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An X-Ray Photoelectron Spectroscopic Study of Several Metal Complexes of 2-Mercaptobenzimidazole and 2-Mercaptobenzoxazole

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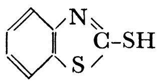
Synopsis. The X-ray photoelectron spectra of several metal complexes of 2-mercaptobenzimidazole and 2-mercaptobenzoxazole were measured in order to examine the mode of coordination of the ligands. From their N(1s) and S($2p_{3/2}$) chemical shifts, it was suggested that the ligands are coordinated through both the sulfur and nitrogen atoms in most of the complexes.

Heterocyclic thiols, such as 2-mercaptobenzothiazole, **1**, 2-mercaptobenzimidazole, **2**, and 2-mercaptobenzoxazole, **3**, are widely used as organic reagents for inorganic ions. The complexing properties of these ligands, which exhibit thioketo-thiol tautomerism, have been studied by the use of a variety of techniques: IR, far IR, UV, magnetic measurements, and NMR.[1)]



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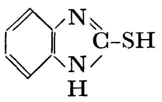

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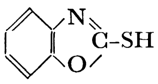

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X-Ray photoelectron spectroscopy (XPS) is sensitive to the charge distribution.[2)] The XPS study of several metal complexes of **1** has been reported.[3)] In that paper, it was proved that the copper was present in a (+1) oxidation state in the complexes obtained from Cu(II) salts and **1**.

The purpose of the present study is to examine the mode of the coordination of the ligands in several metal complexes of **2** and **3** and the oxidation state of copper in their copper complexes by means of XPS.

Experimental

The X-ray photoelectron spectra were measured on an AEI ES200 spectrometer. MgK_α (1253.6 eV) X-ray radiation was used as the excitation source. The samples were ground to powder and then dusted onto double-backed adhesive tape. The measurements were run at room temperature under a vacuum of about 10^{-7} Torr. The binding energy of the C(1s) electron peak was used as the energy standard throughout the present experiments; it was taken to be 285.0 eV. The reproducibilities of the values thus obtained were within ±0.1 eV. All the compounds used and their binding energies are given in Table 1.

Chemicals. Benzimidazole as a reference compound, 2-mercaptobenzimidazole, and 2-mercaptobenzoxazole (abbreviated as L'', LH, and L'H respectively) were obtained commercially and were of an analytical grade. They were used after recrystallization from ethanol. The sodium salt (abbreviated as LNa) of LH was obtained by treating LH with NaOH, but the attempt to prepare L'Na was unsuccessful.

Preparations of Metal Complexes. *CuL*: A solution of LH (4 mmol) containing an equivalent amount of NaOH in ethanol (50 ml) was added to a solution of CuX_2 (X= Cl, NO_3, 1/2(SO_4), CH_3COO, ClO_4) (2 mmol) in water (50 ml). A grey-colored compound thus precipitated was digested on a water bath for an hour. The suspension was cooled, and then the precipitate was filtered and washed with ethanol. The yield of the complex was more than 95%, as in other copper complexes.

Cu(LH)Cl, *$Cu(LH)_{1.5}(SO_4)_{0.5}$*, *and* *$Cu(LH)_{1.5}NO_3\cdot H_2O$*: A solution of LH (4—6 mmol) in ethanol (50 ml) was added to each solution of $CuCl_2$, $CuSO_4$, and $Cu(NO_3)_2$ (2 mmol) in water (50 ml). The ivory-white compounds thus precipitated were treated in a way similar to the procedure for CuL. *CuL'*: A solution of L'H (4 mmol) in ethanol (50 ml) was used instead of the solution of LH containing NaOH in the above procedure for preparing CuL. The color of the compound was ivory-white.

Pb(L–H): An ethanol solution of LH was added to an aqueous solution of $Pb(NO_3)_2$, and the mixed solution was neutralized with aqueous ammonia; a white complex was thus precipitated. *$PbL(CH_3COO)$*: An ethanol solution of LH was added to an aqueous solution of $Pb(CH_3COO)_2$, and then the solution was digested on a water bath; a pale yellow white compound was thus precipitated.

$NiL(OH)\cdot H_2O$ and $NiL'(OH)\cdot H_2O$: An aqueous solution of LH (L'H) containing an equivalent amount of NaOH was added to an aqueous solution of nickel salts, whereby a dark-brown (greenish-brown) compound was precipitated.

Other Metal Complexes: The other metal complexes were prepared based upon the literature.[1)]

All the compounds used were dried in an air oven at 95 °C for at least 2 h and then analyzed elementally.

Results and Discussion

The N(1s) spectra of LH and L'H showed a single peak, and the peak could be assigned to the protonated nitrogen atom from its binding energy.[3)] This indicates that both LH and L'H exist entirely in the thioketo form. This conclusion is consistent with the results obtained by IR.[4)] The N(1s) spectra of LNa and L'' showed two peaks with nearly equal intensities; these peaks could easily be assigned to protonated and deprotonated nitrogen atoms, based upon their binding energies.

