Ultraviolet Photoelectron Spectra of some Transition-metal Diethyldithiocarbamates

By **Carla Cauletti** and **Claudio Furlani**,* CNR/TSECS Laboratory and Institute of General Chemisty of the University, Rome, Italy

He(I) photoelectron spectra of the diethyldithiocarbamates of Cr^{III}, Fe^{III}, Co^{III}, Ni^{II}, Cu^{II}, and Zn^{II} are reported, and a tentative assignment is proposed. 'd'-Orbital ionization is observed as early and distinct bands for the complexes of Cr, Co, and Ni, while the bands in the 7.5—9.5 eV region, present in all the complexes and related to the known spectrum of $NMe_2{\cdot}CS{\cdot}SMe$, probably arise from the following sequence of molecular orbitals of the chelate rings, $\pi_3 > \sigma_{M-S}(n_-) > \pi_2 > \sigma_{M-S}(n_+)$, mainly derived from sulphur 3*p* atomic orbitals.

As a part of a series of investigations on the applications of photoelectron (p.e.) spectroscopy to the elucidation of the electronic structure of co-ordination compounds, we report the vapour-phase He(I) p.e. spectra of the diethyldithiocarbamates $[M^{II}(S_2CNEt_2)_2]$ (M^{II} = Ni, Cu, or Zn) and $[M^{III}(S_2CNEt_2)_3]$ (M^{III} = Cr, Fe, or Co), which are sufficiently volatile to be amenable to gas-phase investigations. The results of the present study suggest that the electronic structure of the metal chromophore is similar to that offered by the vapour-phase p.e. spectra of other sulphur-containing metal complexes, such as β-diketonates and their thio- and dithio-analogues of nickel[1] and of cobalt and copper,[2] as well as transition-metal difluorodithiophosphates $[M(S_2PF_2)_n]$.[3]

EXPERIMENTAL

All the investigated complexes were prepared by literature methods[4] and purified by sublimation *in vacuo*. Photoelectron spectra were recorded on a Perkin-Elmer PS 18 instrument at sample temperatures ranging from *ca.* 160 to 250 °C. The calibration was made with inert gases (Ar $3p_{\frac{1}{2}}$, $3p_{\frac{3}{2}}$; Xe $5p_{\frac{1}{2}}$, $5p_{\frac{3}{2}}$) allowed into the sample chamber.

RESULTS AND DISCUSSION

Spectra of the six complexes are in Figures 1 and 2, and values of the vertical ionization energies are listed in the Table; adiabatic ionization potentials (i.p.s) could not usually be distinguished. The spectral patterns consisted of: (*a*) a region of resolved or partly resolved bands between *ca.* 6 and 8 eV,* with different patterns for each metal (such bands will be assigned as ionizations of orbitals of predominantly '*d*' character); (*b*) a common region of more intense ionization bands between *ca.* 7.5 and 9.5 eV, sometimes coalesced into a single, broad, band profile (arising from ionization of ligand orbitals involved in co-ordination bonds); and (*c*) several overlapping bands beyond 10—11 eV, mainly associated with ionization of σ_{C-H} and σ_{C-C} bonding orbitals, giving rise to a broad, intense, and ill defined band contour.

(a) *The Region* <7.5 eV; *Ionization of the* 'd' *Shell.*—Only three of the investigated complexes, namely $[Cr(S_2CNEt_2)_3]$, $[Co(S_2CNEt_2)_3]$, and $[Ni(S_2CNEt_2)_2]$, showed p.e. bands at energies of *ca.* ⩽7 eV; we take this as an indication that such bands arise from ionization of orbitals of mainly metal '*d*' character, at 7.02 eV from $^4A_2(t_{2g}{}^3)$ of Cr^{III}, at 6.95 and 7.13 eV from the two highest orbitals of the d^8 configuration of Ni^{II}, and at 6.67 eV from the pseudo-octahedral d^6 configuration of Co^{III}. As to the region 7—9.5 eV, where all the complexes exhibited a series of bands, with somewhat different profiles, a hint to the assignment is suggested by the work of Guimon *et al.*[5] on the p.e. spectrum of *S*-methyl dimethyldithiocarbamate. They reported a

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

[1] C. Cauletti and C. Furlani, *J. Electron Spectroscopy*, 1975, **6**, 465.

