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UV Photoelectron Spectra of Some Substituted Iron Dithiocarbamates

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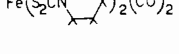
Photoelectron spectra (He(I)) are reported for several $Fe(dtc)_2(CO)_2$ complexes, which, in vapor phase under experimental p.e. spectroscopic conditions, lose their CO and behave as $Fe(dtc)_2$ (dtc^- = N,N'-disubstituted dithiocarbamate anion). p.e. Spectra are not well resolved, but can be interpreted on the ground of a comparison with already known transition-metal diethyldithiocarbamates. Substituent effects due to the groups bonded to the dithiocarbamate nitrogen are particularly large, and their possible mechanisms are discussed.

Introduction

In continuation of previous photoelectron investigations of sulfur-containing metal complexes [1, 3], including particularly transition metal dithiocarbamates [2], we have studied the He(I) p.e. spectra of some substituted dithiocarbamates of iron, prepared and characterized for the first time by N. V. Duffy and J. B. Zimmermann [4]. Our present work aims at a better understanding of the electronic structure of dithiocarbamates as ligands, and at the effect of alkyl and aryl substituents at the dithiocarbamate nitrogen, on the p.e. spectra of the corresponding complexes. The investigated complexes include:

$Fe(S_2CN(CH_3)_2)_2(CO)_2$ (I)



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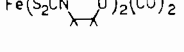

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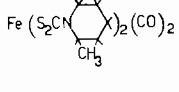
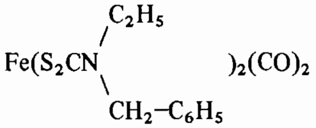


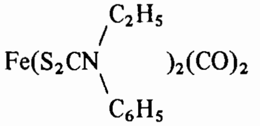
(IV)

$Fe(S_2CN(C_6H_5)_2)_2(CO)_2$ (VIII)



$Fe(S_2CN(C_2H_5)(CH_2-C_6H_5))_2(CO)_2$ (V)

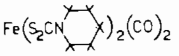
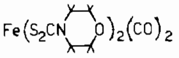
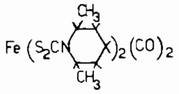
$Fe(S_2CN(CH_3)C_6H_5)_2(CO)_2$ (VI)



$Fe(S_2CN(C_2H_5)(C_6H_5))_2(CO)_2$ (VII)

While simple diethyldithiocarbamato complexes [3] have sufficient volatility and thermal stability for p.e. measurements, the present compounds undergo decompositiom under the experimental conditions of p.e. spectra; it proved namely necessary to heat the solid samples up to temperatures between 150 and 240 °C in order to achieve a sufficient vapor phase concentration in the spectrometer chamber, and at such temperatures a nearly complete loss of CO occurs. T.G. analyses confirm that the investigated products undergo around 150 °C a weight loss closely corresponding to two CO molecules. Mass spectra exhibit a very strong peak at m/e = 28 (free CO^+), and parent peaks at m/e values corresponding to the mass of the original compound minus 56 ($Fedtc_2^+$, where dtc^- = N,N'-disubstituted dithiocarbamate anion); other strong peaks occur at the above m/e value minus the m.w. of one ligand ($Fedtc^+$). Easy loss of CO is confirmed by detection of intense p.e. bands of free CO, *i.e.* by CO evolution, in the initial stage of p.e. measurements on the solid samples. As a consequence, we assume that the vapor-phase species present in the experimental measuring conditions are $Fedtc_2$ molecules containing iron in the formal oxidation state +2. Mass spectral results under conditions similar to the photoelectron spectra reported in this study show no evidence of dimeriza-

TABLE I.

