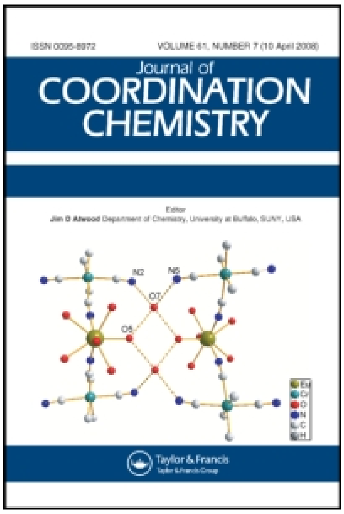

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THE RELATIVE ORBITAL ENERGIES OF METAL AND LIGAND ELECTRONS IN SOME TRIS(HEXAFLUOROACETYLACETONATO) TRANSITION-METAL COMPLEXES

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The He(I) photoelectron spectra of the first row transition metal tris(hexafluoroacetylacetonato) M(III) complexes are described, and the trends in the orbital energies of metal and ligand electrons are elucidated.

Despite the rapid development of inorganic UV photoelectron (PE) spectroscopy, there have been few systematic investigations of extended series of related transition metal compounds. Moreover, the limited amount of published work on such materials has concerned, for the most part, systems incorporating relatively 'soft' ligand species such as CO, PF_3 and π-cyclopentadienyl. We have studied[1] the PE spectra of a wide range of complexes of the hexafluoroacetylacetonato ligand (*hfa*$^-$),* the primary motivation, in the case of the transition metal complexes, having been to explore the trends in *d* orbital energies in a set of isostructural molecules. We report here some results obtained for the tris-chelates, M(*hfa*)$_3$.†

The helium-(I) spectrum‡ of one of these compounds, Ti(*hfa*)$_3$ is reproduced in Figure 1. The high ionisation energy (IE) structure above about 14 eV is characteristic of the M(*hfa*)$_3$ system (as may be seen by reference to the previously reported spectrum of Fe(*hfa*)$_3$),[4] and is similar to that observed in the *enol* form of the free protonated ligand:[6] it arises mainly from ionisation of the ligand σ electron framework and the fluorine 'lone-pair' electrons. The region between about 10 and 13 eV is also broadly similar in each of the spectra, and these bands (B–D in Figure (1)) are believed to derive from the leading metal-ligand bonding orbitals. Comparison with the PE spectrum of Sc(*hfa*)$_3$ reveals that the additional band (A) observed at 7.98 eV in the Ti(*hfa*)$_3$ spectrum must be due to ionization of the single unpaired electron localised mainly on the metal. The situation is reminiscent of the relationship between the PE spectrum of $TiCl_4$ and VCl_4,[7] where the latter compound exhibits a band at 9.41 eV with no counterpart in the $TiCl_4$ spectrum.

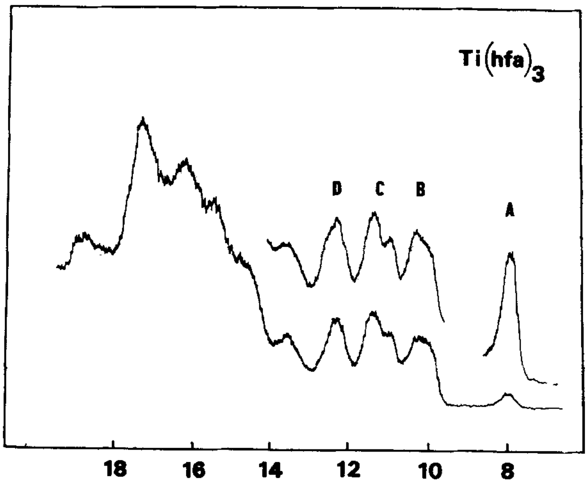

FIGURE 1 The He(I) photoelectron spectrum of Ti(*hfa*)$_3$ (the electron count rate is plotted against ionisation energy in eV).

The '*d* ionizations' are also clearly evident in the PE spectra of V(*hfa*)$_3$ and Cr(*hfa*)$_3$, though at chromium the band in question partially overlaps the first 'ligand band' (B):* there is no evidence for

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* This work will be described in greater detail elsewhere.[1]

† Lloyd[2,3] has published the low ionisation energy parts of the PE spectra of Fe(*hfa*)$_3$, Cr (*hfa*)$_3$ and Co(*hfa*)$_3$ while the full He(I) spectrum of the iron complex has been reported by the present authors.[4]

‡ The PE spectra were measured on the spectrometer described by Evans *et al.*[5]

* In this respect our assignment of the Cr(*hfa*)$_3$ spectrum agrees with that proposed by Lloyd.[3]

a large trigonal splitting of the e and a_1 d levels derived from the t_{2g} orbitals of octahedral symmetry.* The vertical ionization potentials of these molecules are: V(*hfa*)$_3$ 8.68 eV, Cr(*hfa*)$_3$ 9.53 eV.