[2] C. Cauletti and C. Furlani, unpublished work.

[3] A. Flamini, E. Semprini, C. Furlani, and M. V. Andreocci, unpublished work.

[4] G. D. Thorn and R. A. Ludwig, 'The Dithiocarbamates and related Compounds,' Elsevier, Amsterdam, 1962.

[5] C. Guimon, D. Goubeau, G. Pfister-Guillonzo, L. Åsbrink, and J. Sandström, *J. Electron Spectroscopy*, 1974, **4**, 49.

series of bands between 8 and 10 eV, assigned to ionizations of the sulphur lone pairs and of the highest π orbitals, mainly localized on the sulphur atoms. Since such bands are expected to shift to lower orbital energies on involvement of the corresponding orbitals in dative co-ordination bonds, ionization peaks occurring at $\leqslant 7$ eV should have a different origin, and are more plausibly associated with ionization of '*d*' orbitals. This assignment is further supported by the relatively lower intensity of the peaks in this region, consistent with the smaller cross section for the ionization of metal '*d*' than of sulphur '*p*' orbitals.[6]

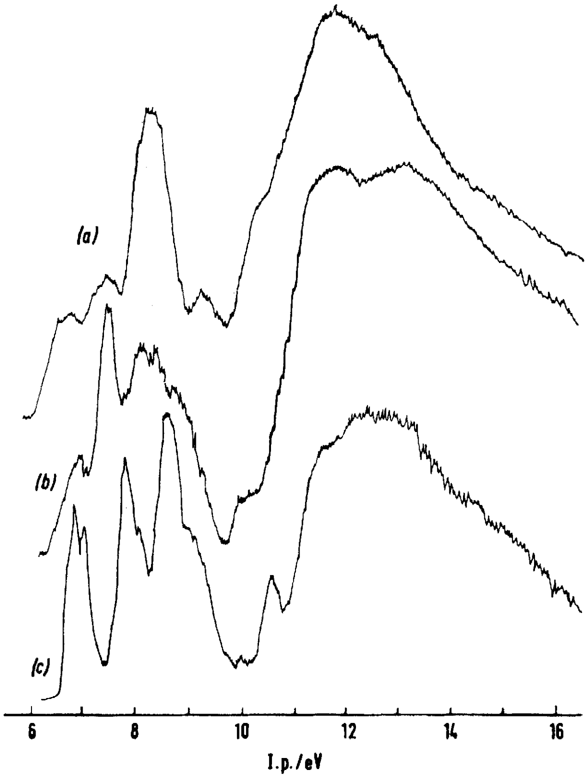

FIGURE 1 He(I) photoelectron spectra of: (*a*) $[Co(S_2CNEt_2)_3]$; (*b*) $[Cr(S_2CNEt_2)_3]$; (*c*) $[Ni(S_2CNEt_2)_2]$

Lower-symmetry splitting effects were not evident in the p.e. bands of $[Cr(S_2CNEt_2)_3]$ and $[Co(S_2CNEt_2)_3]$, although an effective symmetry D_3 should split pseudo-octahedral d t_{2g} levels according to $t_2 \rightarrow a_1 + e$; however, a more extensive mixing of ligand and metal '*d*' orbitals probably occurs in the states of lower i.p. of $[Co(S_2CNEt_2)_3]$. In the quadratic chromophore of the planar nickel(II) complex, the effective ligand field of symmetry D_{2h} is expected to split the '*d*' orbitals into four levels, of which at least the two or three of higher energy are contained under the bands at **6.95** and **7.13** eV; similar patterns appear in the p.e. spectra of other quadratic $[NiS_4]$ complexes.[1,3]

