An X-Ray Photoelectron Spectroscopic Study of 2-Mercaptobenzothiazole Metal Complexes

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(Received March 1, 1979)

The X-ray photoelectronic spectra of 2-mercaptobenzothiazole (LH) and its metal complexes have been measured. On the basis of the chemical shifts of the N(1s), S(2p), and Cu($2p_{3/2}$) electron binding energies, the coordination mode of the ligand and the oxidation state of the copper atom have been examined. It is suggested that, in HgL_2, PbL_2, AgL, and CuL_3H_2Cl complexes, the ligand is solely coordinated through the exocyclic sulfur atom, and that, in CuL, CuL_2, PtL_2, PdL_2, NiL_2, and CdL_2 complexes, the ligand is coordinated through both the exocyclic sulfur and nitrogen atoms. In CuL_2 and CuL_3H_2Cl, it was found that the copper was present in a (+1) oxidation state, and that part of the ligand molecules, bis(benzothiazol-2-yl) disulfide, resulted from oxidation of LH by the Cu^{2+} ion on complex formation.

The use of 2-mercaptobenzothiazole as an analytical reagent has been known for a long time,[1-3] and the structures of its complexes with several metal ions have been investigated using a variety of physical techniques.[4-9]

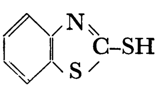
In the copper complex prepared from the reaction of 2-mercaptobenzothiazole with copper(II) chloride, the copper has been reported to be in a (+2) oxidation state, in spite of its diamagnetism.[7,9] Clear evidence for this assignment has however not been given. Furthermore, it is well known that sulfur-containing ligands often reduce the Cu(II) ion to Cu(I) on complex formation.[10]

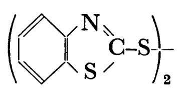
X-Ray photoelectron spectroscopy (XPS) is sensitive to charge distribution and is suitable for the detection of protonated atoms and the oxidation state.[11]

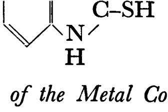
The purpose of the present study is to confirm the oxidation state of copper in complexes with 2-mercaptobenzothiazole, and to examine the mode of coordination of the ligand in several metal complexes.

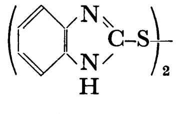
Experimental

Chemicals. 2-Mercaptobenzothiazole, the sodium salt, and 2-mercaptobenzimidazole (abbreviated as LH, LNa, and L′H, respectively) were obtained commercially and were of analytical grade. They were used after recrystallization from ethanol. Bis(benzothiazol-2-yl) and bis(benzimidazol-2-yl) disulfides (abbreviated as L–L and L′–L′) were obtained by standard methods: the oxidation of LH and L′H in ethanol by H_2O_2 and I_2, respectively. L′H and L′–L′ were used as reference compounds. All the copper salts used were analytical reagents. All ligands and metal complexes were analysed elementally.

LH: 

L–L: 

L′H: 

L′–L′: 

Preparation of the Metal Complexes. *CuL*: Method (a) (according to the literature). An ethanol solution of LH was added to an aqueous solution of copper(I) chloride saturated with KCl[3] which gave an orange yellow precipitate. Found: C, 36.86; H, 1.71; N, 6.09; S, 27.47; Cu, 27.50%. Calcd for CuL: C, 36.60; H, 1.74; N, 6.10; S, 27.89; Cu, 27.67%. Method (b). A solution of LH (4—6 mmol) in ethanol (100 ml) was added to a solution of CuX_2 (X=CH_3COO or NO_3) (2 mmol) in ethanol (50 ml). The orange-yellow and pale yellow compounds precipitated were digested on a water bath for approximately 1 h. The suspension was cooled and filtered on a suction pump through a qualitative filter paper to give a pale yellow crystalline precipitate (L–L). The filtrate, containing a fine orange-yellow precipitate was filtered through a quantitative filter paper and the resulting amorphous precipitate (CuL) washed with hot ethanol. The yields were approximately 90% for CuL and L–L. Found: C, 37.00; H, 1.67; N, 6.11; S, 27.57; Cu, 27.90%.