Compound	Vertical I.P.s. (eV) (Shoulders in parentheses)							
$Fe[S_2CN(CH_3)_2]_3$	7.72	8.04	8.37		10.87	11.84		13.91
$Fe[S_2CN(CH_3)_2]_2(CO)_2$	(7.79)	(8.14)	8.51	(8.90)	11.02	11.92		
	(7.63)	(8.34)	8.57	(8.72)	11.31		12.88	
	(7.90)		8.64		10.24			
	(7.90)	8.26	(8.52)			11.79		
$Fe[S_2CN(C_6H_5)_2]_2(CO)_2$	7.58	(7.95)	(8.26)	9.12		12.00	12.72	13.94
$Fe[S_2CN(C_2H_5)(C_6H_5)]_2(CO)_2$	7.76	(8.01)	(8.22)	9.20	11.92	12.15	12.82	14.00
$Fe[S_2CN(CH_3)(C_6H_5)]_2(CO)_2$	7.77		(8.73)	9.42		12.80	13.76	14.48
$Fe[S_2CN(C_2H_5)(CH_2C_6H_5)]_2(CO)_2$	7.90		(8.69)	9.16	11.58			

tion to produce $(Fe(dtc)_2)_2$ in which the iron has been reported to be in a distorted trigonal bipyramidal environment [5]. In the species, $Fe(dtc)_2$, indicated in these gas phase measurements, deviations from the ideal tetrahedral environment should be even greater than distortions in $(Fe(dtc)_2)_2$ [6–8] (trigonal bipyramidal) [5] or $Fe(dtc)_3$ (octahedral) because of the small bite angle of the dithiocarbamate ligand.

Results and Discussion

P.e. Spectra

The He(I) p.e. spectra of compounds (I)–(VIII) are reported in Figures 1 and 2, and the relevant I.P. values are listed in Table I. Observed p.e. bands are generally broad and unresolved, and show a well-defined trend, with a single broad envelope, including several shoulders, between 7.5 and 8.5 eV (*I.E.*) approximately, followed by another band in the region 9.0–9.5 eV (for the phenyl-substituted compounds only), and by a much broader and more intense band system between 11 and 16 eV approximately. We shall disregard the latter band system, which is due to the ionisation of the σ_{CC}, σ_{CH}, and presumably also σ_{CS} and σ_N bonding electrons of the ligands; we shall instead concentrate our discussion on the former bands, which are more directly involved in the ionisation of the actual chromophore, hence more significant for the elucidation of its electronic structure.

In Fig. 1 we report also for comparison the p.e. spectrum of $Fe(S_2CN(CH_3)_2)_3$; it resembles clearly the previously reported spectrum of $Fe(S_2CN(C_2H_5)_2)_3$ [3] in having its first, broad peak between 7.5 and 8.5 eV, only slightly better resolved in the dimethyl derivative, and confirms that in this energy region we have to expect the ionisations of both the d electrons of iron, and the ligand bonding orbitals. We recall that, according to previous calculations [3], in the order $n_- < \pi_3 < n_+ < \pi_2$, which is expected to pond to the two highest occupied orbitals of the π system of the conjugated skeleton NCSS, and to two linear combinations of the in-plane sulfur lone pairs, in the order $n_- < \Pi_3 < n_+ < \pi_2$, which is expected to become $\pi_3 < n_- < \pi_2 < n_+$ in the actual metal complexes, since the n electron pairs become σ-bonding in the chelate rings and are therefore shifted to lower orbital energies, or to higher *I.E.'s*. At least two, if not more, of the above types of ligand orbitals are present under the envelope between 7.5 and 8.5 eV, together with the (predominantly) d-metal occupied orbitals, in such a way that no single identification or specific assignment is possible.

