

XPS of Coordination Compounds: Data on the Electronic Structure of a Series of Cu(II) N,N'-cyclic Substituted Dithiocarbamates

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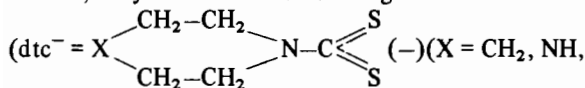
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A series of copper(II) dithiocarbamates $Cudtc_2$ with $dtc^- = X \begin{array}{l} \text{CH}_2-\text{CH}_2 \\ \text{CH}_2-\text{CH}_2 \end{array} \text{N}-\text{C} \begin{array}{l} \text{S} \\ \text{S} \end{array} \begin{array}{l} \text{(-)} \\ \text{(-)} \end{array} \text{ (X = CH}_2, \text{NH, NCH}_3, \text{O)}$ has been investigated by XPS. The compounds proved sufficiently stable under X-irradiation; b.e. data confirm substantial identity of the electronic structure of the metal chromophores throughout the series, in which remote ligand effects find evidence in a linear correlation between relative intensity of $Cu2p_{3/2}$ satellite peaks and variations of magnetic moments of the Cu(II) species.

Introduction

Among the numerous applications of XPS (X-ray photoelectron spectroscopy) to coordination chemistry, increasing interest is being devoted to possible detection of finer structural effects, and to a more systematic and enlarged search for transferability of electronic structure parameters derived from XPS measurements.

Following the latter trend, we have investigated by XPS a series of copper(II) dithiocarbamates $Cudtc_2$, with N,N'-cyclic substituted dtc^- ligands

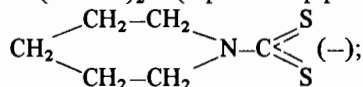


Metal dithiocarbamates in general, and copper(II) dithiocarbamates in particular, have been the subject of numerous previous investigations by XPS [1–5], which however did not always give coincident quantitative results. This suggested problems of chemical instability under XPS conditions [4], and indicated the usefulness of further and deeper investigations. In particular, referencing procedures are critical, since the usual procedure of referring to the C1s signal of contamination carbon taken as 285.0 eV is obviously complicated by the presence of carbon atoms in the ligand moieties; more elaborate referencing procedures have to be adopted, which

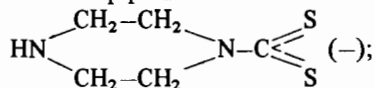
also require quantitative evaluation of intensities. Only then can significant b.e. data be obtained, and these reveal a substantial similarity in the electronic structure of the chromophores. The effect of remote substituent groups is not reflected in any significant chemical shift on the b.e. value; it nevertheless receives evidence in other features of the XPS spectra, namely in the satellite bands accompanying the copper(II) 2p_{1/2} ionization signals.

Experimental

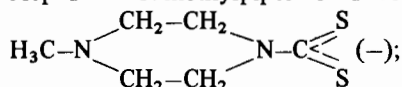
The investigated copper(II) complexes $Cu(\text{Pipdte})_2$, $(Cu\text{Pzdte})_2$, $Cu(\text{Mepzdtc})_2$, $Cu(\text{Morphdte})_2$ and $Cu(\text{Timdte})_2$ ($\text{Pipdte}^- = \text{piperidinedithiocarbamate}$



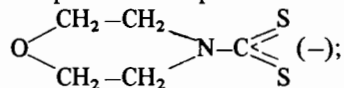
$\text{Pzdte}^- = \text{piperazinedithiocarbamate}$



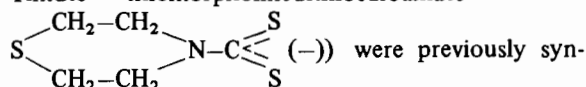
$\text{Mepzdtc}^- = \text{N-methylpiperazinedithiocarbamate}$



$\text{Morphdte}^- = \text{morpholinedithiocarbamate}$



$\text{Timdte}^- = \text{thiomorpholinedithiocarbamate}$



thesized and described by some of us [6–8]. For the present work the above Cu(II) complexes were prepared, together with the corresponding Na salts, according to the previously published methods [6–8] and their purity checked by elemental analysis and physical constant values; a further check of the elemental composition was accomplished through intensity ratios of XPS signals (see next section).