CuL_2: Method (a). A solution of CuX_2 (X=Cl, CH_3COO, NO_3, 1/2(SO_4)) (2 mmol) in water (50 ml) was substituted for the solution of CuX_2 in ethanol in the above preparation procedure for CuL by method (b). The orange-yellow precipitate was washed with water and ethanol (yield>95%). Found: C, 42.34; H, 2.03; N, 7.08; S, 32.12; Cu, 16.20%. Calcd for CuL_2: C, 42.48; H, 2.02; N, 7.08; S, 32.36; Cu, 16.06%. Method (b). A solution cotaining LH and L–L (2 mmol and 1 mmol, respectively) in a mixture of ethanol (100 ml) and *N,N*-dimethylformamide (DMF) (50 ml) was added to a solution of CuCl (2 mmol) in an aqueous solution saturated with KCl (30 ml). The pale orange-yellow precipitated was digested with stirring on a water bath for approximately 1 h. The suspension was cooled and filtered and the collected precipitate washed with water, an ethanol–DMF mixture (30 ml, 2: 1), and ethanol (yield 80%). Found: C, 42.26; H, 1.99; N, 7.00; S, 32.02; Cu, 16.11%.

CuL_3H_2Cl: A solution of $CuCl_2$ (2 mmol) in ethanol (50 ml), in a procedure similar to method (b) above for CuL, gave a pale yellow complex (yield>95%). Found: C, 42.43; H, 2.17; N, 7.04; S, 31.23; Cl, 5.80; Cu, 10.63%. Calcd for CuL_3H_2Cl: C, 42.07; H, 2.34; N, 7.01; S, 32.05; Cl, 5.93; Cu, 10.60%. In the preparation of CuL_3H_2Cl, more than 5% water produced a mixture of CuL_2 and CuL_3H_2Cl, and greater than 20% gave CuL_2 quantitatively.

Other Metal Complexes: PtL_2, PdL_2, NiL_2, CdL_2, HgL_2, PbL_2, and AgL were prepared according to the literatures.[7,8]

All compounds used were dried in an air oven at 105 °C for a minimum of 2 h.

The structures of the two complexes prepared by methods (a) and (b) in the cases of CuL and CuL_2 were analysed by powder X-ray diffraction analysis.

Physical Measurements. The X-ray photoelectron spectra were measured on an AEI-ES200 spectrometer. Al *K*α (1486.6 eV) X-ray radiation was used as the excitation source. Samples were ground and dusted onto a double-backed adhesive tape. The measurements taken at room temperature under vacuum (about 10^{-7} Torr). The binding energy of the C(1 s) peak assigned to the carbon of benzene was used as the energy standard throughout the experiments and taken to be 285.0 eV. The reproducibility was ±0.1 eV.

The IR spectra of LH and the copper complexes were recorded on an IR spectrometer, model IR-G (Japan Spectroscopic Co., Ltd.). The spectrum of CuL_3H_2Cl was the only one which exhibited a similar N–H band to that of LH in the region 2800—3150 cm^{-1}. Magnetic measurements were conducted at room temperature using the Faraday method on a magnetic balance, model MB-2 (Shimadzu Co., Ltd.). The diamagnetic corrections were estimated by the use of Pascal's Constants[12] and all copper complexes were found to be diamagnetic.

Results

The measured binding energies are given in Table 1.

Free Ligands. The N(1s) electron spectra of L′H and L′–L′, and the S(2p) electron spectrum of L′H are shown in Fig. 1. The N(1s) spectrum of L′H showed a single peak with the full-width at a half-maximum height (FWHM) of 1.7 eV. L′–L′ showed two peaks with almost equal intensities. The S(2p) spectrum of L′H as well as that of L′–L′ showed an unsymmetrical peak with a FWHM of 2.3 eV. Two peaks, p_1 and p_2, indicated by broken lines in the figure, have been attributed to $S(2p_{1/2})$ and $S(2p_{3/2})$ electrons, respectively. The S(2p) spectra of LH, LNa, and the metal complexes were resolved graphically on the basis of the shape L′H containing one type of sulfur atom.

