Note

Formation of an anchored copper(II) complex on a thiourea-functionalized silica gel by *in situ* modification of the tethered ligating function

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Abstract

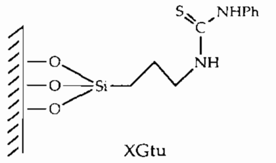
Copper(II) chloride reacts with a double-thiourea ligand tethered on a silica xerogel through a reduction–oxidation process. XPS data suggest that the main products are copper(I) chloride supported on the matrix and a tethered copper(II) compound containing a heterocyclic ligand derived from the double thiourea by oxidative mono-desulfurization. The presence of this anchored complex is also substantiated by ESR measurements.

Key words: Copper complexes; Anchored complexes; Thiourea-functionalized xerogels

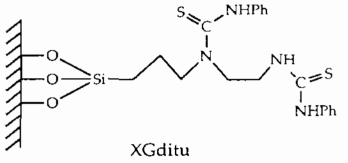
Introduction

Thiourea and its substitution derivatives represent a well-known class of sulfur ligands extensively studied by many researchers in the last decades [1]. In addition, thiourea ligands are of interest in catalysis owing to the specific catalytic properties of the thiourea/PdX_2 complexes, which were found efficient in catalyzing carbonylation of alkynes [2] and in inducing ring closure processes of diynes [3].

Recently, we started to study the reactivity of N,N′-disubstituted thioureas towards metal species, in order to obtain easy-to-study molecular models for certain surface complexes anchored on new thiourea-functionalized silica xerogels, namely XGtu and XGditu, derived from $(EtO)_3Si(CH_2)_3NHC(S)NHPh$ and $(MeO)_3Si(CH_2)_3N\{C(S)NHPh\}(CH_2)_2NHC(S)NHPh$, respectively, by hydrolysis and co-condensation with $Si(OEt)_4$.



XGtu



XGditu

These functionalized polysiloxanes, which belong to the family of inorganic–organic hybrid sol–gel materials [4], are able to bind palladium(II) and metal carbonyl species. In the case of the system Pd/XGtu, treatment with dihydrogen affords supported colloidal metal particles with selective hydrogenating activity [5]. Moreover, $Ru_3(CO)_{12}$ reacts with both xerogels, giving tethered metal carbonyl clusters whose structures have been recognized by comparing their IR spectra with those of the corresponding clusters obtained from the non-siloxanized thioureas PrNHC(S)NHPh (tu) and $PhNHC(S)N(Et)(CH_2)_2NHC(S)NHPh$ (ditu) [6, 7].

Continuing these investigations on the interactions between thiourea-functionalized xerogels and metals useful in catalysis, we decided that it would be of interest to study the reactivity of XGditu and of its model molecule ditu towards copper salts, in particular $CuCl_2$.

Results and discussion

The reaction between the double thiourea ditu and copper(II) chloride takes place in ethanol at room temperature, as shown below, giving [Cu(ditu)Cl] as a yellowish white powder and red crystals of the complex $[CuCl_2\{(C_7H_4NS)N(CH_2)_2N(Et)C{=}NPh\}]$ (hereafter $[Cu(ditu^*)Cl_2]$). Its molecular structure, fully elucidated by a previous X-ray study [8] (Scheme I of Fig. 1), shows an unexpected N,N-bidentate heterocyclic ligand (ditu*) derived from oxidative mono-desulfurization of ditu followed by cyclization [8].

$$3CuCl_2 + 3ditu \xrightarrow[\text{r.t.}]{\text{EtOH}}$$
$$2[Cu(ditu)Cl] + [Cu(ditu^*)Cl_2] + S + 2HCl + 2[H]$$

$\mathrm{ditu = Ph{-}NH{-}C({=}S){-}N(Et){-}(CH_2)_2{-}NH{-}C({=}S){-}NH{-}Ph}$
$\mathrm{ditu^* = Ph{-}N{=}\overline{C{-}N(Et){-}(CH_2)_2{-}N}{-}Bt}$ (Bt = benzothiazolyl)

