A Study of the Bonding in Some Compounds of Aluminium using Al-$K\beta_{1,3}$ X-Ray Emission spectra

By **C. J. Nicholls** and **D. S. Urch,*** Department of Chemistry, Queen Mary College, University of London, Mile End Road, London E1 4NS

The aluminium $K\alpha$ and $K\beta_{1,3}$ X-rays have been studied in the following compounds, alumina, microcline, kyanite, cryolite, aluminium trifluoride, aluminium trichloride, topaz, aluminium acetylacetonate, aluminium 8-hydroxyquinolinate, and the metal itself. The relative intensities of the two peaks can be related to bond length and the degree of ionic character. It is proposed that the fine structure of the $K\beta_{1,3}$ peak is due to varying Al $3p$ participation in different molecular orbitals. Evidence for both σ and π bonding between the metal and the ligands is discussed.

X-RAY emission spectra result from electronic transitions to vacancies in inner orbitals. If the electron originates from the valence band then the fine structure of the X-ray peak reflects the various molecular orbital energy levels present in the molecule.[1] The relative intensities of the components of such a peak can be related to the degree of atomic orbital participation in particular molecular orbitals. X-Ray emission (XRE) spectroscopy also permits a study of the bonding role of specific types of orbitals; this is because the atomic selection rule $\Delta l = \pm 1$ operates. Thus a vacancy in an s orbital can be used to probe the bonding role of p orbitals; similarly a p vacancy would attract transitions only from s or d orbitals, or molecular orbitals with s or d character. For these reasons high resolution X-ray emission spectroscopy is a particularly attractive method for the study of bonding in molecules.

The intensity of a K X-ray emission line is governed by the integral $\int\phi_{1s}\mathbf{P}\psi_{\text{ex}}$ (1) where $\mathbf{P}$ is the transition probability operator and ψ_{ex} is the wave function for the orbital from which the electron came to fill the $1s$ vacancy. If ψ_{ex} is a molecular orbital it will have, in the LCAO approximation, the form

$$\psi_{\text{ex}} = a \,.\, \psi_{np} + (1 - a^2)^{-\frac{1}{2}}\psi_{\text{l}} \qquad (2)$$

where a is a coefficient. ψ_{np} Is a p orbital of principal quantum number n on the atom in which the vacancy was created and ψ_{l} is an appropriate ligand wave function. Substituting (2) into (1) enables (1) to be broken down into two parts, one essentially located on the central atom and another which involves ψ_{l} and ϕ_{1s}. A consideration [2] of the amplitudes of ψ_{l} and ψ_{np} in the ϕ_{1s} region shows that the overwhelming contribution ($>99{\cdot}9\%$) to (1) comes from the former of these two terms. This means that the direct 'cross-over' transition from ψ_{l} to ϕ_{1s} is negligible. Relative X-ray emission intensities can therefore be used to estimate ratios of coefficients in equations of type (2) for the different molecular orbitals. Simple molecular orbital theory can be used to generate a qualitative energy level diagram and to suggest approximately the degree to which particular atomic orbitals will participate in given molecular orbitals. Such a diagram can then be correlated with the observed X-ray emission spectrum.[2] This technique is used in this paper to study the bonding role of aluminium $3p$ orbitals in compounds and complexes of aluminium.

EXPERIMENTAL

All the spectra reported in this paper were obtained using a Philips PW 1410 X-ray fluorescence spectrometer with a chromium anode X-ray tube operated at 40 kV, 60 mA.

---

[1] D. S. Urch, *Quart. Rev.*, 1971, **25**, 343.

[2] D. S. Urch, *J. Physics C, Solid State*, 1970, **3**, 1275.

Pentaerythritol (002), ' P.E.,' with a $2d$ spacing of 874·2 pm, was chosen as the diffracting crystal since it diffracts aluminium $K\beta_{1,3}$ radiation at a high angle ($2\theta = ca.\ 130°$) and dispersion, as a function of energy, increases with angle. The overall resolving power in this angular region was estimated by means of high order iron $K\alpha_{1,2}$ lines. The doublet gave rise to a main peak and a shoulder from which $E/\Delta E$ was estimated to be 800. Thus in the aluminium region it would not be possible to resolve features separated by less than about 2·0 eV. The natural width of the $K\alpha_{1,2}$ doublet from aluminium metal is of the order of 0·7 eV; it would be unreasonable to suggest that the $K\beta_{1,3}$ should be narrower than this. The degree of resolution observed in the spectra reported in this paper was therefore controlled by the resolving power of the instrument. The spectra were calibrated with respect to the $K\alpha$ line of aluminium metal (1486·7 eV, angular setting for P.E. crystal 145·07 °2θ). A proportional counter with a thin (1 μm) polypropylene window, coupled to Harwell 2000 series electronics, was used to detect the X-rays. The spectrometer was evacuated ($<10^{-3}$ Torr) and fine collimation (150 μm) was used to enhance resolution.