Table 1. Binding energies

Compound	Binding energy/eV		
	N(1s)	$S(2p_{3/2})$	$Cu(2p_{3/2})$
LH	400.6	164.5; 162.3	
LNa	398.9	164.2; 162.2	
L–L	399.0	164.5	
L′H	400.6	162.4	
L′–L′	400.5; 399.1	164.5	
CuL	399.4	164.4; 162.8	933.5
CuL_2	399.4	164.4; 162.8	933.5
CuL_3H_2Cl	400.6; 398.9	164.5; 162.7	933.5
PtL_2	399.8	164.5; 162.9	
PdL_2	399.7	164.5; 162.9	
NiL_2	399.6	164.4; 162.6	
CdL_2	399.4	164.4; 162.6	
HgL_2	399.0	164.2; 163.1	
PbL_2	399.0	164.3; 162.4	
AgL	399.1	164.4; 162.7	
$CuCl_2$			935.8
$Cu(CH_3COO)_2$			935.2

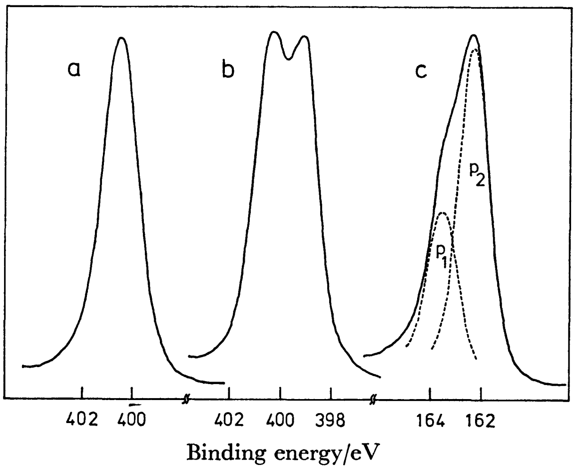


Fig. 1. Electron spectra of the reference compounds. a: N(1 s) of L′H, b: N(1 s) of L′–L′, c: S(2 p) of L′H.

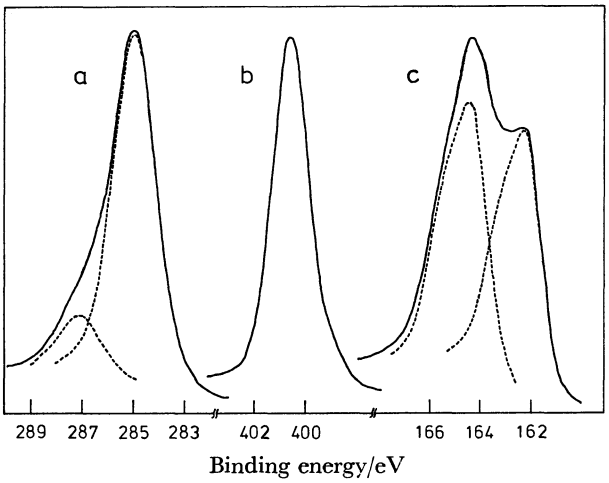


Fig. 2. Electron spectra of LH.
a: C(1 s), b: N(1 s), c: S(2 p).