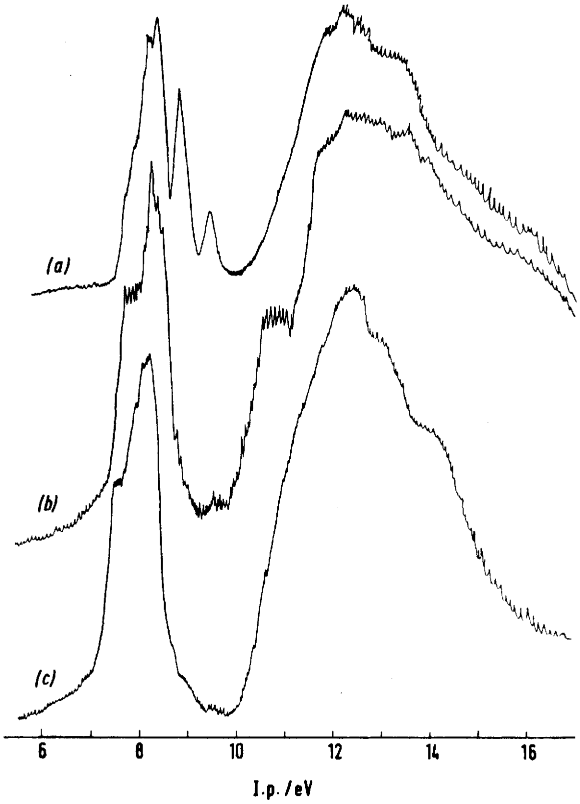

FIGURE 2 He(I) photoelectron spectra of: (*a*) $[Zn(S_2CNEt_2)_2]$; (*b*) $[Fe(S_2CNEt_2)_3]$; (*c*) $[Cu(S_2CNEt_2)_2]$

Ionization-energy data (eV) * for some diethyldithiocarbamato-complexes

$[Ni(S_2CNEt_2)_2]$	6.95		7.13	7.84	8.10		8.66	9.07	
$[Cr(S_2CNEt_2)_3]$		7.02		7.48	8.15		8.42	8.83	
$[Co(S_2NEt_2)_3]$		6.67		7.35		8.25		9.45	
$[Cu(S_2CNEt_2)_2]$				7.63	(7.93)		8.13		
$[Fe(S_2CNEt_2)_3]$				7.75 (7.69) (7.85)		8.19		8.39	
$[Zn(S_2CNEt_2)_2]$					8.13		8.31	8.75	9.41

* Shoulders are given in parentheses.

Early p.e. peaks specifically, or mainly, due to '*d*' ionizations were either absent or not clearly identified in the spectra of the dithiocarbamates of Fe^{III}, Cu^{II}, and Zn^{II}. This is in line with the trend of decreasing '*d*' orbital energies with increasing atomic number, which is generally observed also in other series of transition-metal complexes, although not always in a simple monotonous

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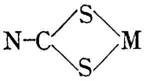
[6] S. Evans, J. C. Green, and S. E. Jackson, *J.C.S. Faraday II*, 1972, 249.

way. Actually, ' *d* ' ionizations are reported at $\geqslant$16 eV for zinc compounds, although the investigated molecules (linear dihalides and dialkyls) [7-10] are not necessarily comparable to pseudotetrahedral [$Zn(S_2CNEt_2)_2$]. Our zinc spectrum showed at most a band at 9.41 eV, which is however not likely to correspond to ionization of the pseudo-tetrahedral $d\ t_2$ levels and could be related to one of the low-symmetry split products of the co-ordination bond orbital n_+ [see section (b)].

Less obvious is the absence of distinct ' *d* ' ionization peaks from the spectra of [$Fe(S_2CNEt_2)_3$] and [$Cu(S_2CNEt_2)_2$], where all the ' *d* ' ionizations are apparently masked under the broad unresolved envelope of ligand orbitals between *ca.* 7.5 and 9.5 eV. This is even more surprising since Cu^{II} has a single antibonding b_{2g} (D_{4h}) electron of presumably low i.p., which is actually not observed below 7.5 eV [compare 6.95 eV for the highest, non-σ-bonding, ' *d* ' level of the nickel(II) complex]; again however the same behaviour is observed in analogous, nearly quadratic, copper(II) chromophores such as β-diketonates and their thio- and dithio-analogues.[2]