Energies/eV of X-rays from aluminium compounds

Sample	$K\alpha$	$K\beta_{1,3}$	$K\beta'$	$K\beta - K\beta' = \Delta$	$\frac{\text{Intensity } K\beta_{1,3}}{\text{Intensity } K\alpha}$
Aluminium metal (reference)	1486·7	1556·6	None		1·3
α-Alumina	1487·1	1552·8	1537·3	15·5	2·2
Kyanite	1487·2	1552·9	1537·9	15·0	1·9
Microcline	1486·8	1551·4	1537·1	14·3	1·9
Aluminium trifluoride [a]	1487·2	1551·8	1538·3 1532·7	13·5 19·1	1·9
Aluminium trichloride	Not determined	1553·0	None		Not determined
Cryolite	1487·1	1551·6	1532·3	19·3	0·4
Topaz	1487·2	*b*	1538·0 1532·0	*c*	1·5
Aluminium acetylacetonate	1487·0	*b*	1535·6	*c*	3
Aluminium 8-hydroxyquinolinate	1487·0	*b*	1537·5 1545·0?	*c*	3

[a] Contaminated sample, see text. [b] $K\beta_{1,3}$ Peak has complex structure, see Figure 1. Δ Not given, since unique value for $K\beta_{1,3}$ not determined.

Under these conditions low count rates at the aluminium $K\beta_{1,3}$ peak were obtained, varying from 100 to 250 counts s^{-1} depending upon the sample. The background count for all samples was of the order of 5 counts s^{-1}. In order to obtain spectra characterised by reasonable counting statistics the angular range of interest was scanned at the slowest possible speed (0·25° 2θ per min) using a time constant of 5 s (the time to traverse 0·13 eV).

In the case of aluminium tris(acetylacetonate) an even slower technique was employed, that of counting for fixed periods (1 min) at preset angular positions. This gives larger numbers of counts and therefore a more accurate spectrum.

The compounds studied were:

α-Alumina, Cryolite, Kyanite, Microcline, and Topaz	All mineralogical specimens supplied by Geology Department Queen Mary College.
Aluminium fluoride	A commercial sample obtained from the laboratory of the Government Chemist.
Aluminium chloride	B.D.H. Ltd.

Aluminium tris(8-hydroxyquinolate). Prepared from equivalent quantities of aluminium sulphate and 8-hydroxyquinoline in aqueous solution. Optimum conditions for precipitation were brought about by the addition of 2M-ammonium acetate. The yellow compound was washed thoroughly and dried at 150°.

Aluminium tris(acetylacetonate). An ammoniacal solution of acetylacetone (6 g) in water was added to a solution of aluminium sulphate (6 g) in water. The precipitate was washed, dried, and vacuum sublimed, m.p. 193—195° (lit. 194·6°).

A disc of pure aluminium metal supplied by Philips Ltd. was used as a reference standard. Apart from the metal all the samples were crushed to a powder and mounted into discs of terephthalic acid under pressure. These discs were then inserted into the spectrometer for the $K\alpha$ and $K\beta$ aluminium emission spectra to be recorded.

RESULTS AND DISCUSSION

The experimentally determined X-ray emission energies are summarised in the Table. For the most part, the main $K\beta_{1,3}$ peak from the compounds of aluminium is without structure and is much more symmetrical than from the metal itself. The spectra of the compounds is also characterised by the presence of the low energy satellite peak $K\beta'$. In some cases, however, much more complex $K\beta_{1,3}$ peaks are observed and these spectra are shown in Figure 1. In these spectra a smooth line has been drawn through the noise of the ratemeter trace. The average level of this noise has been indicated on some of the spectra. Various features of the spectra deserve comment, (a) peak position, (b) peak intensities, (c) satellite peaks, and (d) structure of the main $K\beta_{1,3}$ peak.