TABLE I. Binding Energies (FWHM)^a (eV), Intensities (10³ counts at 0.1 eV/sec), Number of atoms^b.

Compound	Cu 2p _{3/2}	Cu 2p _{3/2} sat.	Cu 3p	S 2p _{av}	S 2s _{av}	N 1s _{av}	C 1s	C 1s components	Cu A	O 1s	μ
Cu(Pipdte) ₂	933.1(2.0)	$\Delta E = 10.5(4.6)$	76.0(4.4)	162.0(2.4)	226.1(2.8)	399.7(2.2)	284.9(2.9)	284.1(28%) 285.0(52%) 286.3(20%)	916.7(4.3)	531.5(2.4)	1.81
	75.7	16.8% ^c	11.1	35.1	25.4	18.3	99.5				
Cu(Pzdtc) ₂	933.4(2.3)	$\Delta E = 10.4(4.9)$	76.7(4.8)	162.1(2.5)	226.1(2.8)	399.5(2.4)	285.5(2.4)	285.0(42%) 285.9(58%)	916.6(4.4)		1.9
	77.8	22.5%	11.2	38.0	24.7	398.8	57.0				
		1.00		4.35	4.01	400.0	12.47				
Cu(Mepzdtc) ₂	933.3(2.2)	$\Delta E = 10.7(5.3)$	76.4(4.5)	162.3(2.5)	226.3(2.7)	399.4(2.4)	285.6(2.3)	285.0(55%) 285.9(45%)	916.1(4.0)		1.84
	83.4	19.2%	11.1	34.0	22.1	398.9	78.3				
Cu(Morphdte) ₂	933.2(2.0)	$\Delta E = 10.5(5.4)$	76.6(4.5)	162.4(2.5)	226.4(2.8)	400.0(2.0)	286.0(2.2)	285.0(25%) 285.7(34%) 286.3(41%)	916.2(3.4)	532.2(2.4)	1.88
	69.7	22.7%	9.7	31.6	20.3	15.9	61.0				
		1.00		4.04	3.67	2.14	15.11				
Cu(Timdte) ₂	933.1(1.9)	$\Delta E = 10.6(5.2)$	75.6(4.7)	162.3(2.9)	226.4(3.2)	399.5(1.7)	285.0(2.4)	284.3(36%) 285.0(41%) 286.1(23%)	916.5(3.2)	531.6(3.0)	1.81
	71.5	18.55%	9.0	161.9	225.9	13.0	51.8				
		1.00		47.4	32.1	1.72	13.10				
					6.09						
PipdteNa·2H ₂ O	62.7(1.8)		7.3	161.4(2.4)	225.4(2.6)	399.3(1.8)	286.0(2.5)	284.1(39%) 285.0(34%) 285.6(27%)			
	1.45		1.45	45.9	29.6	22.5	93.5				
				2.00	1.03	7.70					
PzdtcNa·2H ₂ O	63.0(1.8)		5.5	161.7(2.4)	225.7(2.6)	399.5(2.0)	285.5(2.5)	285.0(57%) 286.1(43%)			
	1.45		1.45	33.5	22.6	399.1	61.1				
				2.00	1.62	6.76					

MePzdtcNa·2H ₂ O	63.0(1.9)	161.6(2.5)	225.5(2.6)	399.3(2.0)	285.4(2.2)	285.0(49%) 285.6(51%)
	3.5	30.9	19.1	399.0 399.6 26.7	70.8	
	1.03		2.00	1.84	8.79	
MorphdtcNa·3H ₂ O	62.9(1.8)	161.7(2.4)	225.7(2.7)	399.6(1.8)	285.7(2.4)	285.0(30%) 285.7(31%) 286.3(39%)
	5.7	37.8	25.3	18.5	73.8	
	1.34		2.00	1.01	7.28	
TmdtNa·2H ₂ O	62.7(1.8)	162.1(3.4)	226.1(3.5)	399.4(1.8)	285.8(2.3)	284.4(40%) 285.0(39%) 286.1(21%)
		161.1	225.1			
		162.8	226.9			
	6.3	61.4	41.1	16.8	67.9	
	1.36		0.85	6.17		

^aFWHM = Full Width at Half Maximum.
both satellite and the main line Cu 2P_{3/2}.

^b Referred to 1.00 Cu atom (complexes) or 2.00 S atoms (Na salts).

