Study of the Metal-Oxygen Bond in Simple Tris-chelate Complexes by He(I) Photoelectron Spectroscopy

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Vapour-phase He(I) photoelectron spectra are reported for a variety of tris-chelates of the form ML_3, where L is the enolate anion of a β-diketone (commonly hexafluoroacetylacetone) and M is one of the metals: Al, Ga, Sc, Ti, V, Cr, Co, Mn, Fe, Ru. The spectra yield information concerning the details of the metal–ligand bonding and, in the case of the transition metal complexes, information about the relative energies of the metal d and ligand orbitals.

We report the results of an extended investigation of the vapour-phase He(I) photoelectron (PE) spectra of tris-(β-ketonato) complexes. The primary aim of this work has been to explore, by the use of Koopmans' approximation,[1] the leading valence MOs of these systems and thereby gain information concerning the details of the metal–ligand binding. The hexafluoroacetylacetonato complexes, being highly volatile materials, are particularly amenable to gas-phase studies. Some of our earlier results have already been described.[2, 3]

EXPERIMENTAL

The β-diketones, obtained from commercial sources, were triply distilled under reduced pressure before use. For the most part, the β-diketonato complexes were synthesized by well established methods [4-13] and purified by recrystallization followed by sublimation under vacuum. The following details are particularly important:

Co(hfa)$_3$ was prepared by the reaction of CoF$_3$ and hexafluoroacetylacetone using NaF as a scavenger for the liberated HF. The preparation from a Co(II) salt using hydrogen peroxide as an oxidizing agent [14] is unduly hazardous.

Be(hfa)$_2$ was obtained by refluxing anhydrous BeCl$_2$ with hexafluoroacetylacetone in rigorously dried benzene or CCl$_4$. The product is extremely volatile (subliming at 30°C, 10^{-2} Torr, very easily) and is therefore unusually dangerous.

Mn(hfa)$_3$ could be obtained only in very poor yield by the literature [12] preparation, which involves a ligand exchange reaction between tristrifluoroacetylacetonato-Mn(III) and hexa-fluoroacetylacetone. A more satisfactory method was found with the reaction of *braunite* Mn$_2$O$_3$ and hexafluoroacetylacetone in petroleum ether. A dark green solution is obtained after some 24 h; this deposits Mn(hfa)$_3$ on cooling to -120°C. The dark green crystals sublime smoothly at 50°C, 10^{-3} Torr.

The tris-hexafluoroacetylacetonato complexes of Sc, V, and Ga have apparently not been reported previously.

Sc(hfa)$_3$ was prepared by gently refluxing hexafluoroacetylacetone with commercial ScCl$_3 \cdot$ 6H$_2$O in CCl$_4$ for 12 h. (It is necessary to remove a substantial quantity of white material, presumably the hydrate of hexafluoroacetylacetone, which collects in the reflux

condenser.) White crystalline Sc(hfa)$_3$ was obtained from the resultant solution after concentration and cooling. The material is rather hygroscopic and requires careful drying. It sublimes very easily at 50°C, 10^{-3} Torr.

V(hfa)$_3$ and Ga(hfa)$_3$ were prepared by refluxing anhydrous VCl$_3$ and Ga$_2$Cl$_6$ respectively with hexafluoroacetylacetone in carefully dried benzene. The light orange crystals of Ga(hfa)$_3$ were also prepared from Ga$_2$Br$_6$ and are particularly volatile. V(hfa)$_3$ was obtained as dark brown crystals, subliming readily at 60°C, 10^{-3} Torr and, like Ti(hfa)$_3$, which has similar volatility characteristics, was sensitive to air.

The purity of these compounds was established by melting point, infra-red and mass-spectroscopic measurements.

RESULTS

Vapour-phase He(I) PE spectra of the β-diketones, fig. 1-4, the M(hfa)$_3$ complexes, fig. 5, 7-11, 13, 15a, 16a and 17 and of the beryllium bis-chelates, Be(hfa)$_2$ and Be(acac)$_2$, fig. 6, were measured in a spectrometer having a 127° electrostatic analyzer combined with a retarding field.[15,*] The hexafluoroacetylacetonato complexes proved adequately volatile for room temperature study, yielding electron count-rates of up to 500 counts/s. Mn(hfa)$_3$ proved rather difficult to study, however, causing a progressive deterioration of the performance of the analyzer (though it recovered after prolonged pumping). Its spectrum, fig. 15b, was accordingly also measured on a commercial Perkin-Elmer PS 15 spectrometer which does not contain carbon-coated equipotential surfaces: however, the dynode multiplier used in this instrument suffered some damage. The spectrum of Fe(tfa)$_3$ (fig. 16) was also recorded on both instruments, while the spectra of Al(tfa)$_3$ and Cr(tfa)$_3$ (fig. 12) were obtained only on the PS 15.[†]
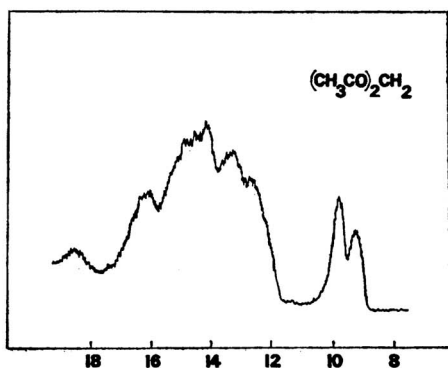

FIG. 1.—The He(I) PE spectrum of Acetyl-
acetone.
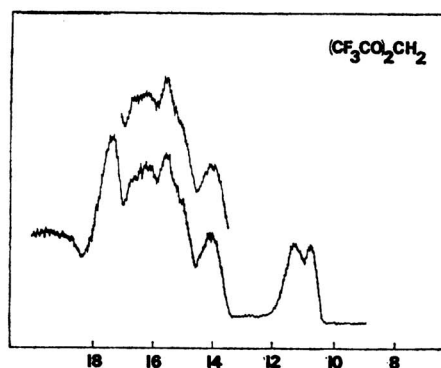
FIG. 2.—The He(I) PE spectrum of Hexa-
fluoroacetylacetone.

The tris(acetylacetonato) complexes of the transition elements are however insufficiently volatile for study at room temperatures. The He(I) PE spectra of Cr(acac)$_3$, Fe(acac)$_3$, Fe(dpm)$_3$, and Co(acac)$_3$ were accordingly investigated using another spectrometer,[16] based on a 90° electrostatic analyzer and incorporating a target chamber heated by fluid circulating in a surrounding jacket. This arrangement has so far permitted measurements up to about 200°C. The spectra presented here (fig. 14 and 16) were recorded between 96°C and 100°C.

* Abscissae for all spectra illustrated in this paper are quoted in eV.

† The scanning mode of the PS 15 (analyzer potential) is such that the electron count rates must be divided by the electron kinetic energy to render the spectra comparable with those obtained on the spectrometer of ref. (15).
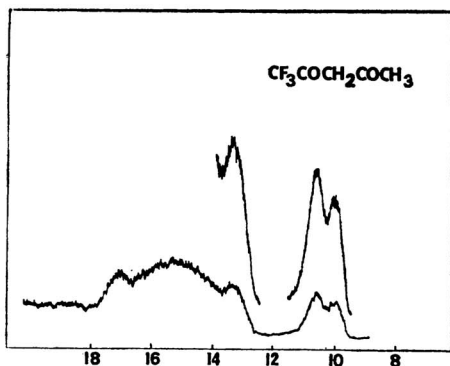
CF₃COCH₂COCH₃

FIG. 3.—The He(I) PE spectrum of Tri-fluoroacetylacetone.
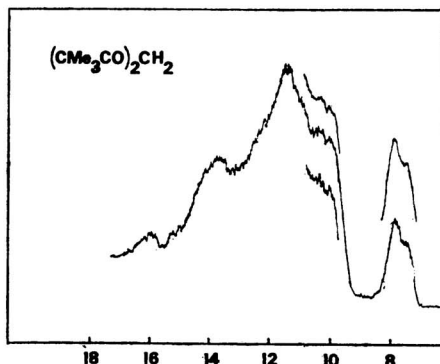
(CMe₃CO)₂CH₂

FIG. 4.—The He(I) PE spectrum of Dipivaloyl-methane.

Al(hfa)₃

FIG. 5.—The He(I) PE spectrum of tris-(hexa-fluoroacetylacetonato)-Aluminium (III)

Be(hfa)₂
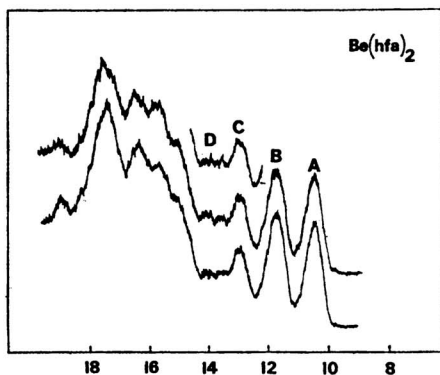
FIG. 6.—(a) The He(I) PE spectrum of bis-(hexafluoroacetylacetonato)-Beryllium (II).

Be(acac)₂
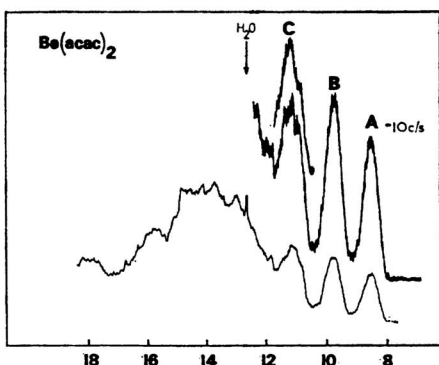
(b) The He(I) PE spectrum of bis-(acetyl-acetonato)-Beryllium (II).

Ga(hfa)₃

FIG. 7.—The He(I) PE spectrum of tris-(hexa-fluoroacetylacetonato)-Gallium (III).