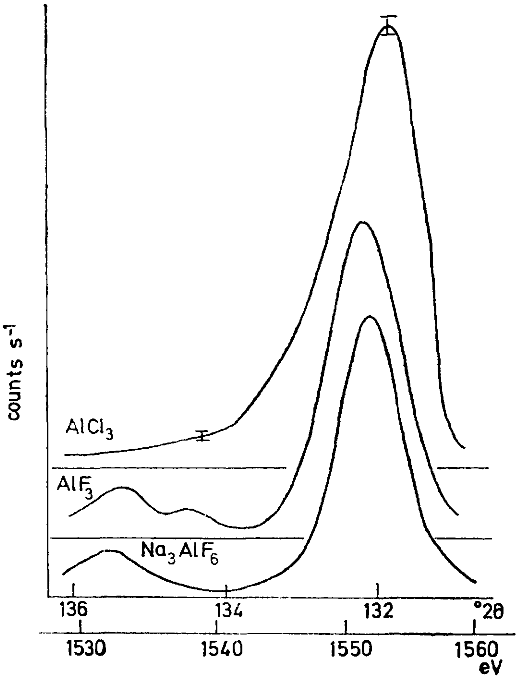
(a) *Peak Positions*.—The $K\alpha$ emission peak arises from the transition between the inner orbitals $2p$ and $1s$. Both are, as X-ray photoelectron spectroscopy has shown,[3] subject to ionisation energy perturbations which can be correlated with co-ordination number. However, the absolute magnitude of these perturbations is not quite the same for both orbitals and so small changes in the $K\alpha$ emission energy can be observed, and these changes can be correlated with co-ordination as was originally shown by Day.[4] The results presented here are very much in agreement with Day's general con-

---

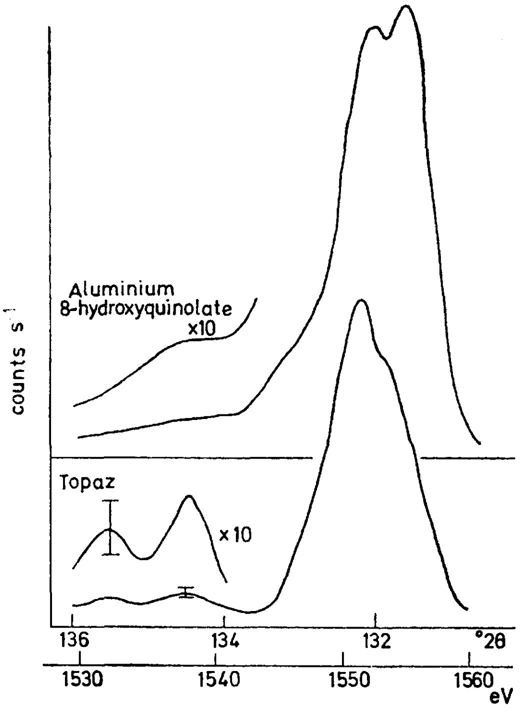
[3] C. J. Nicholls, D. S. Urch, and A. N. L. Kay, *J.C.S. Chem. Comm.*, 1972, 1198.

[4] D. E. Day, *Nature*, 1963, **2000**, 649.

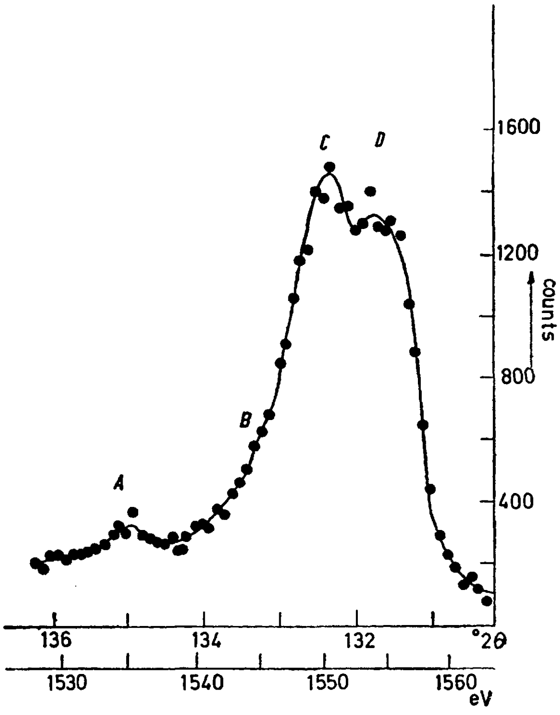
clusions. The Al-$K\alpha$ energy from microcline (four-co-ordination) exceeds that of the metal itself by only 0·1 eV whereas the $K\alpha$ energies from aluminium in six-co-ordination are greater than from the metal by 0·3—0·6 eV. The reasons for these variations could be many, *e.g.* the nature of the ligands, their bond lengths to the aluminium, *etc.* But it is interesting to note that the most energetic $K\alpha$ emissions appear to be associated with ligands which would be expected to form rather ionic bonds whereas the lower energy $K\alpha$ X-rays are associated with the complexes, where the aluminium–ligand bond is perhaps more covalent.