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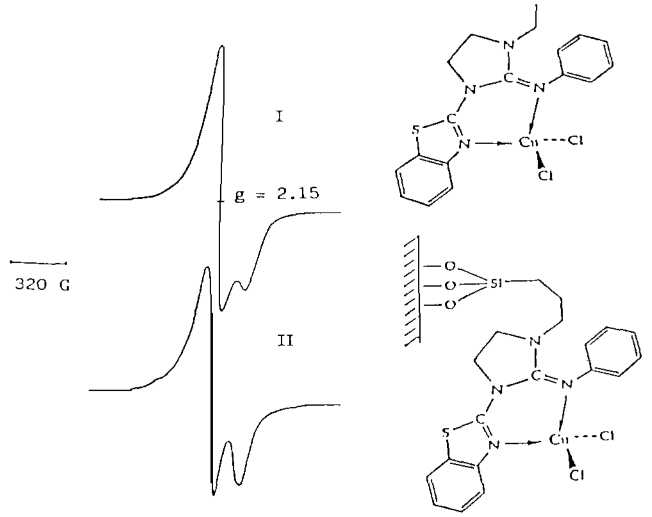

Fig. 1. Comparison between (I) the powder ESR spectrum of Cu(ditu*)Cl$_2$, diluted (4%) with silica gel, and (II) that of the system Cu/XGditu obtained from XGditu by treatment with CuCl$_2$; both recorded at room temperature.

It is well known that the reactions of thiourea and substituted thioureas with copper(II) are, in fact, redox processes, giving rise to different copper(I) complexes [9]. Moreover, in the present process the double thiourea ditu plays an unprecedent triple role, acting as reductant for copper(II) and as complexing agent for copper(I) and for copper(II), through its oxidation derivative labelled as ditu*. As regards the copper(I) complex [Cu(ditu)Cl], its insolubility in the common organic solvents suggests a polymeric nature probably favoured by the expected bridging behaviour of the dithiourea ligand. Coordination through sulfur is indicated by the small but significant shifts of the thiourea bands in the IR spectrum.

In the light of these results we have reacted CuCl$_2$ with the dithiourea-functionalized xerogel XGditu (S% 1.4) derived from $(MeO)_3Si(CH_2)_3N\{C(S)NHPh\}$-$(CH_2)_2NHC(S)NHPh$ by hydrolysis and co-condensation with $(EtO)_4Si$ [7]. Under the same experimental conditions adopted in the case of the reaction with ditu, the suspended xerogel is able to bind copper (Cu/S atomic ratio 0.4, from XPS data), turning pale pink in colour (the Cu(II)–ditu* complex, described before, is red), and is easily filtered, washed and dried without loss of metal. The IR spectrum of this material (Cu/XGditu) is lacking in information; it appears practically identical to that of unreacted XGditu. This is not surprising, as the spectrum is dominated by the absorption bands due to the O–H and Si–O groups and the peaks attributable to the ligand functionalities are very weak in these diluted systems. Only in the case of metal carbonyl complexes do their spectra give valuable data [5–7], owing to the presence of the strong CO stretching bands. Nevertheless, complexation of the thiourea groups should produce slight shifts of the relevant, even weak, bands as observed for the model compound [Cu(ditu)Cl]. However, in the present case, a careful examination of the spectrum reveals, in addition to the bands due to the uncomplexed dithiourea function, the presence of a pair of very weak extra peaks at 1471 and 1430 cm^{-1} that could account for the formation of a new anchored species similar to the Cu(II)–ditu* complex.

In this regard, the ESR spectrum of this system evidenced the presence of at least one anchored copper(II) compound. In particular, as shown in Fig. 1, the ESR pattern is strictly comparable with that found for [Cu(ditu*)Cl$_2$], mechanically diluted with silica gel (4% in weight) in order to obtain almost the same copper(II) concentration of Cu/XGditu (0.5% from XPS). This substantial matching of the two spectra strongly suggests the presence of an anchored copper(II) complex of the same nature of [Cu(ditu*)Cl$_2$], or, in other words, that the tethered dithiourea function of XGditu has partly undergone the same oxidation process observed for the ligand ditu.