The C(1s), N(1s), and S(2p) electron spectra of LH are shown in Fig. 2. The C(1s) spectrum showed a main peak and a weak peak on the higher energy side. The former has been assigned to the carbon in the benzene ring and the latter to the thioamide group. The N(1s) spectrum together with the L′H showed a single peak, but the S(2p) spectrum showed a broad peak with a shoulder suggesting two types of sufur atoms. The two peaks indicated by the broken lines which were obtained by a graphical resolving, were almost equal in intensity. The peak with the lower binding energy of the two appeared to weaken with X-ray radiation time. Such X-ray damage in the S(2p)

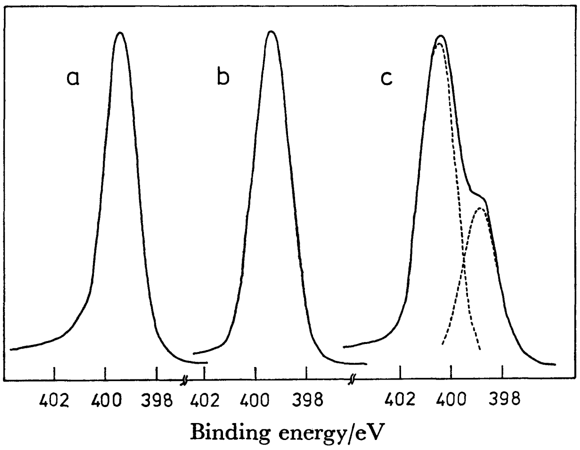


Fig. 3. N(1 s) electron spectra of the copper complexes.
a: CuL, b: CuL_2, c: CuL_3H_2Cl.

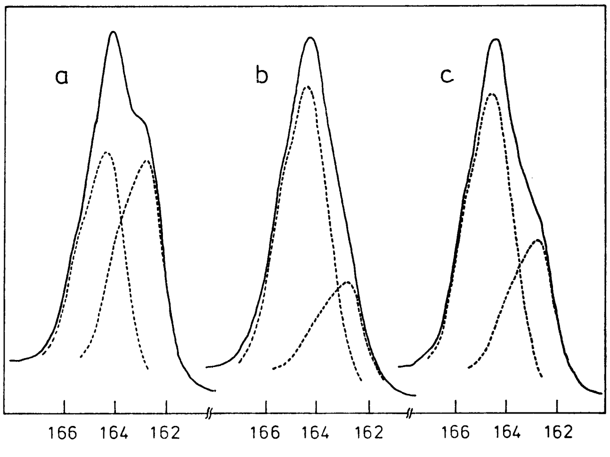


Fig. 4. S(2 p) electron spectra of the copper complexes. a: CuL, b: CuL_2, c: CuL_3H_2Cl.

spectra was not observed in the other samples. The N(1s) and S(2p) spectra of LNa were similar to those of LH in shape. The S(2p) spectrum of L–L, which contains two types of sulfur atoms, was almost the same as those of L′–L′ and L′H in shape.

Complexes. The N(1s) and S(2p) spectra of CuL CuL_2, and CuL_3H_2Cl are shown in Figs. 3 and 4. The N(1s) spectra of CuL and CuL_2 as well as those of the other metal complexes showed a single peak with a FWHM of 1.5—1.7 eV. The N(1s) spectrum of CuL_3H_2Cl showed two peaks with an intensity ratio of approximately 2: 1. The S(2p) spectra of the three copper complexes as well as those of the other metal complexes showed the presence of two types of sulfur atoms. The two peaks, indicated by broken lines in the figures were obtained by graphical resolving. The approximate intensity ratio of the two peaks of CuL as well as the other complexes was 1: 1, however, that of CuL_2 was 3: 1, and that of CuL_3H_2Cl 2: 1.

The $Cu(2p_{3/2})$ electron region spectra of CuL_2, $CuCl_2$, and $Cu(CH_3COO)_2$ are shown in Fig. 5. In the case of CuL_2 as well as CuL_3H_2Cl the broad satellite was not observed in the higher energy region than a main peak as was seen for $CuCl_2$ and $Cu(CH_3COO)_2$.