The spectra were calibrated individually, usually by the *simultaneous* admission of inert gases into the target chamber of the instrument. This often proved essential since the action of several of the hexafluoroacetylacetonato complexes on the equipotential surfaces caused substantial shifts in the energy scale. The ionization energy
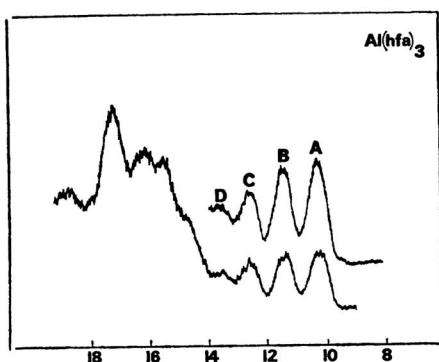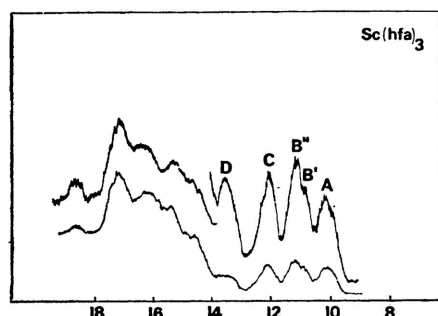
FIG. 8.—The He(I) PE spectrum of tris-(hexa-fluoroacetylacetonato)-Scandium (III).
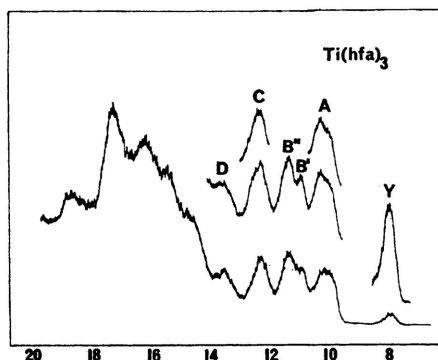
FIG. 9.—The He(I) PE spectrum of tris-(hexa-fluoroacetylacetonato)-Titanium (III).

FIG. 10.—The He(I) PE spectrum of tris-(hexa-fluoroacetylacetonato)-Vanadium (III).
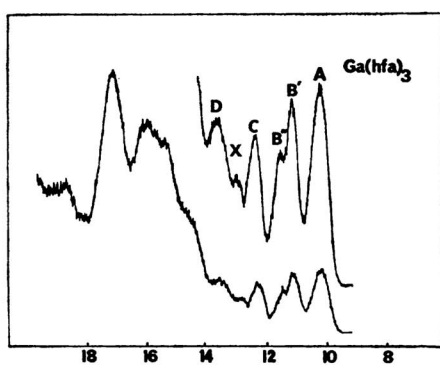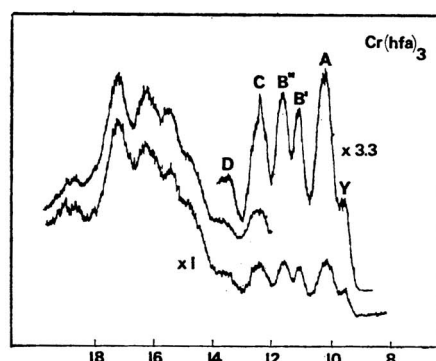

FIG. 11.—The He(I) PE spectrum of tris-(hexa-fluoroacetylacetonato)-Chromium (III).
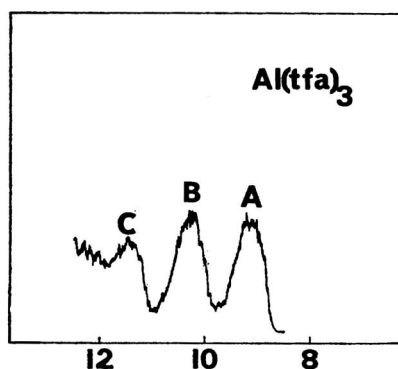
FIG. 12.—(a) The He(I) PE spectrum of tris-(trifluoroacetylacetonato)-Aluminium (III); low IE region.
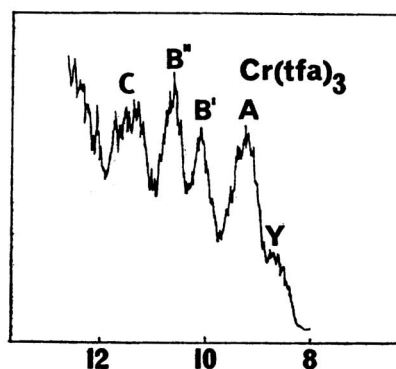
(b) The He(I) PE spectrum of tris-(trifluoroacetylacetonato)-Chromium (III); low IE region.

(IE) data given in the tables is accurate to ± 0.07 eV for the sharper bands. The instrumental resolution was usually *ca* 50 mV for the spectra recorded on the instrument of ref. (15) and the PS 15, and *ca* 90 mV for the high temperature spectra.
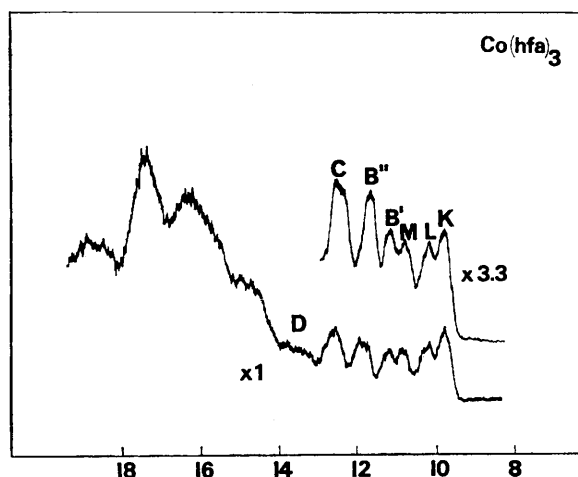
Co(hfa)₃

C B"

B'
M L K

× 3.3

D

× 1

18 16 14 12 10 8

FIG. 13.—The He(I) PE spectrum of tris-(hexafluoroacetylacetonato)-Cobalt (III).

−2 c/s

Co(acac)₃

C B"

B'

M L K

12 10 8 6

C

D B" B' A

Cr(acac)₃

Y

12 10 8 6
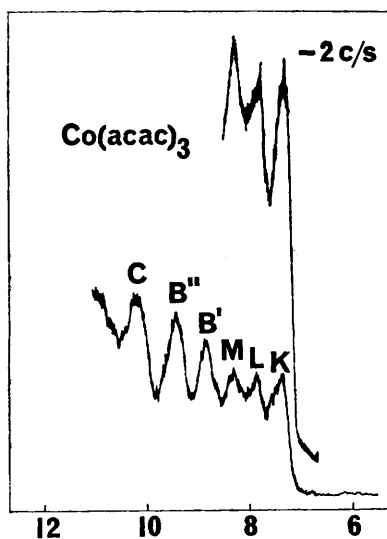
FIG. 14.—(a) The He(I) PE spectrum of tris-(acetylacetonato)-Cobalt (III); low IE region.

(b) The He(I) PE spectrum of tris-(acetylacetonato)-Chromium (III); low IE region.

Mn(hfa)₃

D

C B" A
B'

₁1

₁3

18 16 14 12 10 8

B" B' Mn(hfa)₃⁻

D C

A

18 16 14 12 10 8
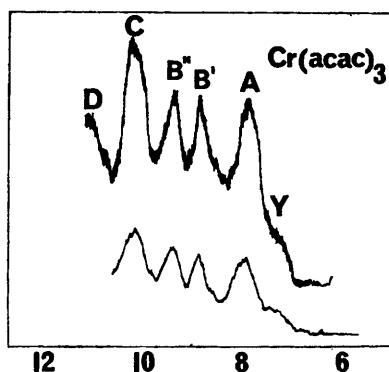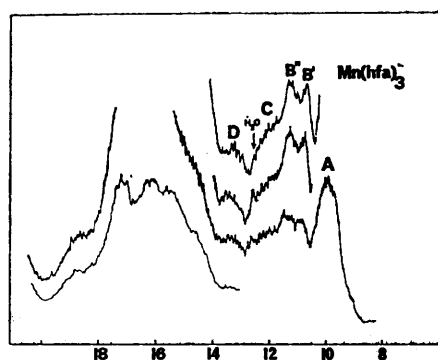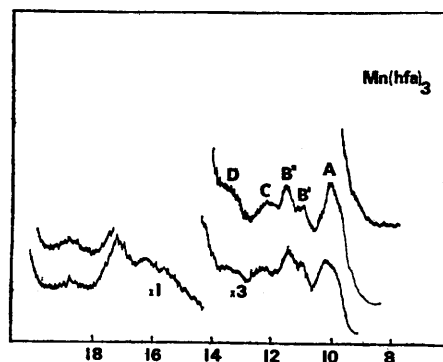
FIG. 15.—The He(I) PE spectrum of tris-(hexafluoroacetylacetonato)-Manganese (III); recorded (a) on the instrument of ref. (15); (b) recorded on a PS 15 spectrometer.

An intense band at 20-21 eV was observed in all the spectra of the hexafluoro-acetylacetonato complexes, which has been confirmed by preliminary studies using He(II) radiation.
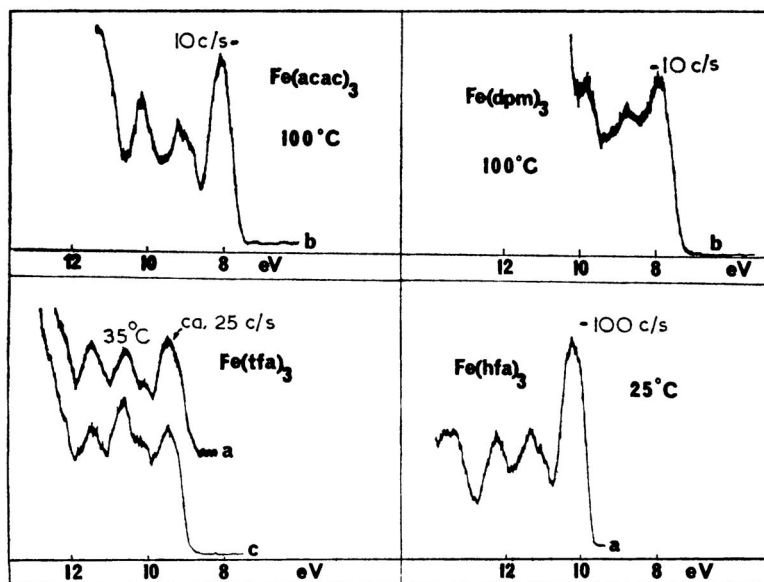
FIG. 16.—The He(I) PE spectra of some tris-chelates of Iron(III) [(*a*) recorded on the spectrometer of ref. (15), (*b*) recorded on the 90° sector instrument of ref. (16), (*c*) recorded on a PS 15 spectro-meter].
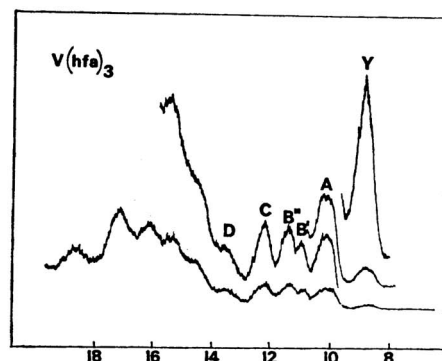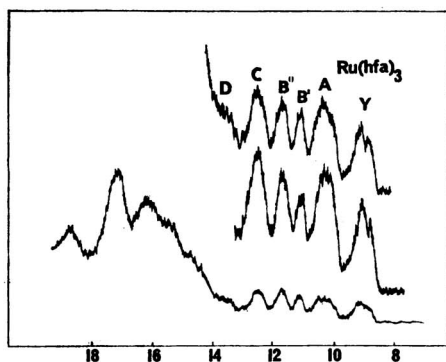