The N(1s) binding energies of the protonated and deprotonated nitrogen atoms of LNa were 0.3—0.5 eV lower than those of L''. The S($2p_{3/2}$) binding energy of LNa is fairly close to that of LH. These findings may suggest that, in LNa, the contribution of $-\overline{N}-\overset{|}{C}=S$ dominates that of $-N=\overset{|}{C}-\overline{S}$, and that an apparent unit negative charge on the nitrogen is delocalized by conjugation within the hetero five-membered ring.[5)]

The N(1s) spectra of AgL, HgL_2, $CdL_2\cdot 0.5H_2O$, $PbL(CH_3COO)$, CuL, $NiL(OH)\cdot H_2O$, $PdL_2\cdot 2H_2O$, and $PtL_2\cdot H_2O$ showed the presence of two kinds of nitrogen atoms, that is, protonated and deprotonated nitrogens, similarly to LNa. Those of the other metal complexes showed a single peak, indicating only one kind of nitrogen atom, that is, a deprotonated nitrogen atom for Pb(L–H), in addition to all the com-

TABLE 1. MEASURED BINDING ENERGIES

Compound	Binding energy/eV			
	N(1 s)	$S(2p_{3/2})$	O(1 s)	$Cu(2p_{3/2})$
LH	400.6	162.4		
$LNa \cdot H_2O$	400.3, 398.5	162.2		
AgL	400.4, 398.9	162.7		
HgL_2	400.3, 398.9	162.9		
$CdL_2 \cdot 0.5H_2O$	400.4, 399.0	162.5		
Pb(L-H)	398.9	162.7		
$PbL(CH_3COO)$	400.4, 398.8	162.4		
CuL	400.4, 399.0	162.8		933.4
Cu(LH)Cl	400.7	163.1		933.2
$Cu(LH)_{1.5}(SO_4)_{0.5}$	400.6	163.0		933.3
$Cu(LH)_{1.5}NO_3 \cdot H_2O$	400.6	163.0		933.4
$NiL(OH) \cdot H_2O$	400.6, 399.1	162.7		
$PdL_2 \cdot 2H_2O$	400.6, 399.5	162.9		
$Pd(LH)_2Cl_2$	400.6	163.0		
$PtL_2 \cdot H_2O$	400.6, 399.6	163.0		
$Pt(LH)_2Cl_2$	400.6	163.2		
L'H	400.9	162.5	534.6	
AgL'	399.4	162.8	534.5	
HgL'_2	399.3	163.1	534.6	
$CdL'_2 \cdot H_2O$	399.5	162.7	534.6	
PbL'_2	399.3	162.6	534.5	
CuL'	399.5	162.9	534.5	933.5
$NiL'(OH) \cdot H_2O$	399.4	162.7	—	
PdL'_2	400.0	163.2	534.7	
PtL'_2	400.0	163.2	534.7	
L''	400.6, 399.0			

plexes of L'H, and a protonated nitrogen for the remaining complexes of LH.

In general, the coordination of a ligand to a metal ion causes a decrease in the electron density on the coordination atom, giving rise to an increase in the core-electron binding energy of the atom.

In the series of the complexes of LH, the chemical shifts of the N(1 s) binding energy of a deprotonated nitrogen atom or of the $S(2p_{3/2})$, which are the differences between the N(1 s) or the $S(2p_{3/2})$ binding energies of the complexes and LNa, were 0.2—1.1 eV. These chemical shifts were comparable with the values reported for the complexes with other ligands.[6] This seems to suggest that, in all the complexes, the ligand is coordinated through the sulfur atom, and that in the complex containing a deprotonated nitrogen atom the ligand is also coordinated through the nitrogen atom.

It was difficult to confirm the presence of the bond between a metal ion and a protonated nitrogen atom because of the absence of any appreciable difference between the N(1 s) binding energies of the protonated nitrogen atoms of a complex and LH.

In the series of the complexes of L'H, the N(1 s) and $S(2p_{3/2})$ chemical shifts were 0.3—1.0 eV and 0.1—0.7 eV respectively. In this case, the N(1 s) binding energy (399.0 eV) of the deprotonated nitrogen atom of L'' and the $S(2p_{3/2})$ binding energy (162.5 eV) of L'H were used as the standard energies in determining the chemical shifts, because L'Na could not be obtained. The chemical shifts thus obtained seem to suggest that, in all the complexes, the ligand is coordinated through both the sulfur and nitrogen atoms. The O(1 s) electron spectra of all the complexes showed a single peak. There was no appreciable difference between the O(1 s) binding energies of a complex and L'H. This seems to suggest the absence of a metal–oxygen bond. These conclusions were consistent with the results obtained by IR and far IR.[1d)]

The N(1 s) electron binding energies of L'H and its complexes were 0.3—0.5 eV higher than those of LH and the deprotonated nitrogen atom of its corresponding metal complexes. This finding suggests that the electron densities on the nitrogen atom of the former compounds are smaller than those of the latter. This seems to be consistent with the fact that the dissociation constant ($pK_{N-H}=6.58$) of L'H was smaller than that ($pK_{N-H}=9.18$) of LH.[7]

The Cu $(2p_{3/2})$ electron-region spectra of all the copper complexes in this study did not show at all a satellite characteristic of cupric compounds.[8] Furthermore, the $Cu(2p_{3/2})$ binding energies were 2—4 eV lower than those of cupric compounds.[8] These findings indicate that the copper in the complexes is in a (+1) oxidation state, as in the copper complexes of 2-mercaptobenzothiazole.[3] This is apparent also from the stoichiometric analyses of the complexes in the present study.

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