^c Relative satellite intensity with respect to the total area of

XPS measurements were performed on a VG ESCA-3 spectrometer with Al K_{α1,2} ($h\nu = 1486.6$ eV) source. Samples were dusted as thin film on a gold bearing plate, whose Au 4f_{7/2} signal at 84.0 eV was used for checking the energy scale. These compounds proved essentially stable under X-ray (typical X-ray power 12 kV × 10 mA through a 0.04 mm Al window), except after several hours of irradiation (as discussed in more detail in the next section). Vacuum in the spectrometer chamber was typically 1×10^{-9} torr, and the resolution was about 1.6 eV on the Au 4f_{7/2} peak. Measured b.e. values were corrected for surface charging phenomena (usually 1–2 eV) by adopting the value of 285.0 eV for the C1s signal of contaminant carbon; however, detection of the C1s peak was not straightforward, since it was mixed with the signals from other kinds of (ligand) carbon. To overcome the difficulty two procedures were adopted, which gave coincident results: a) deconvolution of the composite C1s peak, so as to identify the component due to adventitious carbon; b) mixture with inert filling materials (KCl, CaSO₄, BaSO₄) and referencing to their previously determined b.e. values.

Quantitative evaluation of atomic ratios in the XPS sampling layer from the intensities of XPS signals was accomplished by the usual formula $n_a/n_b = I_a \sigma_b \lambda_b S_b e^{-d/\lambda_b} / I_b \sigma_a \lambda_a S_a e^{-d/\lambda_a}$ [9], where σ values were taken from Scofield [10], IMPF values λ from the formulas given by Seah and Dench [11], luminosity factor S from ref. [12] ($\sim E_k^{-1/2}$). Overlayer thickness d was in the present case negligible; in fact, the amounts of adventitious carbon, estimated from atomic ratios in the overall sampling layer, were between *ca.* 2 and 5 atoms of C per molecule of metal compound, which is in the sub-monolayer range.

Auxiliary UPS measurements in gas phase were performed on a Perkin Elmer PS-18 spectrometer with HeI (21.2 eV) radiation in the interval 230–270 °C, and calibrated by CH₃I and Ar signals.

Results and Discussion

Some representative XP spectra of the investigated Na and Cu(II) dithiocarbamates are reported in Fig. 1, and all numerical data are listed in Table I.

Reduction of metal compounds in high oxidation states under X-ray irradiation in the XP spectrometer chamber is of common occurrence, and is not excluded *a priori* for Cu(II) compounds. For Cu(II) dithiocarbamates, Thompson *et al.* [4] maintain that immediate reduction to Cu(I) occurs, so that measured XP spectral data refer actually to a Cu(I) decomposition product. This view finds further apparent support also in some of our findings, since our measured Cu 2p_{3/2} peaks are narrow (FWHM 1.9–2.1 eV), whereas Cu(II) peaks are often

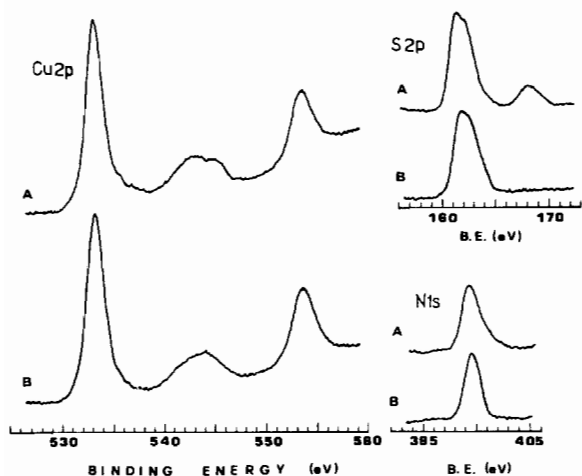


Fig. 1. Copper $2p_{3/2, 1/2}$, sulfur $2p$ and nitrogen $1s$ spectra of (A) $\text{Cu}(\text{Pipdtc})_2$, (B) $\text{Cu}(\text{Pzdtc})_2$.

