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THE BONDING OF DIBENZYLDITHIOCARBAMATE METAL COMPLEXES
BY X-RAY PHOTOELECTRON SPECTROSCOPY

Key words: XPS, Dibenzylidithiocarbamate, Zinc, Copper,
Bismuth, Bonding

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ABSTRACT

Core orbital binding energies for N 1s and S 2p_{3/2} in the metal chelates of dibenzylidithiocarbamic acid M(DBDTC)_n for n=2, M=Cu(II) and Zn(II), and for n=3, M=Bi(III), have been measured using x-ray photoelectron spectroscopy. The nature of the spectral peaks and the core binding energies indicates that the nitrogen atom in the DBDTC is not intramolecularly bound with the metal as had been previously suggested. The relatively high binding energies for the N 1s orbitals indicate planar geometry

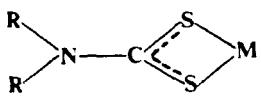
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for the ligands, and the form $\overset{\delta-}{S_2} \overset{\delta+}{C}=\overset{\delta+}{N}R_2$ to reasonably represent their structure, which agrees with previous infrared studies.

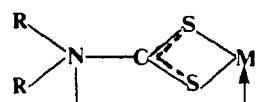
INTRODUCTION

Dithiocarbamate metal chelates are used in a wide variety of chemical processes including rubber vulcanization and the production of agricultural fungicides and pesticides.¹ Soluble dithiocarbamate salts have found extensively application in the extraction of metal chelates from acid solutions,² and the chemical and physical properties of these complexes are of much interest, particularly the nature of the nitrogen-metal bonding.

Previous experimental data from NMR,^{3,4} IR^{5,6} and electron spectroscopy,⁷ as well as x-ray photoelectron spectroscopy (XPS)^{8,9,11,12,15} have indicated two possibilities for the bonding in these compounds:



TYPE I



TYPE II

Structure I illustrates the long-held view that the ligand forms a stable four-membered chelate ring.

Early XPS studies supported this idea solely on the basis of the existence of only one broad sulphur 2p_{3/2} peak^{8,9,11,15} : however recent XPS studies on N 1s binding energies in Cu(II)-, Pb(II)- and Sn(II)-diethyldithiocarbamate complexes by Cheng et al¹² suggested that there may exist an additional bond between the N atom and the metal M (structure II) to form a second four-membered ring, since they found the binding energy of the N 1s peak to be approximately the same as that in the EDTA chelate (ethylenediaminetetraacetic acid),¹⁰ where the N atoms are certainly coordinated to the metal ion.

In order to clarify this issue, we extended the XPS studies to include the more stable Cu(II), Zn(II) and Bi(III) dibenzyldithiocarbamate (DBDTC) compounds.

EXPERIMENTAL

1. Preparation of Metal-Dibenzyldithiocarbamate Chelate:

The metal {Cu(II) and Bi(III)} chelates were synthesized by the general procedure outlined for the synthesis of diethyldithiocarbamic acids.¹² Zinc-DBDTC was obtained from Eastman Kodak Chemical Company and was recrystallized using a 1:1 mixture of chloroform and ethanol as solvent. The sodium salt of DBDTC was prepared from Zn-DBDTC by ion exchange, and the other chelates were then synthesized from the

sodium salt.¹³ The chelate precipitates were filtered, washed with water, dried in vacuum, and finally recrystallized from another chloroform-ethanol solvent.

2. Instrumental

X-ray photoelectron spectra were taken with a Varian IEE-15 spectrometer, using magnesium K α radiation (1253.60 eV) at 280 watts. Each sample was lightly dusted onto the 3M scotch tape of the sample holder and inserted into the spectrometer (operating pressure $< 10^{-7}$ torr). All binding energies (BE's) were calibrated with reference to the carbon 1s peak (284.0 eV) from graphite, or the potassium 2p_{3/2} peak from potassium chloride (295.0 eV).

RESULTS AND DISCUSSION:

The main usefulness of XPS in determining bonding configurations lies in its ability to detect changes in an atom's electrostatic environment, as evidenced by shifts in BE's of core electrons.¹⁴ We obtained N 1s BE data on the dibenzyldithiocarbamate metal complexes containing Cu(II), Zn(II), and Bi(III), choosing benzyl compounds in preference to the less stable ethyl derivative compounds used in previous studies.¹² -

TABLE I

XPS data on some dibenzyldithiocarbamates, and Cu(II)H₂-EDTA and Bi(III)H-EDTA

PEAK (eV)*	SAMPLE	BINDING ENERGY (eV)*	PEAK WIDTH (eV)*
N 1s	Zn(DBDTC)	400.50	2.10
	Cu(DBDTC)	400.55	2.16
	CuH ₂ (EDTA)	400.20	2.85
	Bi(DBDTC)	400.50	1.95
	BiH(EDTA)	402.25	2.47
S 2p _{3/2}	Zn(DBDTC)	162.20	2.75
	Cu(DBDTC)	162.20	2.61
	Bi(DBDTC)	162.60	2.67

* Estimated errors \pm 0.05 eV

even so, with the lowest practical x-ray power and sample probe cooled by liquid nitrogen, the hydrogen and sodium complexes decomposed in the spectrometer. The data obtained from the remaining complexes are given in table I.

Our results show that from Zn(II) to Bi(III) DBDTC the S 2p_{3/2} BE increases, but the N 1s BE's

remain essentially unchanged, as opposed to the case of the similar molecules $\text{CuH}_2\text{-EDTA}$ and BiH-EDTA , where there is N-M bonding, and where we see a difference in N 1s BE of approximately 2.0 eV. This is a strong indication that N is not bonded to the metal in the DBDTC complexes. Furthermore, the N 1s electrons in the DBDTC complexes have a BE of about 1.0 eV greater than 'neutral' nitrogen in triphenylamine, which suggests the N-C bond in $\text{R}_2\text{N}=\overset{\delta+}{\text{C}}\text{S}_2$ is polar and would cause this group to be planar, as has been previously observed in the diethyl complexes.^{16,17}

CONCLUSION

In the DBDTC complexes studied, S 2p_{3/2} binding energies are shown to vary with the oxidation state of the metal. The same change in oxidation state has no effect on the N 1s peak, -strong evidence that there is no metal-nitrogen interaction and consequently no intramolecular N-M bond.

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