In each of the PE spectra of Sc(*hfa*)$_3$, Ti(*hfa*)$_3$ and Cr(*hfa*)$_3$, the structure between 10 and 13 eV consists of three distinct bands, the central one of which (labelled C in Figure (1)) shows an asymmetrical splitting which increases somewhat and becomes progressively more resolved on going from scandium to chromium. This splitting is, however, clearly absent in the spectrum of Al(*hfa*)$_3$.[1] Simple theoretical arguments,[1] and a close comparison with the PE spectra of hexafluoroacetylacetone and related species, indicate that the second PE band (C) of Al(*hfa*)$_3$ results from ionization of the near degenerate e and a_2 bonding molecular orbitals which may be constructed from metal p orbitals and the out-of-phase combinations of oxygen 'lone-pair' orbitals (n_-) on each of the three bidentate ligands. The splitting observed in the corresponding bands of the transition metal M(*hfa*)$_3$ molecules may then be understood in terms of d, rather than p, valence orbitals on the central metal atom, since the a_2 molecular orbital should now be relatively non-bonding and may be sufficiently separated in energy from the e bonding orbital to permit the resolution of two distinct PE bands. This is just what we observe, the less intense component of band C appearing at lower ionization energy.† The first ligand band, B, almost certainly arises from unresolved ionizations of another pair of e and a_2 molecular orbitals, but according to the theory, these orbitals should be only rather weakly bonding in Al(*hfa*)$_3$, corresponding essentially to the third orbital (π_3) of the ligand π-system, and only slightly differentiated in energy in the transition metal M(*hfa*)$_3$ species.

The compounds Ti(*hfa*)$_3$, V(*hfa*)$_3$ and Cr(*hfa*)$_3$ form a series in the ligand field configuration, $t_{2g}{}^n$, although this must be significantly perturbed by the trigonal field present. The remaining member of this series is Co(*hfa*)$_3$, which exhibits a particularly complex spectrum with six distinct band maxima in the 10–13 eV region. A detailed comparison with the PE spectra of the preceeding members of the t_{2g} series indicates without doubt that the d ionizations occur at a higher energy than the ionizations of the predominantly ligand electrons, as electron-impact spectroscopy has suggested.[11] It is also clear that the e and a_1 trigonal components of the t_{2g} shell are substantially separated in energy: the appearance of six, instead of five band maxima in the low energy region of the Co(*hfa*)$_3$ PE spectrum is otherwise very difficult to understand. Now, in the case of Ti(*hfa*)$_3$, V(*hfa*)$_3$ and Cr(*hfa*)$_3$, a linear relationship is found between the a_2—e (n_-) splitting discussed above and the inverse of the mean energy separation of the metal d and the ligand a_2 and e levels. Extrapolation to the Co(*hfa*)$_3$ case, and independent theoretical considerations, suggest an assignment which implies a trigonal splitting of some 0.6 eV for the metal e and a_1 orbitals.*

Our conclusion that the d electrons of Co(*hfa*)$_3$ have orbital energies lower than the highest ligand level, π_3, is perhaps surprising at first, especially since it appears to be at variance with the results of conventional visible and UV spectroscopy, from which it is clear that the first ligand field transitions, $t_{2g} \rightarrow e_g$, occur at lower energy than the $\pi_3 \rightarrow e_g$ or $n_- \rightarrow e_g$ charge-transfer transitions.[12] There is, however, no conflict of evidence: the *d–d* bands are expected to appear first in the ordinary optical spectrum because the *d–d* electron repulsion integrals, $J(t_{2g}, e_g)$, are likely to be very much larger than any ligand-metal coulomb integrals such as $J(\pi_3, e_g)$.†

The main result of this work is illustrated by Figure (2), where the various orbital ionisation energies for the $t_{2g}{}^n$ M(*hfa*)$_3$ species are plotted across the first transition series. There is relatively little variation in the energies of the molecular orbitals composed mainly of ligand π_3 and n_-, but in marked contrast, the t_{2g} d orbitals are rapidly

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* The molecular point group is taken to be D_3, so the metal d orbitals transform as $a_1 + 2e$, and the p orbitals as $a_2 + e$. We have assumed that the M(*hfa*)$_3$ species have the same molecular symmetry as the analogous tris(acetylacetonato) complexes, M(*acac*)$_3$:[8] with the exception of Mn(*acac*)$_3$, which has a highly distorted molecular structure, these have geometries corresponding quite closely to an octahedral configuration of oxygen atoms about the central metal atom, though the actual molecular symmetry can never of course be higher than D_3.