Discussion

Free Ligands. The peak with the higher binding energy of the two in the N(1s) spectrum of L′–L′ may be assigned to the protonated nitrogen atom and the other to the deprotonated atom, considering that the N(1s) binding energy of a protonated nitrogen atom is approximately 1.5 eV higher than that of a deprotonated one.[13]

LH and L′H are able to exist in two tautomeric conformations, the thiol form and the thioketo form. IR, NMR, and X-ray analysis studies[6,8,14] have indicated that the thioketo form dominates in LH and L′H in the solid state. The results in this study indicate that both LH and L′H exist entirely in the thioketo form, since the N(1s) spectra showed a single peak with a binding energy corresponding to the –NH type.

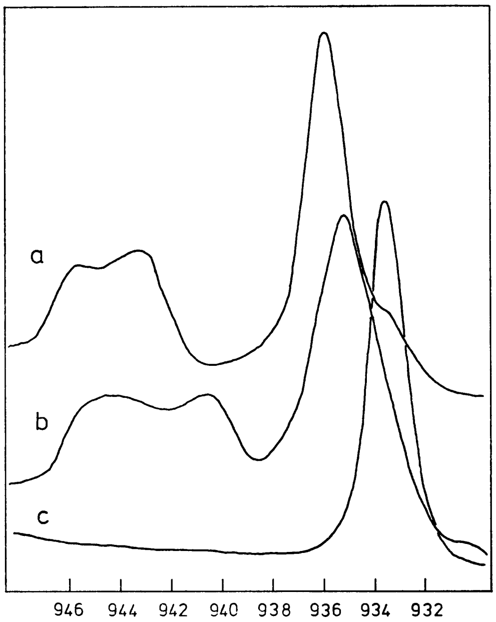


Fig. 5. $Cu(2\,p_{3/2})$ electron region spectra. a: $CuCl_2$, b: $Cu(CH_3COO)_2$, c: CuL_2.

The peak with the higher binding energy of the two in the S(2p) spectrum of LH can be readily assigned to the endocyclic sulfur atom and the other to the exocyclic, by comparing the binding energies (164.5 and 162.3 eV) with that of L′H, which has only the exocyclic atom. The binding energies of two types of sulfur atoms of LNa, when compared with those of the corresponding sulfur atoms of LH, give a difference of 0.3 eV for the endocyclic sulfur atom and 0.1 eV for the exocyclic atom. Furthermore, the N(1s) binding energy of LNa was only 0.2 eV lower than that of the deprotonated nitrogen of L′–L′. From these results, it is suggested that in LNa, the contribution of $-\bar{N}-\overset{|}{C}=S$ dominates that of $-N=\overset{|}{C}-S^-$, and that an apparent unit negative charge on the nitrogen atom is delocalized by conjugation within the hetero five-membered ring.

Complexes. It has been reported that CuL_2 may be prepared by the reaction of $CuCl_2$ with LH in ethanol.[7,9] Repeated attempts to prepare CuL_2 in this way however failed and a complex with an elemental analysis of CuL_3H_2Cl was obtained. CuL_2 was obtained only in the presence of some amount of water as described above.

CuL_2 involves only one type nitrogen atom, a deprotonated type, whereas CuL_3H_2Cl involves both protonated and deprotonated nitrogen atoms, with a ratio of 2: 1. This result supports the experimental evidence that CuL_2 does not show the N–H band in the IR spectrum, whereas CuL_3H_2Cl does.

The diamagnetism of Cu(II) complexes has been explained by two theories. One is that the paramagnetism is quenched by a strong spin-spin interaction between the two copper(II) ions,[15] and the other is a reduction of the Cu(II) ion to Cu(I) by a ligand on complex formation.[10] The diamagnetism of the complex of the copper(II) salt with LH has been explained by the former theory.[7,9] This explanation was however found to be completely excluded on the basis of the following evidence obtained.