broadened by unresolved multiplet splitting, and since $\text{Cu}2p_{3/2}$ b.e. values fall around 933.2 eV (*vide infra*), which is a very low, although still acceptable, value for a $\text{Cu}(\text{II})$ species. On the grounds of our observations we came however to the conclusion that $\text{Cu}(\text{II})$ dithiocarbamates are essentially stable under X-ray since: a) the shape of the XP spectra does not change in the first few minutes of irradiation within the XP spectrometer, which implies that radiation damage is either immediate (which we do not consider likely) or negligible; b) $\text{Cu}2p_{3/2}$ signals are accompanied, as typical of $\text{Cu}(\text{II})$, by satellites whose position and intensity are reproducible and constant in the initial irradiation times; c) $\text{S}2p$ and $\text{S}2s$ signals are narrow, as expected for one kind of sulfur atom present in the sampling layer (only in some instances did we observe small components of impurities at sulphate or sulphone level ($\text{S}2p$ ca. 168.1 eV) of irreproducible intensity); d) atomic ratios from XP spectral intensities are in good agreement, within the usual approximation limits, with the $\text{Cu}(\text{II})$ formulation; e) only after prolonged irradiation ($>1-2$ hr) does a genuine X-ray reduction process of $\text{Cu}(\text{II})$ dithiocarbamates become detectable: the main peaks of $\text{Cu}2p$ become broader, develop a foot on the low b.e. side, and the b.e. of the maximum decreases slightly, while the satellites decrease in intensity. Such radiation damage is however so slow and partial that XPS data taken at exposure times not exceeding ca. 1–2 hr can be considered as truly representative of $\text{Cu}(\text{II})$ structures.

As for XPS spectral referencing procedures, the usual method of taking the $\text{C}1s$ maximum as 285.0 eV proves here unsatisfactory, and leads to gross inconsistencies such as apparent shifts of the whole XP spectrum of some member of the investigated series. Referencing to contamination carbon can still be done, but requires additional care and less direct

procedures: the $\text{C}1s$ bands have a composite structure, where several kinds of carbon atoms are present: from contamination as well as from the organic part of the dithiocarbamate ligands. The latter in turn comprises several kinds of C atoms, whose $\text{C}1s$ signals can be identified by deconvolution of the composite band. The signals are assigned the following b.e. values, which result from comparisons between different ligands and repeated trials, aided by a rough evaluation of the amount of excess (contamination) carbon on the basis of atomic ratios from XPS intensities: aliphatic secondary C (e.g. in the piperidine chain), or C singly bonded to S at 284.2 ± 0.1 eV; contamination at 285.0 eV; dithiocarboxylate at 285.0 eV or slightly higher; C–N at 286.1 ± 0.2 eV; C–O at 286.3 eV (see Table I and Fig. 2).

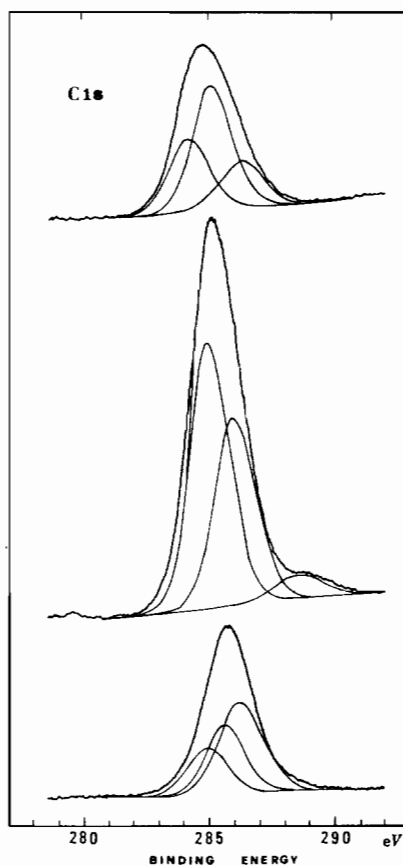


Fig. 2. Representative $\text{C}1s$ photoelectron spectra with deconvolution of (from top to bottom) $\text{Cu}(\text{Pipdtc})_2$, $\text{Cu}(\text{Pzdtc})_2$ and $\text{Cu}(\text{Morphdtc})_2$.

Such referencing procedure is internally consistent and yields reasonable results, but its accuracy is decreased by the uncertainty inherent in the deconvolution. Therefore, we attempted also another referencing procedure based on admixing the investigated substances with some suitable inert support of known b.e. such as KCl , CaSO_4 or BaSO_4 ; we adopted

TABLE II. Some Examples of Different Referencing Procedures (b.e. values in eV).