(a)



(b)



(c)

FIGURE 1 (a) and (b), Al-$K\beta_{1,3}$ emission spectra. All spectra have been ' hand-smoothed ' by drawing the best line through a ratemeter trace. The usual level of concomitant noise ($\pm$ one standard deviation) is indicated on the AlCl$_3$ and the topaz spectra (thus I). Note that the AlF$_3$ sample is contaminated with an oxygen containing species (see text). Typical count rates at the peak and for background are given in the text; (c), Al-$K\beta_{1,3}$ emission spectrum from aluminium trisac(etylacetonate) using the step-scanning technique

That the $K\beta$ emission energy should also respond to changes in the chemical environment of the aluminium atom is intuitively more reasonable. White and Gibbs[5] have succeeded, in a series of closely related alumino-silicates, in correlating $K\beta$ emission energies with bond length and co-ordination number. However, in the series of compounds discussed in this paper the position is more complex since a wide variety of bonding situations is being considered. Also in some examples the $K\beta_{1,3}$ peak itself shows considerable structure and no single energy can reasonably be chosen as the $K\beta_{1,3}$ emission energy for that compound. Even so it is of interest to notice that the general effect of chemical bond formation, by comparison with the metal, is for the $K\beta$ peak to move to lower energies (by a few eV) whilst the $K\alpha$ peak moves to higher energies (by a few tenths of an electron volt). The changes in $K\beta$ energies can be rationalised by making the reasonable assumption that chemical bond formation causes greater perturbations in valence shell, than in inner orbital, energies. Electrons

---

[5] E. W. White and G. V. Gibbs, *Amer. Mineralogist*, 1967, **52**, 985; *ibid.*, 1969, **54**, 931.

become more tightly bound in molecular orbitals and so the transition energies to inner orbitals are reduced.

(b) *Peak Intensities.*—If it is assumed that the intensity of the Al-$K\alpha$ emission is not affected by chemical bonding then it can be used as a standard, relative to the $K\beta_{1,3}$ peak. Changes in the ($K\beta/K\alpha$) intensity ratio should reflect changes in the Al $3p$ contribution to particular molecular orbitals and therefore to changes in the electronic charge associated with the $3p$ orbitals. (A direct relationship with the total effective charge at aluminium will *not* be possible since the $3s$ contribution cannot be measured by this technique.) $K\beta/K\alpha$ Intensity ratios are given in the Table. If a series of six-co-ordinate aluminium compounds is chosen it would seem that there is a correlation between the $K\beta/K\alpha$ intensity ratio and bond length (Figure 2).

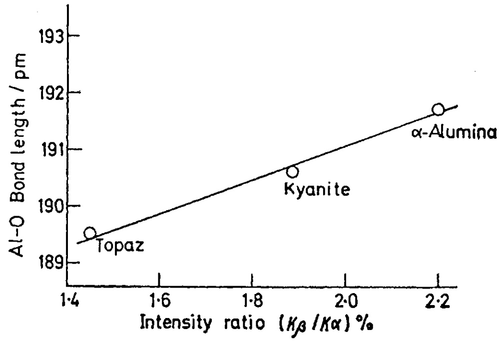


FIGURE 2 Correlation between the $K\beta/K\alpha$ peak intensity ratio and Al–O bond length

Such a correlation would seem to suggest an increase in $3p$ character with increasing bond length and therefore with an increase in the overall ionic nature of the bond. If this is so then there would have to be a rather larger diminution in the aluminium $3s$ character. Very simple molecular orbital calculations do indeed suggest[2] that when aluminium does form bonds with considerable ionic character then the greatest donation of electronic charge comes from the $3s$ orbitals and that there may be back donation, *via* $3p$ orbitals, to aluminium. In this way an increase in the total electronic charge in the aluminium $3p$ orbitals can be reconciled with an increase in the effective positive charge at the same atom.

