu(pdz)Cl_2$ and $Cu(pym)Cl_2$ polymer materials.



$Cu(pdz)Cl_2$



$Cu(pym)Cl_2$

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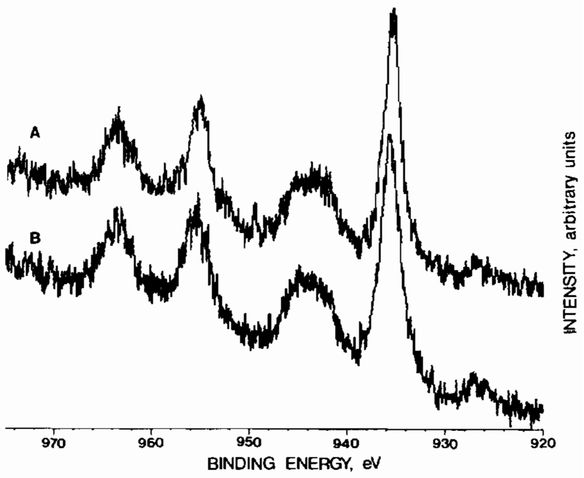

Fig. 3. Cu(2p) emission lines observed from XPS spectra of (A) $Cu(pdz)Cl_2$ and (B) $Cu(pym)Cl_2$ complexes.

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