Sample		Filling support		C1S _{av}	C1S contamination component	Complexes	
		Metal nj ^a	S2p _{av}			Cu2p _{3/2}	S2p _{av}
KCl	c	292.9	—	285.0	285.0	—	—
CaSO ₄	c	348.2	169.6	285.0	<u>285.0</u>	—	—
BaSO ₄	c	178.7	169.1	285.0	<u>285.0</u>	—	—
Cu(Morphdtc) ₂ pure	b	—	—	286.6	—	933.8	162.9
	d	—	—	<u>285.0</u>	284.0	932.2	161.3
	c	—	—	286.0	<u>285.0</u>	933.2	162.3
Cu(Morphdtc) ₂ + KCl	b	294.1	—	286.7	—	934.3	163.4
	d	292.4	—	<u>285.0</u>	—	932.6	161.7
	e	<u>292.9</u>	—	285.5	—	933.1	162.2
Cu(Morphdtc) ₂ + CaSO ₄	b	349.7	170.8	287.6	—	934.8	163.8
	d	347.1	168.2	<u>285.0</u>	—	932.2	161.2
	e	<u>348.2</u>	169.3	286.1	—	933.3	162.3
Cu(Pipdte) ₂ pure	b	—	—	285.7	—	933.9	162.8
	d	—	—	<u>285.0</u>	285.1	933.2	162.1
	c	—	—	284.9	<u>285.0</u>	933.1	162.0
Cu(Pipdte) ₂ + KCl	b	294.0	—	286.0	—	934.2	163.2
	d	293.0	—	<u>285.0</u>	—	933.2	162.2
	e	<u>292.9</u>	—	284.9	—	933.1	162.1
Cu(Pipdte) ₂ + BaSO ₄	b	182.0	172.4	288.3	—	936.5	165.2
	d	178.7	169.1	<u>285.0</u>	—	933.2	161.9
	e	<u>178.7</u>	169.1	285.0	—	933.2	161.9

^aSelected metal inner-core ionization signals are 2p_{3/2} for K and Ca, and 4p_{3/2} for Ba; values for other metal or anion orbitals, e.g. Cl2p or Ba4d_{5/2} (not reported in table) give coincident results when used as reference signals. ^bNot corrected for charging effects. ^cCorrected by referring to C1s (contamination) = 285.0 eV. ^dCorrected by referring to C1s (av) = 285.0 eV.

^eCorrected by referring to metal inner-core reference signals (see a).

Reference signals are underlined.

as convenient reference signals K2p_{3/2} at 292.9 eV, Ca2p_{3/2} at 348.2, S2p_{av} at 169.6 eV (CaSO₄), or 169.2 eV (BaSO₄), Ba4d_{5/2} at 89.9 eV, Ba4p_{3/2} at 178.7 eV, all redetermined from previous literature values [13, 14] by control measurements of the pure supports and assumption of C1s = 285.0 eV for the b.e. of contamination carbon on the pure supports. Table II reports results for a few such measurements, selected among the most representative ones which gave coincident results with the procedure of C1s band deconvolution. The procedure of mixing with a support is however not always applicable, since it gave rise in some other cases to appearance of separate surface charging effects for the two phases of the mixture.

We turn now to analysis of the b.e. data reported in Table 1, and shall discuss first our findings concerning the copper spectra. The Cu2p_{3/2} peaks fall at 933.2 ± 0.1 eV for all investigated Cu(II) complexes, and hence indicate substantial similarity of electronic structure in the copper(II) chromophores, and practical insensitivity to the effect of remote substituents in the organic part of dithiocarbamate ligands. To

further confirm this situation we also ran some UPS measurements in gas phase, and found that the first ionization band under HeI irradiation, known from previous investigations to contain altogether π₃, n₊ and n₋ valence orbitals [15], falls at 8.33 eV for the Morphdte, and at 8.10 eV for the Pipdte Cu(II) complexes. The measured differences are of the order of 0.2 eV, which amounts to the estimated uncertainty of XPS measurements. The value of 933.2 eV for Cu2p_{3/2} is not in good agreement with the prediction (933.8 eV) of the model of additive ligand contribution by Feltham and Brant [16]; however the difference is not so large as to seriously impair either the validity of the model by Feltham and Brant (which is based on statistical considerations), or the assignment to Cu(II) species. The Cu2p main peaks are accompanied by a structureless satellite at ca. 10.5 eV ΔE (FWHM ca. 5.5 eV), with an intensity between ca. 17 and 23% of the total area of both satellite and the main peak. Such a satellite structure is typical of Cu(II) species (satellites are completely absent in the most well-defined Cu(I) cases [17]), and the observed relative intensities fall in the normal range for Cu(II)