FIG. 17.—The He(I) PE spectrum of tris-(hexafluoroacetylacetonato)-Ruthenium (III)
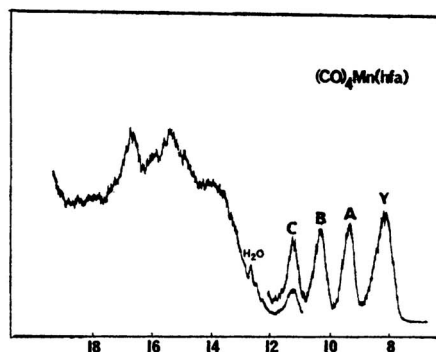
FIG. 18.—The He(I) PE spectrum of tetracar-bonyl(hexafluoroacetylacetonato)-Man-ganese (I).

DISCUSSION

The PE spectra will be interpreted in terms of elementary molecular orbital theory, invoking Koopmans' approximation to connect orbital energies with molecu-lar IE's.[1]   We consider first of all the spectra of the free protonated ligands.

THE PE SPECTRA OF SOME β-DIKETONES

The prototype compound, acetylacetone, exists in the vapour phase as the *enol* form.[17] The six-membered ring is thought to be planar, which confers C_{2v} symmetry on the system. Hexafluoroacetylacetone is known to exist primarily in the enol form even in the liquid phase,[18] and will almost certainly be present as such in the gaseous state. The other β-diketones are also probably present as their enol forms in the gas phase, though there is little direct evidence on this point.[17]

The π-system of the six-membered ring has been extensively discussed. It is formed from the out-of-plane p_π orbitals of the three carbon and two oxygen atoms, the two sets of orbitals transforming as $a_2 + 2b_2$ and $a_2 + b_2$, respectively, in the C_{2v} point group. The five resulting π MOs, $\pi_1-\pi_5$, are shown in fig. 20. The simple Hückel theory leads to the ordering $\pi_1 < \pi_2 < \pi_3 < \pi_4 < \pi_5$ for the orbital energies.[19, 20] With the usual choice of parameters, one finds that π_3 is well separated from both π_2 and π_4, which implies that neither π_4 nor π_5 will be of great importance as regards the bonding in metal chelates. As shown in fig. 20, π_2 may be regarded approximately as an antisymmetric combination of localized C—O π-bonding orbitals, whilst π_3 approximates to an antibonding orbital formed from the symmetric combination of π_{CO} localized orbitals and the p_π orbital on the unique central carbon atom. The two π_{CO} orbitals probably do not interact very strongly, so that one should be able to estimate an approximate orbital energy for π_2 by references to the PE spectra of simple carbonyl compounds. In formaldehyde, for example, the π_{CO} ionization occurs at 14.09 eV[21]: the usual electronegativity arguments would then lead us to predict a rather lower IE for the π_2 electrons in acetylacetone.
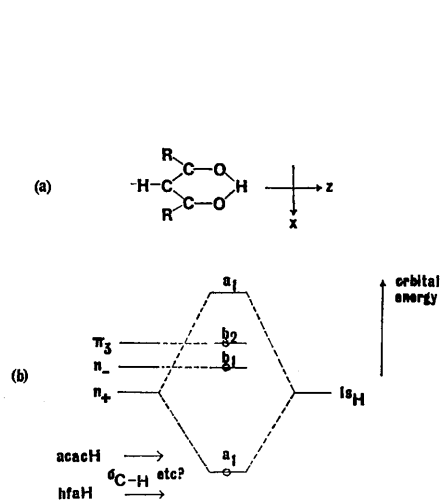

FIG. 19.—(a) The structure of the enol-form of a β-diketone.

(b) A molecular-orbital diagram for the enol-form.
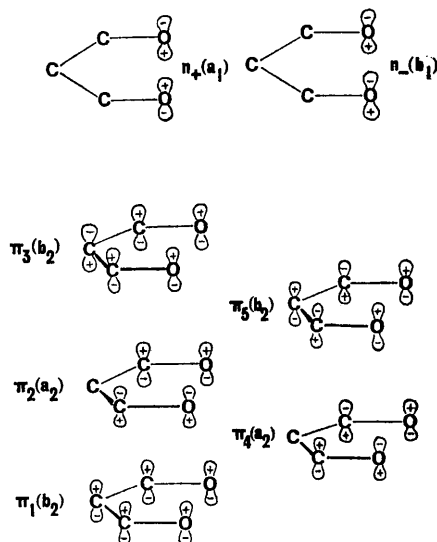
FIG. 20.—The π-MOs and lone-pair combinations for the enol-form.

The oxygen lone-pair orbitals may, as a first approximation, be taken as the in-plane p_x orbitals. The symmetric combination $n_+ (a_1)$ of the two oxygen p_x orbitals interacts with the hydrogen $1s$ orbital, this presumably being the major source of the binding of the proton. The anti-symmetric combination $n_- (b_1)$ is involved only in

the C—O σ-bonding, and probably to much the same extent as the a_1 combination. These lone-pair combinations are pictured in fig. 20. The orbital energy of n_- should not differ greatly from the oxygen lone-pair (n_0) energies inferred from the PE spectra of the simple carbonyls. In formaldehyde, the n_0 ionization is found at 10.88 eV,[21] whilst in acetone it occurs at 9.68 eV.[22]

A tentative energy level scheme for a symmetric β-keto-enol based partly on the foregoing considerations and consistent with the details of the PE spectra, is given in fig. 19. The relative ordering of n_+ and n_- is that which is dictated by the through-space interactions of the two oxygen p_x orbitals. However, this ordering may possibly be reversed by the more subtle through-bond interactions. It is even more difficult to determine the relative energies of π_3 and n_-. The particular ordering $b_2(\pi_3) > b_1(n_-)$ shown in fig. 19 reflects our ultimate conclusions concerning the PE spectra of the metal chelates. It cannot be deduced from the spectra of the free protonated ligands.

The PE spectrum of acetylacetone (fig. 1) shows two partially resolved low IE bands at 9.2 and 9.7 eV, and relatively amorphous structure to higher IE. One of the lower IE bands (we cannot say which) must correspond to ionization of the $b_2(\pi_3)$ electrons, and the other to ionization of the $b_1(n_-)$ oxygen lone-pair electrons. The possibility that the other low IE band is due to ionization from the $a_1(n_+)$ MO may be rejected on energetic grounds: the splitting (0.56 eV) between n_+ and n_- would be unreasonably small. The assignment to $b_2(\pi_3)$ is the more credible. The $a_2(\pi_2)$ and $a_1(n_+)$ PE bands are presumably obscured by the diffuse structure commencing at around 12 eV. This higher IE region of the spectrum, arising from ionization of C—H and C—C σ-bonding electrons, contains too many overlapping bands to merit detailed consideration.

Hexafluoroacetylacetone exhibits a broadly similar spectrum, fig. 2, and in accordance with the high electronegativity of fluorine, there is a substantial shift on the main structural features to high IE. The very characteristic structure beyond about 15 eV must be due in part to the ionization of the fluorine lone-pair electrons. But of particular interest is the PE band now discernible at 14.0 eV. This most probably concerns the $a_1(n_+)$ MO, but might just possibly be due to ionization form the π_2 orbital or from the σ-MO corresponding to the unique C—H σ-bond. The former assignment is preferred on the grounds that the stabilization of orbital energy due to the fluorine atoms should lead to a π_2 IE significantly in excess of the π_{CO} ionization in formaldehyde at 14.09 eV.[21] Similarly, the σ_{C-H} electrons would be expected to ionize at a higher energy than in, for example, methane (13-15 eV).[21] The first two PE bands in hexafluoroacetylacetone, at 10.74 and 11.25 eV, are again assigned to the $b_2(\pi_3)$ and $b_1(n_-)$ ionizations.

An assignment of the dipivaloylmethane PE spectrum, fig. 4, may be advanced along similar lines. Here the electron donor properties of the methyl substituents lead to a low IE shift of the main structure relative to the acetylacetone case, with the result that there is only a very narrow window between the first two PE bands and the onset of the main, diffuse band system.

THE PE SPECTRA OF THE GROUP III COMPLEXES

Al(hfa)$_3$, Ga(hfa)$_3$ and Sc(hfa)$_3$

The PE spectra of Al(hfa)$_3$, Ga(hfa)$_3$ and Sc(hfa)$_3$, fig. 5-8 are very similar, especially in the high IE region. The diffuse structure beyond about 14 eV is characteristic of all simple hexafluoroacetylacetonato complexes (compare the spectrum of Be(hfa)$_2$ in fig. 6, for example). The pronounced peak around 17 eV, which clearly corresponds to the 17.44 eV band in the spectrum of hexafluoroacetylacetone

itself, almost certainly concerns ionization of some fluorine lone-pair combination. The overlapping bands in the 14-17 eV region must arise largely from the ionization of the ligand σ electrons. The low IE structure of the three $M(hfa)_3$ spectra are however significantly different in detail. $Al(hfa)_3$ shows three well resolved bands (A-C) between 10 eV and 13 eV, and a weaker band (D) at 13.6 eV. The spectrum of $Sc(hfa)_3$ is clearly analogous, except that the second band (B) exhibits a shoulder on its *low* IE side. But the $Ga(hfa)_3$ PE spectrum, in addition to showing a clear splitting of the second PE band (B), with the shoulder now appearing to *high* IE, has an extra band (labelled X in fig. 7) at 13.0 eV.