Turning to the p.e. spectra obtained from our substituted iron dithiocarbamates, a very similar situation holds for the first ionisation region, where again the broad band between 7.5 and 8.5 eV is to be considered as an evelope comprising the ionisations of metal d levels, and of some of the σ and π ligand orbitals altogether. Such broad band contains all low-energy ionisations for the alkyl-substituted iron dithiocarbamate complexes; in addi-

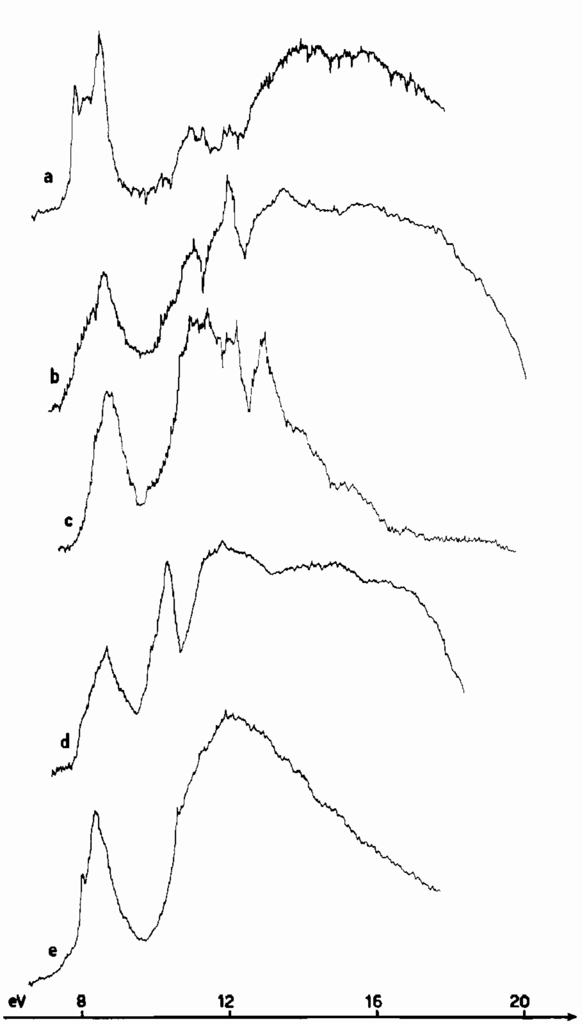
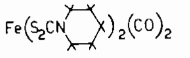


Figure 1. He(I) photoelectron spectra assigned to the species; (a) $Fe(S_2CN(CH_3)_2)_3$, (b) $Fe(S_2CN(CH_3)_2)_2$ (I),



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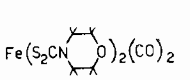

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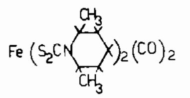


(IV)

(Roman numerals in the same order as the parent $Fe(dtc)_2(CO)_2$ compounds).

tion, the aryl-substituted complexes show another band or band system beginning slightly above 9 eV, clearly assigned as the first ionisation of the conjugated π system of the benzene rings (compare 9.24 eV for benzene itself [9]). The morpholine derivative (III) is unique in this series in showing a ionisation peak also around 10 eV; this is obviously related to the oxygen π lone pair, whose *I.E.* (10.24 eV) compares favorably with that of other compounds containing ethereal oxygen, *e.g.* 10.57 eV in ethylene oxide [10].