e.g. 18% for Cu(II) diethyldithiocarbamate [3], although somewhat higher values have sometimes been reported. It has been suggested [3], that satellite intensities correlate with the spin density on the copper atoms in paramagnetic species or, less accurately, with the magnetic moments; in our case there is approximate linearity between relative satellite intensity and the room temperature magnetic moments previously reported for the substituted copper(II) dithiocarbamates investigated here (see Fig. 3). This is the only evidence for the influence of remote substituent groups on XP spectra, and confirms that satellite structure accompanying the main metal peaks is a sensitive probe for small changes in chemical environment around the chromophore, whereas main peak b.e.s are detectably affected only by major structural variations.

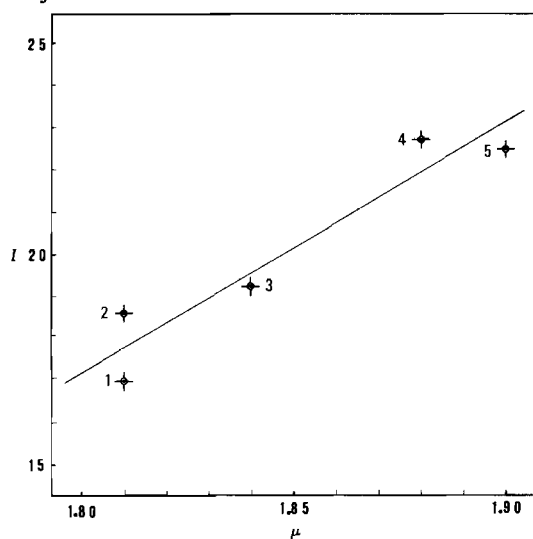


Fig. 3. Plot of total satellite intensity (ratio of the corresponding satellite area to the total area of satellite + the main line $\text{Cu}2p_{3/2}$) versus μ_{eff} . (1) $\text{Cu}(\text{Pipdte})_2$, (2) $\text{Cu}(\text{Timdte})_2$, (3) $\text{Cu}(\text{Mepzdtc})_2$, (4) $\text{Cu}(\text{Morphdte})_2$, (5) $\text{Cu}(\text{Pzdtc})_2$.

$\text{S}2p_{\text{av}}$ b.e.s (taken as the maximum of the composite band, which occurs ca. 0.3 eV higher than the $\text{S}2p_{3/2}$ component) are essentially constant throughout the series at 162.2 ± 0.1 eV; this value is in substantial agreement with most previous literature reports for chelated dithiocarbamates [1, 2, 5], and within the limits quoted by Walton (161.7 to 162.9 eV) [5], and again indicates the absence of any strong effects from remote substituents. It might be argued that two inequivalent sulfur species, in an atomic ratio of 3:1, are present in the molecular structure of Cu(II) dithiocarbamates, if we assume the dimeric, S-bridged structure ascertained by X-ray crystallography, for the N,N'-diethyl derivative by Bonamico *et al.* [18]. However, only some small differences in the band profile of the $\text{S}2p$ peaks are noted with respect to species known to contain only one kind of S atom (e.g. the corresponding Na dithiocarbamates,