(b) *The Intermediate-energy Region; Ionization of Co-ordination Bond Orbitals.*—The bands at i.p. values between *ca.* 7.5 and 9.5 eV are assigned, as anticipated in the preceding discussion, to ionization of orbitals mainly derived from ligand orbitals, predominantly $3p$ orbitals of the donor sulphur atoms, which are the main ingredients of three types of molecular orbitals, *i.e.* for each ligand two π orbitals of the conjugated π system , two M–S σ bonds, and two S–C σ bonds (the latter presumably at lower orbital energies). In fact, CNDO calculations on the ligand [S_2CNEt_2]$^-$ suggest an orbital-energy sequence (approximate eigenvectors) $n_- > \pi_3 > n_+ > \pi_2$, which is expected to change to $\pi_3 > n_-\rightarrow\sigma_{M-S} > \pi_2 > n_+\rightarrow\sigma_{M-S}$ because of the downward energy shift of the sulphur lone-pair combinations n_+ and n_- which become co-ordinatively σ bonding in the complexes, while π_2 and π_3, being co-ordinatively π bonding, are less perturbed; further splittings are possible due to interactions among two or three ligands in the bis- or tris-chelate complexes, and are obviously larger for the σ-bonding orbitals. Actually, [$Cr(S_2CNEt_2)_3$] showed four bands, of approximately equal height and substantially unsplit, which could be accordingly assigned as π_3 (7.48), σ_{Cr-S} from n_- (8.15), π_2 (8.42), and σ_{Cr-S} from n_+ (8.83 eV). Also [$Ni(S_2CNEt_2)_2$] had a sequence of four bands in the same region; however, effects of further splitting were more evident. Compared with an expected D_{2h} splitting scheme of $\pi_3\rightarrow b_{2g} + a_u$, $n_-\rightarrow b_{1g} + b_{3u}$, $\pi_2\rightarrow b_{2g} + b_{2u}$, and $n_+\rightarrow a_g + b_{2u}$, experimentally the first (7.84) and third bands (8.66) were approximately twice as intense as the second (8.10) and fourth bands (9.07 eV). A possible assignment would identify the band at 7.84 eV with the unsplit π_3 orbital, that at 8.10 eV with the b_{3u} component of the Ni–S σ-bonding orbitals from n_-, the large band at 8.66 eV with the other component b_{1g} of n_- plus the π_2 orbitals, and the band at 9.07 eV with levels originating from n_+; it is to be recalled that the splitting of 0.56 eV between the components of n_- is close to that in nickel(II) pentane-2,4-dithionate (0.68 eV).[1]

The assignments for the other dithiocarbamates are subject to further uncertainties. In [$Co(S_2CNEt_2)_3$] there is probably stronger intermixing of metal and ligand orbitals, as reported for other cobalt(III) chelates.[11] With [$Zn(S_2CNEt_2)_2$], the closely spaced peaks between 7.69 and 9.41 eV probably account for the unsplit terms of the $\pi_3 > n_- > \pi_2 > n_+$ sequence [see section (a)], while the p.e. spectra of [$Cu(S_2CNEt_2)_2$] and [$Fe(S_2CNEt_2)_3$] showed only one, rather broad, and partly structured envelope of bands, indicating that probably all the four types of molecular orbitals hitherto discussed are grouped together in a narrow interval of energy levels between *ca.* 7.5 and 8.5 eV, where some portion of the ' *d* ' orbitals is also present. A better characterization of the electronic structure of the [S_2CNEt_2]$^-$ ligand might be achieved by investigating the effect of the substituent groups at the nitrogen; a p.e. study of [$Fe(CO)_2L_2$] (L = variously substituted dithiocarbamates) is now in progress at our laboratory.

(c) *The Region* 11—15 eV.—In all the complexes there was a clear gap, free of ionization peaks, between the previously discussed 7.5—9.5 eV region and *ca.* 11 eV. The next lowest ionized energy levels gave rise to a broad and intense p.e. band profile between *ca.* 11 and 15 eV, not significantly different in the various complexes, and showing only limited resolution evident, at most, as shoulders. This region includes most probably all the σ-bonding orbitals C–C, C–H, and C–S based on atomic ' *p* ' valence orbitals, as well as the nitrogen π-type lone pair. No attempt was made to assign features in this region.

[6/1065 *Received, 4th June,* 1976]

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