These closed-shell tris-hexafluoroacetylacetonato complexes are assumed to possess trigonal symmetry (D_3 point group), like most simple $M(acac)_3$ molecules.[23] The immediate coordination environment of the metal atoms may be described only approximately as an octahedral configuration of the oxygen atoms. Now, our conclusions concerning the low IE structure in the hexafluoroacetylacetone PE spectrum suggest that the leading valence orbitals of the enolate ligand are π_3, n_-, and n_+ (though π_2 should not be forgotten). The ligand symmetry orbitals (SOs) arising from these basis orbitals are as follows:

β-ketonato orbital	tris-chelate SOs
π_3	$e+a_2$
n_-	$e+a_2$
n_+	$e+a_1$

The through-space interaction between the coordinated atoms is often an important source of detail in PE spectra.[24] Now, two forms of interaction may be distinguished in these complexes: there is, first of all, the *intra-ligand* interaction which tends to stabilize n_+ and destabilize n_-, and secondly, there is an *inter-ligand* interaction leading to a small energy differentiation of the SOs. A simple "orbital interaction" model (see Appendix) indicates that the major effect of inter-ligand overlap will be splitting of the n_+ SOs such that $e(n_+)>a_1(n_+)$: the π_3 and n_- SOs should be less affected. The orbital interaction model may also be used to gauge the likely extent of mixing between these ligand SOs and the metal np and ns valence AOs which transform as $e+a_2$ and a_1, respectively, in the D_3 point group. The major source of metal-ligand bonding, as argued in the Appendix, is expected to be the $e(n_+)-e(np)$ and $a_1(n_+)-a_1(ns)$ interactions. The n_--np, and especially the π_3-np interactions, should be significantly less strong. The overlap of the metal np AOs with $e(\pi_3)$ is expected to be similar to that with $a_2(\pi_3)$, so that only a very small splitting of the π_3 ionizations may be anticipated. The e and a_2 MOs arising from n_- should have a larger energy separation since the $e(n)_--e(np)$ interaction is somewhat smaller than that between $a_2(n_-)$ and $a_2(np)$, an effect augmented by the inter-ligand interactions. The largest separation however is expected between the MOs $e(n_+)$ and $a_1(n_+)$, the latter bonding to the ns orbital on the metal, since for these the inter-ligand interactions are the most considerable, and the differentiation on bonding the most pronounced.

We are now in a position to put forward a tentative assignment of the low energy IE bands in the $Al(hfa)_3$ PE spectrum (A-D). Band A must be due to the unresolved $e(\pi_3)$ and $a_2(\pi_3)$ ionizations, whilst band B most probably concerns ionization from the $e(n_-)$ and $a_2(n_-)$ MOs, these also being assumed to lie too close in energy to yield distinct PE bands. The origin of bands C and D is more problematical. One obvious possibility is that both bands arise from ionization of the main bonding electrons, primarily localized as ligand n_+: band C would then be associated with

the $e(n_+)$ orbital and band D with $a_1(n_+)$. Alternatively, it may be that band C represents both the $e(n_+)$ and the $a_1(n_+)$ ionizations, in which case band D must be assigned to some ligand σ ionization (of the unique σ_{CH} orbital, for example), or perhaps even to ionization from the π_2 MOs. The general trend of our arguments, in particular the assignment of bands A and B of Al(hfa)$_3$ to the π_3 and n_- ionizations respectively, receives support from the study of various bis-(β-ketonato) complexes. Thus the PE spectra of Be(hfa)$_2$ and Be(acac)$_2$ (fig. 6), for example, show three low IE bands that are obvious counterparts to bands A-C in the Al(hfa)$_3$ PE spectrum.

The more complex PE spectrum of Ga(hfa)$_3$, fig. 7, is rather difficult to understand. On the whole, the low IE detail is more intelligible if band C in the Al(hfa)$_3$ spectrum is assigned to unresolved $e(n_+)$ and $a_1(n_+)$ ionizations. The splitting of band B observed in the Ga(hfa)$_3$ spectrum might be due to an increased interaction between the n_- ligand SOs and metal $4p$, the $e(n_-)$ ionization at 11.13 eV being now distinguishable from the $a_2(n_-)$ ionization at 11.47 eV: the relative intensities of the overlapping bands are certainly consistent with this interpretation. The fact that band C is distinctly less broad in Ga(hfa)$_3$ than in the case of Al(hfa)$_3$ argues for its assignment to the $e(n_+)$ ionization, while the weaker band X, with no counterpart in the Al(hfa)$_3$ spectrum is most naturally assigned to ionization of the $a_1(n_+)$ electrons. This is rather speculative, but the spectrum is otherwise very difficult to understand. (An alternative explanation of the observed sequence of n_+ orbital energies, $e(n_+) > a_1(n_+)$ involves the possible participation of the Ga $3d$ orbitals-*vide infra*).

However, this assignment of the Ga(hfa)$_3$ spectrum implies a substantial increase in covalency relative to Al(hfa)$_3$. There is independent evidence for this conclusion,[25] though it is perhaps surprising that the spectrum of Ga(hfa)$_3$ exhibits a low IE shift as compared to that of Al(hfa)$_3$. An alternative assignment, in which band C is attributed to ionization from $e(n_+)$ and band D to $a_1(n_+)$, would also imply increased covalency in the Ga(III) compound, since the spacing of bands C and D increases from 0.98 eV in Al(hfa)$_3$ to 1.26 eV in Ga(hfa)$_3$. In addition, the separation of bands C and D is even greater in Sc(hfa)$_3$ (1.47 eV), which cannot be more covalent than Al(hfa)$_3$. Moreover, this assignment leaves band X unaccounted for. Thus we feel that the most plausible explanation of the spectrum of Ga(hfa)$_3$ is the one advanced initially.

The Sc(hfa)$_3$ PE spectrum poses a different problem. It is very similar to the spectrum of Al(hfa)$_3$ except that band B shows an incipient splitting, a shoulder appearing at *low* IE rather than at high IE as in the spectrum of Ga(hfa)$_3$. This phenomenon cannot be understood in terms of a simple $4s$, $4p$ scandium basis set but, as we shall now see, becomes intelligible if the $3d$ orbitals are assumed to play an important part in the metal–ligand bonding. The low IE shift of the first three bands relative to the Al(hfa)$_3$ spectrum is in accord with the expected reduction in covalency in the Sc(III) complex.

THE PE SPECTRA OF THE t_{2g}^n SERIES:
Ti(hfa)$_3$, V(hfa)$_3$ and Cr(hfa)$_3$

We now turn to the PE spectra of the transition-metal complexes Ti(hfa)$_3$, V(hfa)$_3$ and Cr(hfa)$_3$ which, viewed as octahedral complexes, represent a series in the t_{2g}^n configuration. The most striking feature of the Ti(hfa)$_3$ spectrum (fig. 9) is a weak low IE band (at 7.94 eV), with no counterpart in the spectrum of Sc(hfa)$_3$. This additional band (Y) shifts progressively to higher IE in the V(hfa)$_3$ and Cr(hfa)$_3$ (fig. 10 and 11): in Cr(hfa)$_3$ it has apparently merged partially with the envelope of the first strong band (A) which remains at essentially the same position in the three spectra.

TABLE 1.—IONIZATION DATA (eV) FOR SOME β-DIKETONES*

acacH	dpmH	hfaH	tfaH	tmtfaH†
9.18	8.86	10.74	9.92	9.87
9.74	9.23	11.25	10.53	10.19
				(10.29)
12.68	11.37	14.03		11.95
	11.79		13.27	13.14
13.27	12.78	15.05		(14.0)
		15.58	15.23	(15.24)
14.18	(13.66)			
14.8	15.07	16.3	16.99	
16.1	(16.55)	17.42		16.8
18.8	17.32	19.3		
		20.92		

* acacH ; acetylacetone
dpmH ; dipivaloylmethane (2,2,6,6,-tetramethyl-heptane-3,5-dione)
hfaH ; hexafluoroacetylacetone (1,1,1,5,5,5,hexafluoropentane-2,4-dione)
tfaH ; trifluoroacetylacetone(1,1,1,trifluoropentane-2,4-dione)
tmtfaH ; trifluorotrimethylacetylacetone (1,1,1,trifluoro-5,5,dimethyl-hexane-2,4-dione)
Shoulders are indicated by parentheses.

† The low IE structure in the PE spectrum of 1,1,1,trifluoro-5,5,dimethyl-hexane-2,4-dione is complex. There appear in fact to be three bands, the third being indicated by a poorly resolved shoulder at the high IE side of the second band. The reason for this is uncertain, but it may be that the compound is a mixture of *keto* and *enol* forms. The spectrum of this ligand is altogether most discouraging as regards the possibility of studying its complexes by PE spectroscopy, there being virtually no window between the first group of bands and the onset of the main region of ionization. One of its complexes which was studied, Al(tmtfa)$_3$, appeared to exist in two forms (presumably stereoisomers) differing considerably in physical properties.

