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Ultraviolet Photoelectron Spectra of 'Octahedral' (Diethyldithiophosphato)metal(III) Complexes

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Introduction

The O,O′-diethyldithiophosphate (dtp) anion ligand forms very intriguing classes of coordination complexes [1]. The remarkable decrease (with respect to the free ion) of the interelectronic repulsion parameters found in these complexes [1] is evidence of a strong covalent nature of the metal–ligand bonding. Photoelectron (PE) spectroscopy may provide direct evidence as to how covalency effects influence the bonding.

We report here the He–I excited PE spectra of 'octahedral' $M(dtp)_3$(M = In, Cr, Co, Rh) complexes [2].

Experimental

The complexes have been prepared following standard methods [3, 4]. They were purified by crystallization followed by sublimation *in vacuo*. Their purity was checked by mass spectra.

Spectra were run on a Perkin-Elmer PS 18 spectrometer modified by including a hollow cathode discharge lamp (Helectros Developments). They were calibrated by reference to peaks due to admixed inert gases and to He $1s^{-1}$ self-ionization.

Pertinent ionization energy (IE) data are reported in Table I. Present data slightly differ from those reported preliminarily [2]. These minor differences are basically due to more accurate calibration of the low IE region (using He $1s^{-1}$ self-ionization).

Discussion

Low IE regions (up to 11 eV) of the He–I PE spectra of the complexes $M(dtp)_3$ (M = In, Cr, Co, Rh) are reported in Fig. 1. The higher IE regions will

TABLE I. Pertinent IE Data of $M(dtp)_3$ Complexes (eV).

Complex	Band Label	IE	Assign.
$In(dtp)_3$	a′	8.3	$e(n_-)$
	a	8.75	$a_2(n_-)$, $e(\pi_-)$, $a_1(\pi_-)$
	b	9.43	$e(\pi_+)$, $a_2(\pi_+)$
	c	10.59	O 2p lone pairs
$Cr(dtp)_3$	x	7.71	metal d
	a	8.45	$a_2(n_-)$, $a_1(\pi_-)$, $e(\pi_-)$
	b	9.10	$e(\pi_+)$, $a_2(\pi_+)$
	b′	9.35	$e(n_-)$
	c	9.9	O 2p lone pairs +
	c′	10.4	n_+ ligand orbitals (?)
$Co(dtp)_3$	x	7.95	metal d
	a	8.63	$a_2(n_-)$, $a_1(\pi_-)$
	b	9.0	$e(\pi_+)$, $a_2(\pi_+)$
	b′	9.56	$e(\pi_-)$, $e(n_-)$
	c	10.58	O 2p lone pairs
$Rh(dtp)_3$	x	7.70	metal d
	a	8.22	ligand n_-, π_-, π_+
	b	9.33	
	c	10.6	O 2p lone pairs

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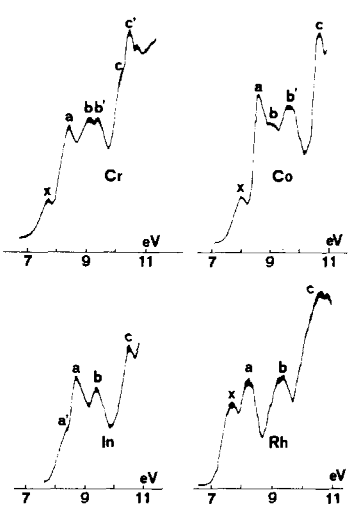

Fig. 1. He–I PE spectra of the studied complexes. Low IE region.

not be discussed because of the diffuse nature of this part of the spectra. Three main bands (labelled *a, b, c*) are present in the low IE region. In In(dtp)$_3$ the band *a* presents a shoulder (*a'*) in the low IE side. In Cr(dtp)$_3$ and Co(dtp)$_3$ the band *b* is split into two components (*b, b'*). Furthermore, the spectra of Cr(dtp)$_3$, Co(dtp)$_3$ and Rh(dtp)$_3$ show at their onset an additional band (labelled *x*), whose intensity and IE dpend upon the nature of the metal atom. Band *c* in all the spectra we propose to represent ionizations of the oxygen 2p lone pairs of the O–C$_2$H$_5$ groups. The absence of this band in the spectra [5] of some M[(CH$_3$)$_2$PS$_2$]$_3$ complexes vindicates the assignment.