their Ni(II) complexes [19], or the supporting sulfates in the mixture spectra), which can be approximately reproduced by a single gaussian curve with two different halfwidths (e.g. FWHM ~ 2.4 , $\delta(-) \sim 1.0$, $\delta(+)$ ~ 1.4 eV in Na dithiocarbamates, against FWHM ~ 2.4 eV, $\delta(-) \sim 0.8$, $\delta(+)$ ~ 1.6 eV for the Cu(II) complexes. Unfortunately, $\text{S}2s$ signals are not informative in this regard; in fact, while falling exactly 64.0 eV higher than $\text{S}2p_{\text{av}}$, and thus confirming all conclusions based on discussion of the latter signals, $\text{S}2s$ peaks are broad (typical FWHM value is 2.9 eV, against 2.4–2.5 eV for $\text{S}2p$) and do not yield evidence for the occurrence of inequivalent sets of sulfur atoms. Only in the thiomorpholine derivatives are $\text{S}2p$ and $\text{S}2s$ signals clearly double and resolvable into two components (2:1), the higher of which is assigned to ring-sulfur and suggests an $\text{S}2p_{\text{av}}$ b.e. value of 163.2 eV for the neutral sulfur atom of thiomorpholine, in agreement with other findings for thio-ethers. The value of 162.2 ± 0.1 eV for $\text{S}2p_{\text{av}}$ in the Cu(II) complexes can be compared with the value 161.5 ± 0.1 eV found for the Na salts; the difference of 0.7 eV sets a lower limit for the σ -donor effect occurring in complexation, but cannot be simply related to the fractional number of transferred electrons since the measured differences of b.e. values are likely to be strongly affected by Madelung potentials. The latter are expected to be small in the copper(II) chelates (charge on Cu probably close to electroneutrality), and to contribute a significant b.e. increase for the Na salts owing to the net +1 charge of the cations. Therefore the actual charge shift from the S donor onto the metal is probably higher than that suggested by the uncorrected figure of $\Delta E \sim 0.7$ eV.

In this regard, we can also compare N1s b.e.s, which fall around 399.8 ± 0.2 eV in the complexed ligands, and around 399.6 ± 0.2 eV in the Na salts. Such values are relatively high, and this can be con-

nected to resonance forms of $\text{N}^+ = \text{C} \begin{matrix} \text{S}^- \\ \text{S}^- \end{matrix}$ type, as

already suggested on the basis of IR evidence [6–8]. The difference in N1s b.e. values between complexed and uncomplexed ligands is within the limits of experimental uncertainty, as expected for absence of direct bond interactions between N and Cu. Only minor b.e. differences would be expected, possibly due to differences in Madelung effects between ionic and non-ionic dithiocarbamates. In the Pzdtc and Mepzdtc derivatives N1s bands are broader and composite in nature, and can be easily resolved into two components (1:1), the less energetic one being assigned to the second ring nitrogen of the piperazine moiety. The difference between the N1s signals of $\text{N}(\text{CS}_2)$ and $\text{N}(\text{ring})$ is ca. 0.7 eV (av) in the Na salts, and 1.1 (av) in the Cu(II) complexes, possibly because of the destabilizing effect of the negative

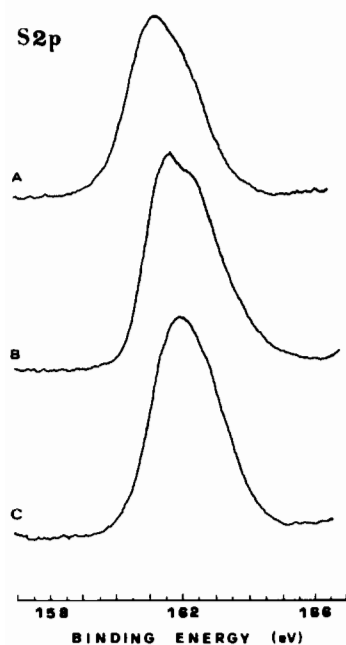


Fig. 4. Sulfur 2p spectra of (A) PipdteNa·2H₂O, (B) Cu(Pipdte)₂, and (C) Ni(Pipdte)₂.

charge on S atoms in the former case. As for b.e. values of C1s signals, we have already discussed the effects due to occurrence of different sets of C atoms in the ligand moieties and their dependence on the nature of the X substituent in the 4-X-piperidine ring of the ligands. Here too, intramolecular Madelung effects can contribute to the observed chemical shifts.

In summary, XPS investigation of the present series of closely similar Cu(II)-dithiocarbamate complexes offers an opportunity on the one hand to confirm some basic features of XP spectra of copper(II) complexes (such as their essential stability, and the limits of radiation damage under X-ray exposure) and of their interpretation (mainly the precautions to be taken in referencing procedures), and on the other to assess the limits of accuracy of XP spectroscopy in detecting smaller structural effects. Donor-

acceptor interactions between ligands and central metal are reflected in chemical shifts of the b.e.s of the involved atoms; however, Madelung corrections are difficult to evaluate, and prevent any simple correlation with the net amount of electronic charge transferred on complexation. Minor effects, e.g. the influence of remote substituents, find evidence only in subsidiary features of the XP spectra such as in the present case, the relative intensity of satellites of metal ionization.

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