TABLE 2.—IONIZATION ENERGY DATA (eV) FOR SOME MAIN GROUP TRIS-CHELATES

PE band	Al(tfa)$_3$	Al(hfa)$_3$	Sc(hfa)$_3$	Ga(hfa)$_3$
A	9.22	10.33	10.13	10.19
B	10.35	11.47	10.82(B′)	11.13(B′)
			11.12(B″)	11.47(B″)
C	11.49	12.64	12.05	12.37
				12.99(X)
D		13.62	13.52	13.63
	14.7	14.81	14.6	14.7
		15.58	15.3	15.5
	16.6	16.20	16.2	16.14
		17.25	17.1	17.24
		18.75	18.5	18.8

TABLE 3.—IONIZATION ENERGY DATA (eV) FOR TWO BIS-CHELATES OF BERYLLIUM

PE band	Be(hfa)$_2$	Be(acac)$_2$
A	10.39	8.41
B	11.66	9.67
C	12.96	(10.86)
		11.13
	13.4-14.3	13.0-14.7
	(15.1)	
	(15.7)	
	16.3	15.8
	17.4	
	18.9	

TABLE 4.—IONIZATION ENERGY DATA (eV) FOR SOME TRANSITION-METAL TRIS-CHELATES

PE band	Ti(hfa)$_3$	V(hfa)$_3$	Cr(hfa)$_3$	PE band	Co(hfa)$_3$
Y	7.94	8.68	9.57	K	9.73
A	10.24	10.10	10.18	L	10.13
				M	10.73
B′	10.87	10.96	11.10	B′	11.15
B″	11.28	11.39	11.61	B″	11.75
C	12.24	12.20	12.44	C	12.56
D	13.50	13.59	13.47	D	13.5
	14.6	14.6	14.86		14.8
	15.39	15.41	15.42		15.5
	16.10	16.16	16.27		16.27
	17.18	17.12	17.24		17.36
	18.68	18.60	18.8		18.56

TABLE 5.—IONIZATION ENERGY (eV) OF SOME TRIS-CHELATES OF Cr(III) AND Co(III)

PE band	Cr(acac)$_3$	Cr(tfa)$_3$	PE band	Co(acac)$_3$
Y	7.46	8.58	K	7.52
A	8.06	9.12	L	8.03
			M	8.49
B′	8.96	10.01	B′	8.99
B″	9.48	10.54	B″	9.54
C	10.26	11.40	C	10.34
	(11.1)			

TABLE 6.—IONIZATION ENERGY (eV) FOR TRIS-CHELATES OF Mn(III)

	Mn(hfa)$_3$		Mn(acac)$_3$
	A	B	C
	(9.2)	(9.2)	(7.32)
	10.1	10.03	8.14
		10.94	
		11.41	
	ca. 12.3	12.31	
	ca. 13.1	13.3	
		14.7	
		15.3	
	16.2	16.2	
	17.2	17.1	
		18.7	

A, measured on the spectrometer of ref. (15); B, measured on a PS 15 spectrometer; C, measured on a Perkin–Elmer spectrometer using a heated inlet at 132°C.

TABLE 7.—IONIZATION ENERGY DATA (eV) FOR SOME TRIS-CHELATES OF Fe(III)

Fe(hfa)$_3$	Fe(tfa)$_3$	Fe(acac)$_3$	Fe(dpm)$_3$
10.13	9.18	8.10	7.92
	(9.92)	(8.93)	
11.30	10.40	9.22	8.76
12.25	11.26	10.16	9.87
13.5		11.4	
14.7		13.2	
15.43			
16.18			
17.22			
18.8			

Clearly, band (Y) must be due to ionization of essentially metal $3d$ electrons. The growth in intensity of this band from $Ti(hfa)_3$ to $Cr(hfa)_3$ is consistent with the increase (from 1 to 3) in the number of $3d$ electrons.

TABLE 8.—IONIZATION ENERGY DATA (eV) FOR $Ru(hfa)_3$ AND $Mn(CO)_4(hfa)$

PE band	$Ru(hfa)_3$	$Mn(CO)_4(hfa)$
Y	8.85	8.11
	9.07	
A	10.30	9.31
B	11.06(B′)	10.31
	11.65(B″)	
C	12.50	11.19
	13.55(D)	13.9
	(14.7)	15.3
	(15.4)	
	16.1	16.7
	17.1	18.0
	18.7	

The relationship between the remaining low IE structure in these spectra and that observed in the $Sc(hfa)_3$ spectrum is fairly clear. The barely discernible structure on band B of $Sc(hfa)_3$ has developed into a definite splitting, and the separation of the components increases steadily from $Ti(hfa)_3$ to $Cr(hfa)_3$, the lower IE component being the less intense.

We now expect that the $3d$ AOs are the leading valence orbitals on the metal atoms. These transform as $a_1 + 2e$ in the D_3 point group. One e set, which we denote e_a, correlates with the t_{2g} set of octahedral symmetry ($t_{2g} \to a_1 + e_a$ for $O_h \to D_3$) and the other, e_b, corresponds directly with the e_g orbitals ($e_g \to e_b$). Recourse, once again, to a simple analysis of the valence orbital interactions (see Appendix) suggests that the major source of bonding lies in the interaction between $e_b(d)$ and the $e(n_+)$, $e(n_-)$ ligand SOs. The interaction of metal $a_1(d)$ and $e_a(d)$ with the ligand SOs is expected to be much less important. The ligand $a_2(\pi_3)$ and $a_2(n_-)$ orbitals are now non-bonding, of course, and only a small interaction is anticipated between $e(\pi_3)$ and the metal $e(d)$ orbitals (but see the discussion of the Co(III) tris-chelates below). Our conclusions concerning the $Al(hfa)_3$ PE spectrum lead us to expect unresolved, or at least overlapping, $e(\pi_3)$ and $a_2(\pi_3)$ bands.

The low IE shoulder on band B in the PE spectrum of $Sc(hfa)_3$, and the appearance of two distinct bands (B″ and B′) in the $Ti(hfa)_3$ $V(hfa)_3$ and $Cr(hfa)_3$ spectra, may thus be understood in terms of a substantial stabilization of $e(n_-)$ with respect to $a_2(n_-)$, an assignment to B″ and B′ respectively being supported by the relative intensities of these two bands. The trend in the separation of these bands, which increases from ca 0.30 eV in $Sc(hfa)_3$ to 0.51 eV in $Cr(hfa)_3$, may be correlated with the simultaneous low IE shift of band Y on going from $Ti(hfa)_3$ to $Cr(hfa)_3$. The extent of the $e(n_-)$–$e(d)$ interactions clearly should increase as the $3d$ orbitals are stabilized.

The first strong band A must be due to unresolved π_3 ionizations, but the assignment of bands C and D is once again uncertain. However, provided the metal $3d$ orbitals play a more important part in the bonding than do the $4s$ AOs, the $a_1(n_+)$ and $e(n_+)$ MOs should lie closer in energy than in the case of $Al(hfa)_3$. For this reason we prefer to assign band C to both the n_+ ionizations. The much greater separation of bands D and C in the transition metal complexes as compared with $Al(hfa)_3$ militates against the assignment of C and D to $e(n_+)$ and $a_1(n_+)$ respectively.

The d-ionizations merit more detailed consideration. The available evidence for these tris-chelate systems suggests the ground state electronic configurations given in table 9. The first PE band of Ti(hfa)$_3$ should thus be due to ionization of the sole $a_1(d)$ electron, while the corresponding band in the V(hfa)$_3$ spectrum must concern ionization of the $e_a(d)$ electrons. (Interestingly, ionization of (V(hfa)$_3$ cannot yield

TABLE 9.—THE PROBABLE GROUND STATES OF SOME TRANSITION-METAL TRIS-(β-DIKETONATO) COMPLEXES AS DEDUCED FROM MAGNETIC MEASUREMENTS (IN PARTICULAR E.P.R.)

complex	ground state	reference
TiL$_3$	$^2A_1\ a_1$	26
VL$_3$	$^3A_2\ e_a^2$	27
CrL$_3$	$^4A_2\ a_1 e_a^2$	28
CoL$_3$	$^1A_1\ a_1^2 e_a^4$	29
RuL$_3$	$^2E\ a_1^2 e_a^3$	30
MnL$_3$	$^5E\ a_1 e_a^2 e_b$	31
FeL$_3$	$^6A_1\ a_1 e_a^2 e_b^2$	32

(L is the bidentate β-ketoenolate ligand)

the ground state of V(hfa)$_3^+$, which is presumably $^2A_1(a_1)$, like Ti(hfa)$_3$.) The d-band (Y) of V(hfa)$_3$ is actually somewhat more broad than that of Ti(hfa)$_3$, and this may be due to vibronic effects in the $^2E(e_a)$ state of the V(hfa)$_3^+$ molecular ion, or possibly to the greater antibonding character of the $e_a(d)$ MO as compared to the $a_1(d)$ (see Appendix). In the Cr(hfa)$_3$ case, ionization of the metal d shell should lead to two distinct ion states, namely $^3A_2(e_a^2)$ and $^3E(a_1 e_a)$—which together correlate with $^3T_{1g}(t_{2g}^2)$ in octahedral symmetry. But the energy separation of these states (which, in crystal-field theory, reflects the trigonal component of the ligand field)
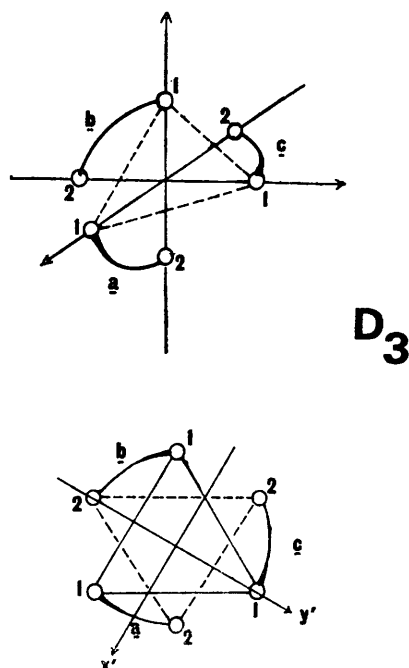

FIG.—21. The axis system and labelling procedure for the tris-chelates.

is expected to be quite small: in all probability the partially resolved band Y corresponds to both ionization processes, a conclusion supported by its measured intensity. The possibility that one of the d-bands, that due to the ^3E state most probably, lies under the strong band A cannot however be absolutely ruled out.

The presence of an open shell in these compounds will mean that ionization of a filled inner shell will yield more than one state of the molecular ion: all states derived from the coupling of the inner shell hole state with the open shell ground term may, in principle, be produced. We do not however find any evidence for a multiplicity of ionization processes, not even in the form of band broadening as observed, for example, in the VCl_4 PE spectrum, when compared to that of $TiCl_4$.[33] Presumably the PE bands are intrinsically too broad in the $M(hfa)_3$ species, and the metal–ligand exchange integrals too small.