A Cu(II) complex typically exhibits a satellite on the higher-energy side of the primary peak in the Cu($2p_{3/2}$) electron region spectrum, as seen for $CuCl_2$ and $Cu(CH_3COO)_2$ in Fig. 5. A Cu(I) complex does not exhibit this.[16] On the basis of the absence of the satellite in the spectra of CuL_2 and CuL_3H_2Cl, it is suggested that CuL_2 and CuL_3H_2Cl are Cu(I) complexes. This agrees with their magnetic moments, *i.e.* both complexes are diamagnetic. Furthermore, the Cu($2p_{3/2}$) binding energies of CuL_2 and CuL_3H_2Cl, as well as CuL, are about 2 eV lower than those of $CuCl_2$ and $Cu(CH_3COO)_2$. This difference in binding energy is comparable to the difference between CuCl and $CuCl_2$ (1.8 eV).[16]

The inequality of intensities of the two types of peaks in the S(2p) spectra of CuL_2 and CuL_3H_2Cl is thought due to the change in the state of a part of the exocyclic sulfur atoms, *i.e.* the change of a thiocarbonyl group to a disulfide group. This is supported by the following facts; the S(2p) binding energy of the sulfur atom of a disulfide group is close to that of an endocyclic one and L–L was obtained from the reaction of LH with copper(II) salts instead of H_2O_2. CuL_2 could be prepared from the reaction of CuCl with LH and L–L.

It is thought that the Cu(II) ion is reduced to the Cu(I) ion by LH on complexing giving CuL_2 and CuL_3H_2Cl, and that the resulting L–L is coordinated to the Cu(I) ion. Therefore, it is thought that, in the stoichiometric forms of CuL_2 and CuL_3H_2Cl, the half and the one-third of the ligands, respectively, should be replaced by 1/2(L–L).

In general, coordination of a ligand to a metal ion causes a decrease in the electron density on the coordinating atom, giving rise to an increase in the core-electron binding energy of the atom. The N(1s) chemical shifts, which are the differences between the N(1s) binding energies of the complexes and LNa, were 0.5—0.9 eV in CuL, CuL_2, PtL_2, PdL_2, NiL_2, and CdL_2, and very small in HgL_2, PbL_2, and AgL. The N(1s) chemical shift of the deprotonated nitrogen atom of CuL_3H_2Cl was not appreciable, and the N(1s) binding energy of the protonated nitrogen of the complex was the same as that of LH.

From these results, it may be concluded that, in CuL, CuL_2, PtL_2, PdL_2, NiL_2, and CdL_2 an M–N bond is present, and in HgL_2, PbL_2, AgL, and CuL_3HCl_2 it is absent.

The S(2p) binding energies of the two types of sulfur atoms of all the present complexes, when compared with the corresponding ones of LNa, were equal to or larger than those of the latter; the differences were 0—0.3 eV for an endocyclic sulfur atom and 0.2—0.9 eV for an exocyclic one. The S(2p) chemical shfts for an exocyclic sulfur were comparable with the values (0.3—0.9 eV)[17] due to the coordination of thiourea or thiazole through the sulfur atom. Therefore, it may be concluded that the exocyclic sulfur atom-metal ion bond is present in all the complexes.

The small positive chemical shifts of an endocyclic sulfur atom appears to suggest the absence of the sulfur-metal ion bond based on the following. The binding energies of the endocyclic sulfur atoms of all the complexes were equal to or smaller than that of the corresponding sulfur atom of LH. The sulfur atom present in the skeleton of the five-membered ring has very weak coordinating ability, since the lone pairs on the sulfur atom are involved in the resonance structures of the molecule.[18]

These results concerning the mode of coordination of LH largely supports the IR results[6–8] in all the complexes. The IR data however suggested that bonding occurred only through the sulfur atom in CuL,[3] and through both the sulfur and the nitrogen in PbL_2 and AgL.[7] This difference of assignments by XPS and IR can not be explained, but may be due to large uncertainties encountered in assigning C=S, M–N, and M–S vibrations in the ligands containing $\mathrm{H{-}\overset{|}{N}{-}\overset{|}{C}{=}S}$ and their metal complexes.[19]

The authors wish to thank Mr. Yukihiro Sato for his aid in performing these experiments, and Mr. Taichiro Hirohara for the elemental analysis.

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