It would be of considerable interest to know the Al–O bond lengths in the two complexes studied in this paper; if the correlation suggested in Figure 2 has any value then the predicted value would be *ca.* 195 pm.

(c) *Satellite Peaks.*—The environment of the aluminium atom in the compounds considered here is either approximately tetrahedral or approximately octahedral. Symmetry arguments can therefore be used to simplify a discussion of the bonding between the central atom and the ligands. When the ligands have $2s$ and $2p$ orbitals that are relatively well separated in their ionisation energies (*i.e.* >10 eV) it is possible to speak of molecular orbitals that have central atom $3p$ character (either t_2 or t_{1u} depending upon the local symmetry, T_d or O_h) and either ligand $2p$ or ligand $2s$ character. The main $K\beta_{1,3}$ emission peak then arises from the $3p$ character in the former orbitals, the $K\beta'$ low energy satellite peak from the small amount of $3p$ character in the latter orbitals. The energy separation between these two sets of t_2 or t_{1u} molecular orbitals will be closely related to the difference in the $2p$ and $2s$ ionisation energies of the free ligand. Hence this difference (Δ) will be diagnostic of the ligand atom (see Table). The spectrum from topaz is particularly interesting in the $K\beta'$ region since two satellite peaks are observed, one with a Δ characteristic of oxygen, the other for a Δ for fluorine. This is clearly in accord with the structure of topaz in which the aluminium atoms are surrounded by four oxygen and two fluorine atoms. The spectrum of aluminium fluoride is also of interest since an ' oxygen ' satellite can be seen as well as the expected ' fluorine ' peak. This shows that the sample is not pure; it is probably contaminated by the presence of water, giving rise to a partially hydrated specimen. In the 8-hydroxyquinolinate sample only the oxygen satellite is clearly resolved. The anticipated position for the nitrogen satellite is covered by low energy structure associated with the main $K\beta_{1,3}$ peak (discussed in more detail in the next section).

Aluminium chloride is of especial interest in that no satellite is observed at all. Again the $K\beta_{1,3}$ peak is broad and indeed may cover the energy region in which the satellite would occur. Even so it would seem that the intensity of such a satellite cannot exceed 5% of the main $K\beta_{1,3}$.[6] This is to be compared with relative intensities associated with oxygen and fluorine ligands of about 20—30%. If the low energy satellites of second row elements are much less intense than those of their first row counterparts, then this shows that $3s$ valence shell orbitals play a much smaller role in bond formation than do $2s$ orbitals, even though they are less tightly bound. This conclusion is, of course, in keeping with the general chemical evidence about the relative bonding importance of $2s$ and $3s$ orbitals. (One very simple manifestation of this effect, by way of example, is the contraction of hydride bond angles in going from the first to the second row, *e.g.* NH_3, 106·6; PH_3, 93·5; H_2O, 104·5; and H_2S, 92·1°.)

(d) *Structure of the* $K\beta_{1,3}$ *Peak.*—As can be seen from Figure 1 the fine structure exhibited by the main Al-$K\beta_{1,3}$ peak is related to the complexity of the ligand. Since the bonding in the various compounds studied is very different each one will be discussed individually.

Cryolite (Na_3AlF_6).—The aluminium is octahedrally surrounded by six fluorine atoms. Orbitals of the correct symmetry (t_{1u}) to interact with the aluminium $3p$ orbitals can be found from: (i), the six fluorine $2s$ orbitals; (ii), the six fluorine $2p$ orbitals pointing towards the central atom; (iii), the other twelve fluorine $2p$ orbitals.

$3p$ Character in the molecular orbital formed by interaction with ligand orbitals (i) gives rise to the $K\beta'$ peak

---

[6] G. Wiech, W. Koppen, and D. S. Urch, *Inorg. Chim. Acta*, 1972, **6**, 376.

and interaction with (ii) to the $K\beta_{1,3}$ peak. The slight high energy tail *ca.* 1556—1559 eV may therefore be due to Al $3p$ interaction with the lone pair orbitals (iii) perpendicular to the Al–F σ bonds, *i.e.* π-bonding. The σ bond between aluminium and fluorine is therefore seen to involve both fluorine $2p$ and $2s$ orbitals and there is also a possibility of some weak π-bonding as well. Further work at higher resolution is required to substantiate the existence of this higher energy peak; a correlation with the fluorine $K\alpha$ emission spectrum would also be valuable. A further source of possible interaction, which does not seem to greatly affect the observed structure of the main $K\beta_{1,3}$ peak, is that of ligand orbitals (ii) with the cations present in the crystal structure. The effects of such interactions may simply be to increase the breadth of the peak.