Further evidence and more details come from XPS investigations carried out in parallel on ditu and its complexes and on XGditu before and after copper chemisorption. The relevant data are quoted in Table 1; Figure 2 shows the Cu2p$_{3/2}$ peak for the three copper-containing materials. As regards ditu and XGditu, the close proximity of corresponding N1s and S2p binding energy (*b.e.*) values confirms the near equivalency of ligand functionalities for both species. In the present experimental conditions N1s and S2p are found as single peaks in both cases as well as in the complex [Cu(ditu)Cl]. On the contrary, the value of N1s full width at half peak maximum (FWHM) found in [Cu(ditu*)Cl$_2$], much larger than in ditu, clearly suggests the presence of two components which can be assigned to the two diazolidine nitrogens (399.5 eV) and to the

TABLE 1. XPS data: binding energies (eV), modified Auger parameter values α' (eV) and Cu/S atomic ratio[a]

Compound	Cu2p	N1s	S2p	α'	Cu/S(total)
ditu		399.8	162.0		
XGditu		399.8	162.4		
[Cu(ditu)Cl]	932.2	400.1	163.5	1847.2	0.5
[Cu(ditu*)Cl$_2$]	933.8	399.5	164.9	1848.2	1.2
		400.8			
Cu/XGditu	932.7	399.6	161.9		0.22 Cu(I)
	934.4	401.0	164.8		0.18 Cu(II)
			169.0		

[a] Experimental errors on binding energies ±0.2 eV, on the atomic ratio ±10–20%.

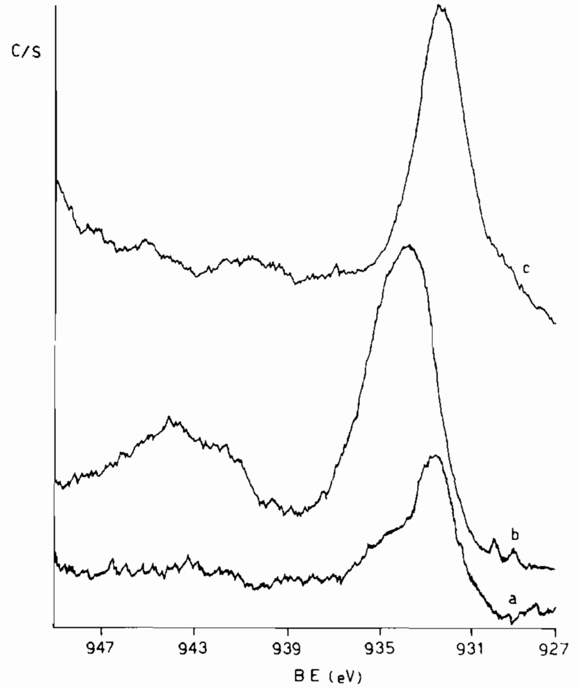

Fig. 2. Cu2p$_{3/2}$XPS peak for: (a) Cu/XGditu; (b) Cu(ditu*)Cl$_2$; (c) Cu(ditu)Cl.

two coordinated imino nitrogens (400.8 eV), on the basis of previous literature reports on related systems [10]. The S2p *b.e.* value is typical for a thioether sulfur atom in the case of [Cu(ditu*)Cl$_2$], while it can be confidently assigned to coordinated C=S groups in [Cu(ditu)Cl]. Cu2p$_{3/2}$ *b.e.* and FWHM, together with the presence of shake-up satellites, which generally accompany main Cu2p ionization peak in Cu(II) species, assign [Cu(ditu*)Cl$_2$] to a Cu(II) complex, whereas [Cu(ditu)Cl] shows a Cu2p spectrum typical for Cu(I) complexes. This is confirmed also by the corresponding values of α' (the modified Auger parameter), differing by 1 eV.

The system Cu/XGditu presents a complex XPS spectrum which supports the formation of the heterocyclic ligand ditu* tethered to the surface of the functionalized silica gel. In particular, the S2p spectrum shows the presence of the thioether group (164.8 eV), along with the uncomplexed thiourea function (161.9 eV) and sulfate sulfur (169.0 eV; it probably derives from the oxidation of elemental sulfur finely dispersed on the xerogel surface). It is worth noting that the residual thiourea function, evidenced also by IR spectroscopy, appears protected or at least not available for the oxidative attack by the copper(II) ions present in excess. The N1s spectrum exhibits two broad peaks compatible with the different functionalities (tethered ditu and ditu*) present on the surface. Finally, the Cu2p spectrum can be assigned to a mixture of Cu(I) and Cu(II) species in a 1.2:1 ratio. The Cu(II) peak at 934.4 eV (although slightly shifted from the value of [Cu(ditu*)Cl$_2$], probably because of matrix effects) is necessarily assigned to the tethered Cu–ditu* complex depicted in Fig. 1 (Scheme II), which is the only Cu(II) complex revealed by ESR, whereas that at 932.7 eV is to be assigned to the simple salt CuCl supported on the gel surface, as there is no detectable evidence of complexed thiourea sulfurs in the S2p spectrum. Actually, the formation of an anchored thiourea complex similar to [Cu(ditu)Cl] could be inhibited by the low density of available thiourea functions on the gel surface, whose presence is substantiated by the IR and XPS spectra, as discussed above.