† We invoke Koopmans theorem[9] and make limited use of the familiar idea that the relative PE band intensities should reflect the occupancies of the two subshells, e and a_2.[10]

* However, the energy separation of the a_1 and e orbitals determined in this way will not be simply related to the separation of the corresponding ligand field levels.

† The energy of the optical transition $a \rightarrow b$ is of the order $\epsilon_b - \epsilon_a - J(a,b)$, where ϵ_a and ϵ_b are average of configuration orbital energies. The electron repulsion integrals, $J(a,b)$, thus determine the relationship between orbital energy differences and optical excitation energies.

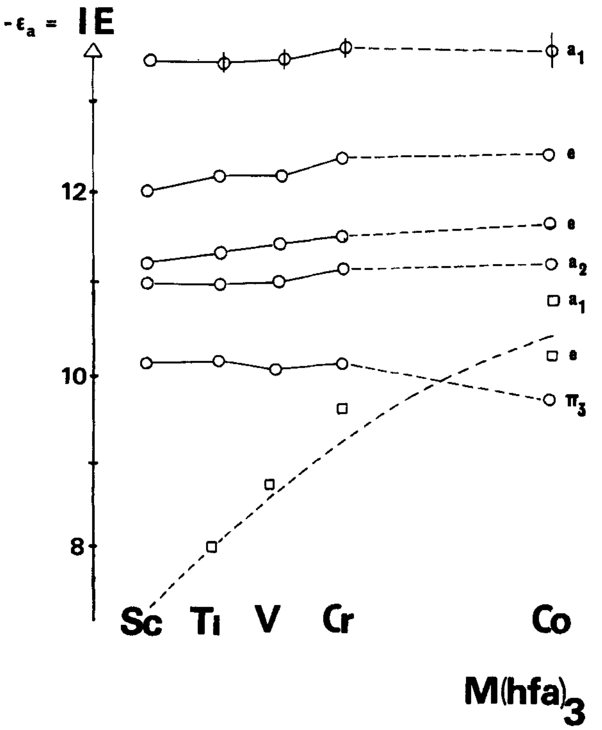

FIGURE 2 Orbital ionization energies in the $t_{2g}{}^{n}$ M(*hfa*)$_3$ complexes. (□ *d* ionization, o ligand ionization.)

tabilised as we traverse the series.* This progressive stabilisation of the *d* electrons, in accordance with the simplest expectations,[13] is not however always observed. In complexes of the softer ligand π-cyclopentadienyl, for example, we have found that the trends in *d* orbital energies are highly complex[14,15]: thus, the average *d* ionization energy in $(\pi\text{-C}_5\text{H}_5)_2\text{V}$ turns out to be greater than in $(\pi\text{-C}_5\text{H}_5)_2\text{Cr}$.

The PE spectra of the high-spin† compounds, Fe(*hfa*)$_3$ and Mn(*hfa*)$_3$, are less informative, the low IE region being rather more diffuse for each of these materials. As an interpolation between Cr(*hfa*)$_3$ and Co(*hfa*)$_3$ would lead us to expect, the *d* ionizations are largely obscured by the ligand bands. Indeed, the only evidence for the *d* ionizations is a very weak shoulder at *ca.* 9.1 eV on the low IE side of the first ligand band of Mn(*hfa*)$_3$: this structure probably relates to the ionization of the *eg* electrons—or, strictly, their counterparts in trigonal, or possibly rhombic symmetry.[8] The conclusion that the partially occupied *d* orbitals may ionize at higher energy than the filled ligand levels is unusual, but is intelligible in terms of a much larger spin pairing energy for the *d* orbitals as compared with, for example, ligand π_3. We hope to learn more about the electronic structures of these two species by investigating the ruthenium, osmium and rhenium analogues.

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* The curve through the *d* ionisations (□) in Figure (2) is intended to represent the trend in the *average of configuration* ionisation energies. It is drawn at lower IE than the points for V(*hfa*)$_3$ and Cr(*hfa*)$_3$ in order to make some allowance for the exchange stabilization of the neutral molecules relative to the ion states.

† We assume that Fe(*hfa*)$_3$ and Mn(*hfa*)$_3$ have the same ground electronic configurations as the M(*acac*)$_3$ analogues.[16]