The low IE data for the t_{2g}^n complexes is displayed in fig. 22, where it may conveniently be compared with the $Sc(hfa)_3$ and $Ga(hfa)_3$ data. The overall shift of bands C, B' and B" to higher IE, as we proceed from $Sc(hfa)_3$ through to $Cr(hfa)_3$ is consistent with the expected increase in covalency as the size of the central M(III) cation diminishes.[25] The behaviour of band A is very irregular, however.
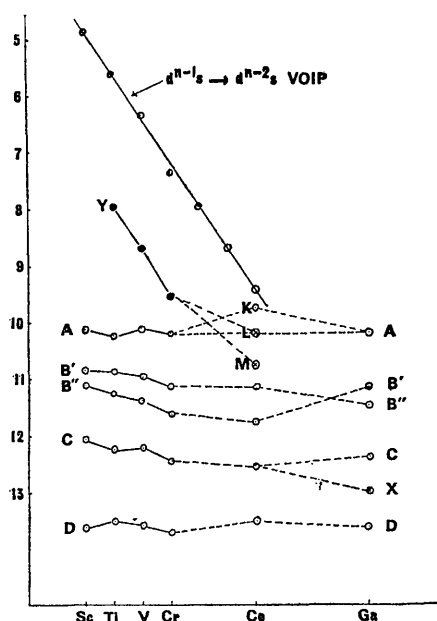
FIG. 22.—A plot of IEs for the tris-hexafluoro-acetylacetonato complexes of the transition metals.
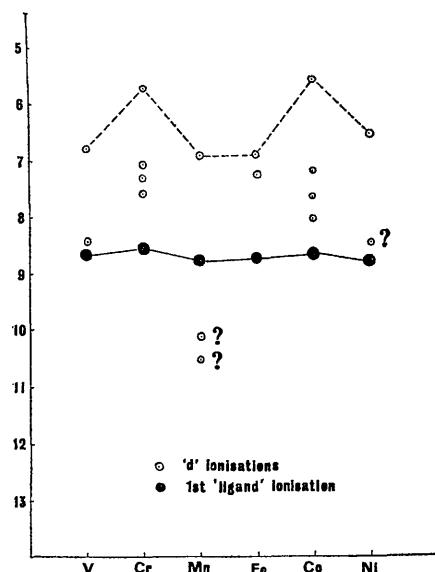
FIG. 23.—A plot of the IEs for the low IE region of the bis-π-cyclo-pentadienyl complexes of the transition metals.

It should be pointed out that the trend in the d electron IEs gives an exaggerated impression of the rate at which the $3d$ orbitals are stabilized across the first transition series. The d band of $Cr(hfa)_3$, for example, relates essentially to the transition $^4A_{2g}(t_{2g}^3) \rightarrow {}^3T_{1g}(t_{2g}^2)$ of octahedral symmetry; that is, the transition from the ground state of t_{2g}^3 to the ground state of t_{2g}^2. But the fully spin and space-randomized $t_{2g}^3 \rightarrow t_{2g}^2$ process will require less energy since $^4A_{2g}$ is more stable relative to the baricentre of t_{2g}^3 than is $^3T_{1g}$ relative to the t_{2g}^2 baricentre.[34] In general, the *average of*

configuration IEs will be lower before the half-filled t_{2g} shell (but greater beyond) than the observed ground term IEs : the difference in IEs for the two processes will increase up to the t_{2g}^3 configuration, then change sign and subsequently decrease until the closed shell t_{2g}^6 configuration, for which case the processes are identical. Thus, the $t_{2g}(3d)$ metal orbitals are expected to stabilize somewhat less dramatically than the IE data in fig. 22 would indicate.

Nevertheless, it is clear that the metal $3d$ orbitals rapidly become stabilized across the first transition series, in accordance with the simplest expectations. This, however, is not always the case. The bis-(π-cyclopentadienyl) complexes, for example, show an extremely complex trend in the d ionizations—fig. 23.[35, 36]

We observe, in passing, that the low IE detail in the Ga(hfa)$_3$ spectrum has conceivably an alternative explanation. The splitting of the n_- band (apparently with $e(n_-) > a_2(n_-)$) and the clear separation of the $e(n_+)$ and $a_1(n_+)$ ionizations postulated earlier, may also be rationalized in terms of interactions with the Ga(III) $3d$ inner-shell AOs. These orbitals are now lower in energy than the ligand SOs so that the $e(d)-e(n_+)$ and $e(d)-e(n_-)$ interactions may contribute to the inferred $e(n_-) > a_2(n_-)$ and $e(n_+) > a_1(n_+)$ orbital energy sequences.

THE PE SPECTRA OF M(acac)$_3$, M(tfa)$_3$ AND M(dpm)$_3$ SPECIES

The PE spectra of Cr(acac)$_3$ (fig. 14b) and Cr(tfa)$_3$ (fig. 12b) are clearly analogous to that of Cr(hfa)$_3$, and the relationship between the Cr(tfa)$_3$ and Al(tfa)$_3$ spectra parallels that between the corresponding tris-hexafluoroacetylacetonato complexes. The general correspondence between the Co(hfa)$_3$ and Co(acac)$_3$ PE spectra (fig. 11 and 14a), the various Fe(III) tris-chelate spectra (fig. 16), and between the Be(hfa)$_2$ and Be(acac)$_2$ spectra (fig. 6), is also fairly obvious.

The main differences between the PE spectra of different tris-(β-diketonato) complexes of a given metal ion may be understood simply in terms of the electronegativities of the terminal groups (R and R′) of the ligands. Corresponding low IE bands (A-C) shift progressively to higher IE in the sequence M(acac)$_3$, M(tfa)$_3$, M(hfa)$_3$: indeed there is a linear variation of IE with the number of substituent CF$_3$ groups, the plots for the different metal ions lying closely parallel to each other. The free protonated ligands also yield straight-line plots, but with reduced gradients. It is remarkable that the predominantly metal $3d$ bands are every bit as sensitive to variation of β-diketonato species as are the low IE ligand bands. Of course, the fact that the ligand σ-ionizations occur at highest IE in hexafluoroacetylacetone makes the M(hfa)$_3$ systems particularly suitable for detailed study.

THE PE SPECTRA OF Co(hfa)$_3$ AND Co(acac)$_3$

Co(hfa)$_3$, with a closed shell ground state $^1A_1$ ($a_1^2 e_a^4$) correlating with $^1A_{1g}(t_{2g}^6)$ in octahedral symmetry, is a further member of the M(hfa)$_3$ series of configuration t_{2g}^6. But a comparison of the Co(hfa)$_3$ spectrum (fig. 13) with those of the preceding t_{2g}^n complexes and of Co(acac)$_3$ (fig. 14a) with Cr(acac)$_3$ provides only limited guidance on the difficult question of assignment. The low IE region of the Co(hfa)$_3$ spectrum shows *six* distinct peaks in addition to an ill-defined band at *ca* 13.5 eV. The latter structure (D), and also the sixth PE band (C), clearly correspond to bands D and C respectively, in the previously considered PE spectra. Furthermore, extrapolation from the Cr(hfa)$_3$ case suggests a correspondence between the fourth and fifth bands (B′ and B″) and bands B′ and B″ in the other spectra (cf. fig. 22). However, the origin of the first three bands (K-M) of the Co(III) complexes is less clear. Four

distinct ionization processes might be expected in the immediate low IE region: these involve the $e(\pi_3)$, $a_2(\pi_3)$, $e_a(d)$ and $a_1(d)$ orbitals. Since there are now six nominally metal $3d$ electrons, the d structure in the spectra should be relatively more pronounced than it is in the case of the Cr(III) tris-chelates, for example.

In a preliminary communication elsewhere,[3b] we assigned the first band K to the energetically similar $e(\pi_3)$ and $a_2(\pi_3)$ ionizations and bands L and M to ionization of the $e_a(d)$ and $a_1(d)$ orbitals, respectively. We have subsequently come to doubt the validity of this assignment. It remains a possibility, but is difficult to reconcile with our analysis of the metal–ligand orbital interactions and is inconsistent with the relative intensities of bands K-M and with the narrow width of band K as compared with the strong band A in earlier spectra. The same objections can be made with regard to an alternative assignment in which the ordering of the $e_a(d)$ and $a_1(d)$ energy levels is reversed.

Whatever the true assignment of these first three bands, one must recognize that the π_3 and $e_a(d)$ basis orbitals are rather close in energy, and therefore now admit the possibility of a substantial interaction between $e_a(d)$ and $e(\pi_3)$. This situation was envisaged by Barnum.[20] If the $3d$ AOs are of greater energy than the π_3 SOs, as we have assumed in the other transition-metal complexes, then the MO energy sequence $e_a(d) > a_1(d) > a_2(\pi_3) > e(\pi_3)$ is expected. This would be in line with either of the alternative assignments (3) and (4) given in table 10. On the other hand, if the $3d$ AOs lie below π_3 in energy, the MO ordering should be $e(\pi_3) > a_2(\pi_3) > a_1(d) > e_a(d)$, which corresponds to assignment (2) in table 10.

TABLE 10.—POSSIBLE ASSIGNMENTS OF THE FIRST THREE BANDS IN THE Co(hfa)$_3$ PE SPECTRUM

PE band	(1)*	(2)	(3)	(4)
K	$e(\pi_3) + a_2(\pi_3)$	$e(\pi_3)$	$e_a(d) + a_1(d)$	$e_a(d)$
L	$e_a(d)$	$a_2(\pi_3) + a_1(d)$	$a_2(\pi_3)$	$a_2(\pi_3) + a_1(d)$
M	$a_1(d)$	$e_a(d)$	$e(\pi_3)$	$e(\pi_3)$

* ref. (3b)

Assignment (3) is unlikely in view of the relative intensities of bands L and M. It appears unreasonable, moreover, that one should observe distinct $e(\pi_3)$ and $a_2(\pi_3)$ bands and yet fail to resolve the $e_a(d)$ and $a_1(d)$ ionizations. This leaves us with assignments (2) and (4), which are difficult to choose between. Both these assignments imply a very substantial trigonal splitting of the Co(III) t_{2g}^6 shell. An $e_a(d)$–$a_1(d)$ separation of ca 0.5 eV is considerably in excess of the t_{2g} trigonal splittings that have been inferred from magnetic measurements on the open-shell tris-chelates.[26, 28]

The trend in the t_{2g} IEs from Ti(hfa)$_3$ to Cr(hfa)$_3$ (fig. 22) leads us to prefer assignment (2). The alternative assignment (4), in which the first band K is assigned to the $e_a(d)$ ionization, would require that this trend be broken in Co(hfa)$_3$. We propose therefore that the first band corresponds to ionization from the π_3 orbitals as originally suggested by Schildcrout et al.[37] The relatively low IE of band K may be attributed to the destabilization of $e(\pi_3)$ through a strong $e(\pi_3)$–$e_a(d)$ interaction. The IE of the second band L, assigned partly to ionization of the $a_2(\pi_3)$ electrons, is however in line with the π_3 IEs inferred from the other spectra.
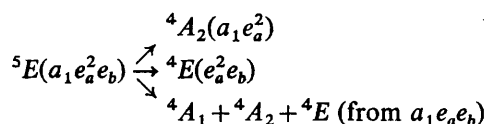
Notice, finally, that the increased separation of bands B′ and B″, as compared with the Cr(hfa)$_3$ complex, is consistent with the assignment to the $a_2(n_-)$ and $e(n_-)$ ionizations, respectively, since the further stabilization of the $3d$ AOs in the Co(III) tris-chelates should result in an increased $e_b(d)$–$e(n_-)$ interaction.