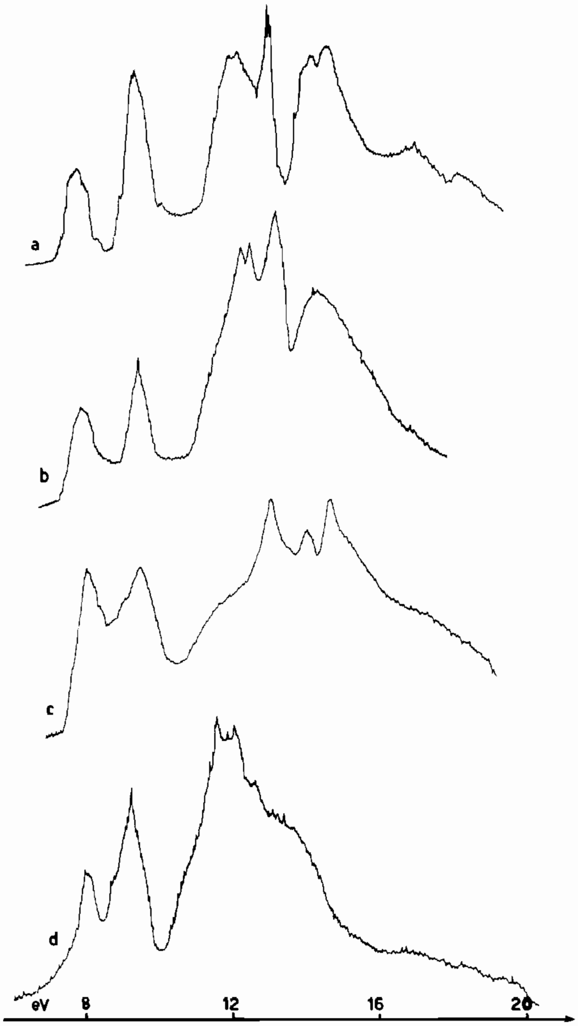
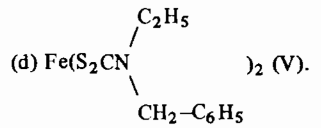


Figure 2. He(I) photoelectron spectra assigned to the species: (a) $Fe(S_2CN(C_6H_5)_2)_2$ (VIII), (b) $Fe(S_2CN(C_2H_5)C_6H_5)_2$ (VII), (c) $Fe(S_2CN(CH_3)C_6H_5)_2$ (VI),



$$(d)\ Fe(S_2CN\overset{C_2H_5}{\underset{CH_2-C_6H_5}{<}})_2\ (V).$$

(Roman numerals in the same order as the parent $Fe(dtc)_2(CO)_2$ compounds).

Substituent Effects

The nature of the substituent groups on the nitrogen atom of the dtc ligands exerts a remarkably large effect on the energy of the lower ionisation processes comprised within the broad envelope in the region 7.5–8.5 eV.

The data collected in Table II indicate that the observed ionisation potentials decrease with changing nitrogen organic substituents in the order (aromatic)$_2$ < (aromatic)(aliphatic) < (aliphatic)$_2$ (In studies of the change in the force constant for the CO stretching frequency of the *cis* carbonyls of the parent $Fe(dtc)_2(CO)_2$ compounds, the separation of the results into these three separate classes was also evident [11]). The compounds with aliphatic substituents have E_{max} of 7.5–7.8 eV, decreasing with the number of phenyl groups bonded to the nitrogen. The presence of phenyl groups lowers therefore considerably the first ionisation energies with respect to aliphatic dithiocarbamato complexes, a fact which can be possibly related to a stabilisation of the ionized species by effect of π electron delocalisation, or alternatively to deviations from Koopmans' behaviour, since the larger mobility of the aromatic π electron systems will obviously favor a more rapid electronic rearrangement after ionisation in the +1 species.

Specific effects for single compounds within each group include: (i) (IV) has I.E. lower by 0.31 eV than (II); such a considerable splitting is probably due to a complex mechanism, and could be related to the electron-releasing effect and to the steric hindrance of the two extra methyl groups in the former compound; (ii) (III) has the highest I.P. within the first group of compounds, probably because of the inductive electron-attracting effect of oxygen; (iv) within the aromatic group of compounds, ionisation energies decrease as the phenyl groups come closer to the nitrogen, and increase in number, *i.e.* as the availability of interactions with the aromatic systems becomes larger. This is generally in line with the suggested interpretations, although it has to be recalled that we consider, for the present correlations, just the maximum intensity peak in the low-energy envelope, which has no precise assignement, while small energy or intensity variations among all component peaks might well change the overall shape, and make more detailed correlations virtually impossible.

Experimental

The $Fe(dtc)_2(CO)_2$ compounds investigated were kindly supplied by N. V. Duffy. UPS spectra were measured on a Perkin Elmer PS 18 instrument, calibrated with argon 3p and xenon 5p signals.

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