The outmost MOs of the presently studied complexes can be usefully described in terms of the appropriate ligand basis set perturbed by interacting with metal valence orbitals. The electronic structure of (R$_2$PS$_2$)$^-$ anion ligands (R = F, O-C$_2$H$_5$) has been already discussed [6, 7]. The four upper filled MOs have been described as in- and out-of-phase combinations of sulfur lone pairs lying in the S–P–S plane (hereafter n$_+$ and n$_-$) as well as combinations of lone pairs orthogonal to the same plane (π_+ and π_-). Their energy ordering is $n_- > \pi_- > \pi_+ > n_+$. This ordering is also in agreement with our CNDO calculations run for dtp$^-$ anion. However, present PE spectra do not show evidence of bands related to n$_+$ ligand orbitals below 11 eV.

In the M(dtp)$_3$ complexes the ligands are arranged in a trigonally distorted octahedral array. It has been shown [8] that D$_3$ point group properly describes the complexes.

In this point group pertinent ligand orbitals transform as

$$n_- \longrightarrow e + a_2$$
$$\pi_- \longrightarrow e + a_1$$
$$\pi_+ \longrightarrow e + a_2$$

The energies of these symmetry orbitals can be differentiated firstly by operation of non-bonded interligand interactions. However, consideration on interligand group-overlaps indicates that such interactions are important only for symmetry orbitals related to n$_-$ manifold. They result in the more stable (than (e(n$_-$)) a$_2$(n$_-$) MO. Further metal–ligand interactions can explain fine details of various PE spectra.

In In(dpt)$_3$ metal–ligand bonding only involves the In 5sp atomic orbitals. Actually, In 4d electrons have been shown [9] to be 'core-like' and sensitive to ligand field only *via* electrostatic perturbation. Group-overlap consideration indicates that significant interactions can involve a$_2$(n$_-$), e(n$_-$) ligand orbitals and In 5p atomic orbitals. However, interactions between orbitals of a$_2$ symmetry are the most favourable. All these arguments lead to the assignment reported in Table I. The shoulder *a'* is taken to represent the e(n$_-$) non-bonding MO while the main band *a* relates to ionizations of a$_2$(n$_-$), e(π_-) and a$_1$(π_-) MOs. Obviously, it is difficult to ascertain, at this stage, whether the energy differentiation of e(n$_-$) and a$_2$(n$_-$) MOs depends simply on interligand interaction or if some bonding interaction could be also cooperative.

In transition metal complexes, the metal–ligand bonding involves metal d atomic orbitals. The e(n$_-$)–e(d) interaction is dominant, but also the e(π_-)–e(d) interaction may be of importance. As a consequence, we expect a remarkable stabilization of the e(n$_-$) MO. The assignments we propose in Table I reflect these considerations: the band *a* in Cr(dtp)$_3$ represents ionizations of non-bonding a$_2$(n$_-$), a$_1$(π_-) and e(π_-) MOs. The following band system *b,b'* we take to represent the remaining e(π_-), a$_1$(π_+) and e(π_+) MOs; the nearly comparable intensity of bands *a* and *b* + *b'* (at variance to the case of In(dtp)$_3$) is in tune with this overall assignment. In more detail, we believe that the band *b'* in Cr(dtp)$_3$ and Co(dtp)$_3$ relates to the bonding e(n$_-$) MO. In fact, the higher IE shift associated with band *b'* on passing from Cr to Co complexes reproduces well the expected higher covalencey [10] in the Co complex. Moreover, the roughly constant IE of band *b* along the same sequence agrees well with the non-bonding nature of corresponding Mos.

In addition, it must be noticed that band *b'* becomes more intense in Co(dtp)$_3$. This may be the consequence of a shift toward higher IE of the e(π_-) MO resulting from some π anti-bonding effect. As far as the spectrum of Rh(dtp)$_3$ is concerned, a general shift toward lower IE is observed. This is likely to be due to the more expanded metal 4d subshells resulting in a lower field experienced by the electrons localized in the chromophore group of the ligand.

Finally, we comment on the band *x* appearing at the onset of spectra of transition metal complexes.

Preliminary measurements [5] indicate that the intensity of this band dramatically increases under He–II radiation. This is a clear evidence for dominant metal contribution in the corresponding MO. In this context it is worthy to note that the 'd' band was not evident in the spectrum [11] of the trisacetylacetonato–Co(III) complex. The appearance of the 'd' band in complexes of sulphurated ligands could be a consequence of the higher (than in β-diketonato complexes) IEs associated to nominally ligands MOs, even though some specific role played by the increased covalency cannot be dismissed.

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