THE PE SPECTRA OF THE HIGH-SPIN Mn(III) AND Fe(III) COMPLEXES

The spectra in fig. 15 and 16 are disappointingly amorphous, especially those of $Mn(hfa)_3$. The lack of well-resolved detail may be due in part to the multiplicity of ionization processes occasioned by the presence of the open d-shells. An additional effect in the Mn(III) complex is the presence of a static Jahn–Teller distortion in the ground state $^5E(a_1e_a^2e_b)$ though the crystal structure indicates that the oxygen atoms are still arranged approximately as an octahedron around the central Mn^{3+}.[12]

The $Mn(hfa)_3$ spectrum shows six overlapping PE bands (A-D) in the low IE region, all of which appear to correspond in a general way with the bands of the $Cr(hfa)_3$ spectrum. The faint, barely discernible shoulder on the low IE side of the prominent band A must be due to the ionization of a metal $3d$ electron, presumably from the $e_b(d)$ orbital correlating with e_g in octahedral symmetry. The ionization cross-section of this orbital is apparently much less than that previously encountered for the $a_1(d)$ and $e_a(d)$ orbitals.

Ionization of the perturbed $3d$-shell may result in several different states of the molecular ion, even if D_3 symmetry is assumed. We have

$$^5E(a_1e_a^2e_b) \begin{array}{l} \nearrow \quad ^4A_2(a_1e_a^2) \\ \rightarrow \quad ^4E(e_a^2e_b) \\ \searrow \quad ^4A_1 + {}^4A_2 + {}^4E \text{ (from } a_1e_ae_b) \end{array}$$

where $^4A_2$ correlates with $^4A_{2g}(t_{2g}^3)$ in octahedral symmetry, and the other quartet states with the configuration $t_{2g}^2e_g$: $^4T_{1g}$ and $^4T_{2g}$.[34] The ligand field analysis of the states of the *molecular ion* $Mn(hfa)_3^+$ shows that the $^4T_{2g}$–$^4A_{2g}$ energy separation is just 10 Dq while $^4T_{1g}$–$^4T_{2g}$ is 12B. The parameter values for neutral $Mn(acac)_3$[12] (10 $Dq = 2.25$ eV, $B = 0.12$ eV) indicate a substantial energy separation for these terms. If band Y represents the $^4A_2$ ion state then the ^4T bands probably lie in the region spanned by bands B′, B″ and C. We cannot however completely rule out the possibility that some of the metal d structure occurs in the region of band A.

The $Fe(hfa)_3$ PE spectrum is deceptively similar in general appearance to that of $Al(hfa)_3$. There is no structure in the low IE region (fig. 16) that may obviously be identified with ionization of essentially Fe(III) $3d$ electrons. Presumably, the $e_b(d)$ orbital is here sufficiently stabilized relative to the $Mn(hfa)_3$ case that the band due to the ionization process $^6A_1(a_1e_a^2e_b^2) \rightarrow {}^5E(a_1e_a^2e_b)$ is lost under the intense band A. The remaining d bands, corresponding to production of the $^5E(a_1e_ae_b^2)$ and $^5A_1(e_a^2e_a^2)$ ion states, are assumed in turn to lie somewhere in the region of bands B and C.

A notable and puzzling feature of the $Fe(hfa)_3$ and $Fe(acac)_3$ spectra is the very high intensity of the first band A.* It seems unlikely, judging from the $3d$ cross-sections encountered in the other transition-metal complexes, that this apparent enhancement in intensity can be due to a near coincidence of the metal $3d$ and ligand π_3 bands. Perhaps the anomalously high intensity of band A arises from an auto-ionizing transition in He(I) radiation : a He(II) spectrum would clearly be very useful evidence on this point.

The PE spectrum of the low-spin d^5 complex, $Ru(hfa)_3$ (fig. 17) presents an interesting contrast to that of $Fe(hfa)_3$. Bands A-D are clearly analogous to the predominantly ligand bands in the spectra of, for example, $Ti(hfa)_3$ and $V(hfa)_3$, and open to essentially the same interpretation. The very pronounced separation of

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* The intensity of band A is fairly normal in $Fe(tfa)_3$ and $Fe(dpm)_3$, fig. 16. However, the relative band intensities and band shapes are not wholly comparable in these spectra.

bands B' and B" (0.59 eV) suggests a high degree of covalency in this compound. The remaining structure Y, consisting of at least two overlapping bands must concern ionization of the ruthenium $4d$ electrons. This structure is vaguely reminiscent of, though different in detail from, the first PE band of $V(CO)_6$, which also formally has a t_{2g}^5 ground configuration : however we cannot be certain that all five t_{2g} electrons ionize in the region of band Y.

CONCLUSIONS

The comparative study by UV–PE spectroscopy of a range of tris-(β-ketonato) complexes yields some otherwise unobtainable information concerning the interaction of metal and ligand valence orbitals. Although some of our conclusions are rather speculative at this stage, the relative energies of the metal $t_{2g}(3d)$ orbitals and the highest occupied ligand orbitals (π_3) in Ti(hfa)$_3$, V(hfa)$_3$ and Cr(hfa)$_3$ have been elucidated beyond doubt. The spectroscopic data for the Co(III), Mn(III) and Fe(III) complexes strongly suggest, moreover, that the ligand π_3 ionizations precede at least some of the metal $3d$ ionizations. This may prove to be not at all unusual in transition metal compounds.[39] The spectra of Co(hfa)$_3$ and Co(acac)$_3$ are intelligible only if fairly substantial $3d_\pi$–π_3 bonding is postulated.

We hope to gain a better understanding of the more problematical spectra, in particular those of the Mn(III) and the Fe(III) complexes by a supplementary investigation using He(II) and X-radiation. We also intend further study of the Co(III) systems and comparative measurements on the corresponding Rh(III) and Ir(III) complexes.

We remark, finally, that a great deal has been learnt about the electronic structures and the mode of bonding of the β-ketoenolate ligands. We are now in a position to undertake the investigation of β-ketonato complexes having a mixed coordination environment. A simple example is provided by (CO)$_4$Mn(hfa), the He(I) PE spectrum of which is given in fig. 18. Bands A, B and C are easily identified as involving predominantly the hfa ligand orbitals, so that band Y must correspond to the ionization essentially of the manganese $3d$ electrons (correlating with t_{2g}^6 in octahedral symmetry.)

APPENDIX

LIGAND SYMMETRY ORBITALS

The important ligand symmetry orbitals (SOs) for the tris-(β ketonato) complexes, D_3 point group, are those arising from the π_3, n_+ and n_- ligand MOs (fig. 20). Using the labels shown in fig. 21a, we have

$$a_2(\pi_3) = 1/\sqrt{3}[\pi_3(a)+\pi_3(b)+\pi_3(c)]$$

$$e(\pi_3) = \begin{cases} 1/\sqrt{6}[2\pi_3(a)-\pi_3(b)-\pi_3(c)] \\ 1/\sqrt{2}[\pi_3(b)-\pi_3(c)] \end{cases}$$

$$a_1(n_+) = 1/\sqrt{3}[n_+(a)+n_+(b)+n_+(c)]$$

$$e(n_+) = \begin{cases} 1/\sqrt{6}[2n_+(a)-n_+(b)-n_+(c)] \\ 1/\sqrt{2}[n_+(b)-n_+(c)] \end{cases}$$

and similarly for $a_2(n_-)$ and $e(n_-)$. The ligand MOs, n_+ and n_- are represented simply by linear combinations of oxygen p_x AOs (perpendicular to the C—O bonds, fig. 19a),

$$n_+(a) = 1/\sqrt{2}(p_{x2}-p_{x1})$$

$$n_-(a) = 1/\sqrt{2}(p_{x2}+p_{x1})$$

etc. The π_3 MO is approximated as an out-of-phase combination of oxygen p_y orbitals: for example,

$$\pi_3(a) = 1/\sqrt{2}(p_{y2}-p_{y1}).$$

The relative energies of the tris-chelate ligand SOs may be estimated by means of a simple overlap model described elsewhere.[24] For simplicity, the coordinated oxygen atoms are assumed to be in exact octahedral array about the metal atom, and the determinative ligand–ligand overlap integrals are evaluated as functions of α, the angle between the oxygen p_x vectors and the usual octahedral cartesian axes. For all reasonable values of α $(0-\pi/4)$ the relative energies of the ligand SOs are as shown in fig. 24. Only the n_+ SOs, $e(n_+)$ and $a_1(n_+)$, are likely to be significantly different in energy. We have assumed the energy ordering $n_->n_+$ for the ligand MOs, which is that dictated by through-space interactions between the oxygen atoms.
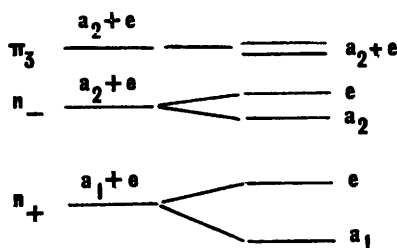

FIG. 24.—A molecular orbital diagram showing the inter- and intra-ligand interactions.