Experimental

Materials

The organic reagents and copper(II) chloride were pure commercial products. The solvents were reagent grade and, when necessary, were dried and distilled by standard techniques before use. All manipulations concerning siloxanized reagents (prior to the sol–gel process) were carried out under dry nitrogen by means of standard Schlenk-tube techniques. The dithiourea ligand ditu [8] and the corresponding xerogel XGditu (S content 1.4%) [7] were synthesized by the methods previously described.

Measurements

Elemental analyses were performed with a Carlo Erba automated analyzer (C, H, N, S). IR spectra were obtained on a Nicolet 5PC FT spectrometer. ESR spectra were recorded at room temperature on a Varian E9 spectrometer, equipped with a cylindrical cavity modulated at 100 kHz. The frequency was measured with a frequency meter XL microwave and the magnetic field was tested with a DTM 141 digital teslameter. XPS experimental measurements were taken on a VG ESCA-3 photoelectron spectrometer equipped with Al Kα and Mg Kα sources. All measurements were performed on thin layers of powder samples, pressed on stainless steel tips. All binding energies (*b.e.*) of supported samples were referenced to the Si2p *b.e.* from the support, taken at 103.5 eV. In the case of free ligands, the C1s *b.e.* from vacuum pumps oil residues was assigned a value of 285.0 eV, and taken as reference. Cu complexes, particularly Cu(II) ones, are known to be sensitive to reduction reactions, under X-ray irradiation. All Cu2p *b.e.* values come from initially recorded spectra, within 5 min from sample exposure to X-rays. This procedure was found to give a fair reproducibility of experimental results.

Reaction of ditu with $CuCl_2$

An ethanol solution (30 ml) of copper(II) chloride (0.24 g, 1.8 mmol) was added to an ethanol solution (20 ml) of ditu (0.64 g) in 1:1 molar ratio, at room temperature. Immediately a yellowish white substance precipitated, which was filtered, washed with ethanol, and ether and dried *in vacuo*. The filtrate produced red crystals of [Cu(ditu*)Cl_2] (yield ~25%). It has already been characterized [8]; main IR bands: 1641vs, 1475vs, 1429vs cm^{-1}. The powder ESR spectrum of Fig. 1 (I) was obtained from a mechanical mixture of [Cu(ditu*)Cl_2] (4%; 0.55% Cu) and silica gel, accurately grinded in order to reach the best dispersion. The pure powder of the complex gave a broader isotropic peak. The precipitate, further washed with chloroform, was recognized as [Cu(ditu)Cl]. Yield ~55%. *Anal.* Calc. for $CuClC_{18}H_{22}N_4S_2$: C, 47.3; H, 4.8; N, 12.2; S, 14.0. Found: C, 46.5; H, 4.5; N, 11.8; S, 14.6%. IR (KBr): 1598ms, 1540vs, 1496ms, 1362m, 1243mw, 708s cm^{-1}; IR of ditu for comparison: 1596ms, 1558s, 1553s, 1495vs, 1359vs, 1315ms, 1249ms, 710s cm^{-1}. The XPS data are given in Table 1.

Reaction of XGditu with $CuCl_2$

The functionalized xerogel XGditu (1 g), suspended in ethanol (30 ml), was added with a large molar excess (with respect to sulfur) of copper(II) chloride (0.3 g) dissolved in the same solvent (30 ml). The mixture was stirred at room temperature. After 1 h it was filtered and the pale pink solid was washed with ethanol and ether and dried *in vacuo*. IR (KBr): 1471vw, 1430vw cm^{-1}, in addition to the bands due to XGditu: 3440vs,br, 1645mw, 1599w, 1547w, 1497w, 1355w, 1077vs,br cm^{-1}. The XPS data are given in Table 1; the ESR spectrum is shown in Fig. 1 (II).

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