THE ORBITAL INTERACTION MODEL

The interactions between different ligand SOs and, in particular, the bonding between the ligand SOs and the metal valence AOs of the same symmetry may be approximately evaluated by use of a simple perturbation model. Suppose that the hamiltonian matrix for a system be written as

$$\mathscr{H} = \mathscr{H}^\circ + \mathscr{H}'$$

where $\mathscr{H}^\circ$ has known eigenvectors $\mathbf{c}_i^\circ$ and $\mathscr{H}$ eigenvectors $\mathbf{c}_i$:

$$\mathscr{H}\mathbf{c}_i = \varepsilon_i\mathbf{c}_i$$

$$\mathscr{H}^\circ\mathbf{c}_i^\circ = \varepsilon_i^\circ\mathbf{c}_i^\circ.$$

Then we have the standard matrix perturbation expressions,

$$\varepsilon_i = \varepsilon_i^\circ + \mathbf{c}_i^{\circ\dagger}\mathscr{H}\mathbf{c}_i^\circ + \sum_k \frac{|\mathbf{c}_i^{\circ\dagger}\mathscr{H}\mathbf{c}_k^\circ|^2}{\varepsilon_i^\circ - \varepsilon_k^\circ}$$

$$\mathbf{c}_i = \mathbf{c}_i^\circ + \sum_k \frac{|\mathbf{c}_i^{\circ\dagger}\mathscr{H}\mathbf{c}_k^\circ|^2}{\varepsilon_i^\circ - \varepsilon_k^\circ}.$$

Now if $\mathscr{H}$ has large diagonal but small off-diagonal terms, we may simplify the problem by taking $\mathscr{H}^\circ$ to be a diagonal matrix and $\mathscr{H}'$ to be a matrix having only off-diagonal elements. The first order terms then vanish so that

$$\varepsilon_i = \varepsilon_i^\circ + \sum_k \frac{|\mathscr{H}'_{ik}|^2}{\varepsilon_i^\circ - \varepsilon_k^\circ}$$

where $\mathscr{H}'_{ik} = \mathbf{c}_i^{\circ\dagger}\mathscr{H}\mathbf{c}_k^\circ = \mathscr{H}_{ik}$.

Regarding $\mathscr{H}$ as a one-electron hamiltonian, we may use the above expression to estimate the effect on ligand SOs of interaction with metal AOs, and *vice versa*, and also the interactions between the ligand SOs themselves. Notice that the extent of each interaction is

inversely proportional to the enregy separation of the orbitals concerned. Also, if we represent the off-diagonal terms by

$$\mathscr{H}_{ik} = S_{ik}\beta_{ik}$$

[cf. ref. (24)] then the interactions depend upon the square of the appropriate overlap integral. Interactions for which the β parameters should be very similar may therefore be compared simply by reference to the overlap integrals and the energy separations.

METAL p VALENCE AOs

To gauge the bonding interactions between metal p AOs and the a_2 and e ligand SOs we first of all construct a set of p orbitals (denoted p') that are quantized about the trigonal axis of the complex: the coordinate system we have used is shown in fig. 21b, and the details of the transformation from octahedral axes are given in table 11. Then we evaluate the overlap integrals collected in table 12. We conclude from these overlaps that the $a_2(\pi_3)$ and $e(\pi_3)$ ligand levels are not split in first order (except very slightly through inter-ligand interactions). For all acceptable values of the parameter α it appears that the main interaction

TABLE 11.—THE TRANSFORMATION OF p AND d AOs BETWEEN OCTAHEDRAL AND TRIGONAL CARTESIAN AXES (fig. 21b)

	p_x	p_y	p_z	
p'_x	$\dfrac{1}{2}$	0	$-\dfrac{1}{2}$	
p'_y	$-\dfrac{1}{\sqrt{6}}$	$\dfrac{\sqrt{2}}{\sqrt{3}}$	$-\dfrac{1}{\sqrt{6}}$	
p'_z	$\dfrac{1}{\sqrt{3}}$	$\dfrac{1}{\sqrt{3}}$	$\dfrac{1}{\sqrt{3}}$	

	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
d'_{z^2}	0	0	$\dfrac{1}{\sqrt{3}}$	$\dfrac{1}{\sqrt{3}}$	$\dfrac{1}{\sqrt{3}}$
$d'_{x^2-y^2}$	$\dfrac{1}{2\sqrt{3}}$	$\dfrac{1}{2}$	$\dfrac{1}{3}$	$-\dfrac{2}{3}$	$\dfrac{1}{3}$
d'_{xy}	$\dfrac{1}{2}$	$-\dfrac{1}{2\sqrt{3}}$	$\dfrac{1}{\sqrt{3}}$	0	$-\dfrac{1}{\sqrt{3}}$
d'_{xz}	$-\dfrac{1}{\sqrt{2}}$	$\dfrac{1}{\sqrt{6}}$	$\dfrac{1}{\sqrt{6}}$	0	$-\dfrac{1}{\sqrt{6}}$
d'_{yz}	$-\dfrac{1}{\sqrt{6}}$	$-\dfrac{1}{\sqrt{2}}$	$\dfrac{1}{3\sqrt{2}}$	$-\dfrac{\sqrt{2}}{3}$	$\dfrac{1}{3\sqrt{2}}$

is between $e(p')$ and $e(n_+)$. The stabilization of $e(n_-)$ and $a_2(n_-)$ should be relatively small and, in normal circumstances, insufficient to produce a significant splitting of these levels. The $a_1(n_+)$ level will presumably be strongly stabilized by interaction with the metal s AO, so that a substantial separation from $e(n_+)$ is possible. This would lead to the energy level diagram of fig. 25.

METAL d VALENCE AOs

The transformation of the octahedral set of d orbitals into a set d', specified in terms of the trigonal coordinate system, is detailed in table 11. However, an even more convenient set may be obtained by a further transformation among the orbitals of e symmetry:

$$e_a^+ = \frac{\sqrt{2}}{\sqrt{3}}d_x'^2 - y^2 + \frac{1}{\sqrt{3}}d_{yz}'$$

$$e_a^- = \frac{\sqrt{2}}{\sqrt{3}}d_{xy}' + \frac{1}{\sqrt{3}}d_{xz}'$$

$$e_b^+ = -\frac{1}{\sqrt{3}}d_x'^2 - y^2 + \frac{\sqrt{2}}{\sqrt{3}}d_{yz}'$$

$$e_b^- = -\frac{1}{\sqrt{3}}d_{xy}' + \frac{\sqrt{2}}{\sqrt{3}}d_{xz}'$$

[cf. Ballhausen [40]].   The symmetry orbitals, $e_a^{\pm}$ and $e_b^{\pm}$, correlate directly with the octahedral symmetry orbitals, t_{2g} and e_g. Specifically, $t_{2g} \rightarrow e_a + a_1$, where $a_1(d) = d_z'^2$, and $e_g \rightarrow e_b$. The general pattern of overlap integrals in table 12 could thus have been anticipated on the basis of octahedral d orbitals.

TABLE 12.—OVERLAP INTEGRALS BETWEEN METAL p AND d AOs AND THE LEADING LIGAND SOs FOR THE TRIS-CHELATES

	$a_2(p_z')$	$e(p_x', p_y')$
$a_2(n_-)$	$\sqrt{2}(S_\pi \sin\alpha - S_\sigma \cos\alpha)$	0
$e(n_-)$	0	$\frac{1}{\sqrt{2}}(S_\pi \sin\alpha - S_\sigma \cos\alpha)$
$e(n_+)$	0	$\frac{\sqrt{3}}{\sqrt{2}}(S_\pi \sin\alpha + S_\sigma \cos\alpha)$
$a_2(\pi_3)$	$\sqrt{2}\,S_\pi'$	0
$e(\pi_3)$	0	$\sqrt{2}\,S_\pi'$

$$[S_\sigma = \langle Op_\sigma(x)|Mp_\sigma'\rangle, \ S_\pi = \langle Op_\pi(x)|Mp_\pi'\rangle, \ S_\pi' = \langle Op_\pi(y)|Mp_\pi'\rangle].$$

	$a_1(d)$	$e_a(d)$	$e_b(d)$
$a_1(n_+)$	$\sqrt{2}\,S_\pi \sin\alpha$	0	0
$e(n_+)$	0	$\sqrt{2}\,S_\pi \sin\alpha$	$-S_\sigma \cos\alpha$
$e(n_-)$	0	0	$\sqrt{3}\,S_\sigma \cos\alpha$
$e(\pi_3)$	0	$\frac{\sqrt{3}}{\sqrt{2}}S_\pi'$	0

$$[S_\sigma = \langle Op_\sigma(x)|Md_\sigma\rangle, \ S_\pi = \langle Op_\pi(x)|Md_\pi\rangle, \ S_\pi' = \langle Op_\pi(y)|Md_\pi\rangle].$$

The major interaction between $e_b(d)$ and ligand $e(n_-)$ may result in a substantial separation between this ligand level and the $a_2(n_-)$ level, which is formally non-bonding. Similarly, $e(n_+)$ should be considerably stabilized with respect to $a_1(n_+)$, unless the metal s valence AOs have an important influence. The identical interaction between the $a_1(d)$ and $e_a(d)$ metal AOs and ligand n_+, depending solely on π overlap, is expected to be quite small. Notice that, apart from the effect of the trigonal potential, which will stabilize $e_a(d)$ somewhat and destabilize $e_b(d)$, a first order separation of the $a_1(d)$ and $e_a(d)$ levels can occur only through the interaction of $e_a(d)$ and $e(\pi_3)$. But this latter interaction, leading also to a splitting of $a_2(\pi_3)$ and $e(\pi_3)$, should normally be quite small. These various conclusions are reflected in the energy level diagram in fig. 26, where we assume that the metal d AOs lie higher in energy than the ligand orbitals.
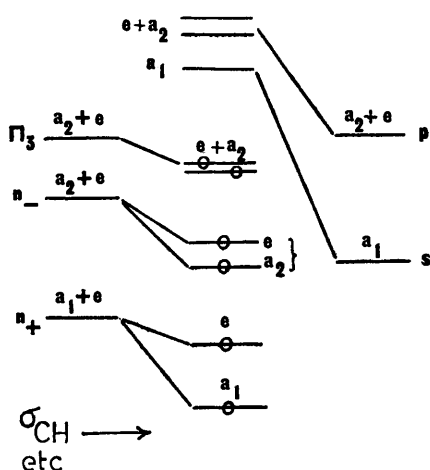
FIG. 25.—A molecular orbital diagram showing the interaction of the tris-ligand system with metal s and p valence orbitals.
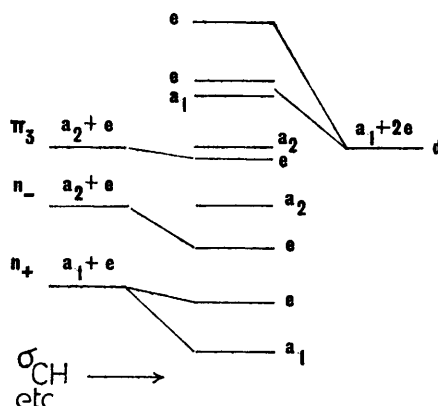
FIG. 26.—A molecular orbital diagram showing the interaction of the tris-ligand system with the metal d valence orbitals.

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