Aluminium Fluoride (AlF_3).—The local environment of the aluminium is very similar to that in cryolite; the difference being that each fluorine is also making σ bonds to other aluminium atoms. The great similarity in the Al-$K\beta_{1,3}$ emission spectra from aluminium trifluoride and from cryolite strongly suggests that those interactions that were important in AlF_6^{3-} are also important in AlF_3, *i.e.* interactions involving fluorine orbitals (i) and (ii). Indeed this similarity shows that orbitals of type (iii) cannot be of importance in either case since it is these orbitals which are used to form σ bonds in aluminium trifluoride.

Aluminium Trichloride.—The Al-$K\beta$ peak is broader in this compound than in either of the fluorides. The reason for this is not clear but may be due to stronger interactions being transmitted from one aluminium atom to another *via* bridging chlorine atoms along Al–Cl bonds that are more covalent than Al–F bonds.

Kyanite and Microcline.—In these two aluminosilicate materials, a single $K\beta_{1,3}$ peak, with no additional structure, was observed. The oxygen ligands, despite the differences in co-ordination number, are heavily committed in the formation of bridging bonds to other atoms such as aluminium, silicon, *etc.*, so there are few lone pair orbitals with π-bonding potential. The Al $3p$ orbitals would therefore seem to form only σ bonds with the oxygen ligands. In the absence of any bonding complications a single Al-$K\beta_{1,3}$ peak is observed.

α-Alumina (Al_2O_3).—Although the bonding commitments of the oxygen in alumina are very similar to those in the aluminosilicates considered above the Al-$K\beta_{1,3}$ peak is sometimes observed[7] to be split into two components of comparable intensity (separation *ca.* 1 eV). Since to a first approximation all the Al–O bonds can be regarded as σ bonds it would seem that this splitting must be due to interactions between σ bonds. Relative to a particular aluminium atom the Al–O bonds which it makes will be σ but the other O–Al bonds arising from the oxygen atoms will give rise to orbitals, some of which will have π-symmetry relative to the original atom.

Topaz.—In topaz each aluminium atom is surrounded by four oxygen atoms and two fluorine atoms. Each fluorine forms a bridge to another aluminium atom whilst the oxygen atoms act as bridges to both neighbouring aluminium and silicon atoms; each oxygen is three-co-ordinate. It is the antisymmetric combination of ligand p orbitals (orientated along ligand–Al axes) from ligand atoms on opposite sides of the central atom that will interact with the $3p$ orbitals of the aluminium. When all six ligands are in position around the central atom, it is also necessary to consider interactions between adjacent ligand atoms. However, it can easily be shown that such interactions will only affect those combinations of ligand orbitals of *gerade* symmetry (*i.e.* a_{1g} and e_g). In the absence of *trans* ligand–ligand interactions the antisymmetric combination of ligand m.o.s will be non-bonding. But when both fluorine and oxygen are ligands the m.o.s of this type associated with O–Al(p)–O will be less tightly bound than those associated with O–Al(p)–F because the F $2p$ ionisation energy is greater than that for O $2p$. There will be one orbital of the former type and two of the latter. One is therefore led to suggest that the interaction of Al $3p$ orbitals with ligand orbitals appropriate for σ bond formation will give rise to two distinct sets of molecular orbitals, the less tightly bound being singly degenerate (O–Al–O) and the other being more tightly bound and doubly degenerate (O–Al–F). The Al-$K\beta_{1,3}$ emission peak should therefore be split into two, and the lower energy component should be the more intense. As can be seen from Figure 1 there is a shoulder on the high energy side of the principal $K\beta_{1,3}$ peak, in accord with the proposed model. π-Bonding has not been considered since it is felt that those ligand orbitals which have π-bonding potential are fully committed in σ-bond formation.

Tris(acetylacetonato)aluminium.—The ligand in this complex is quite different from any that has been considered above and has itself an extensive network of delocalised π-electrons. The $K\beta_{1,3}$ emission spectrum is also much more complex showing two clear peaks and a low-energy shoulder (as well as the $K\beta'$ satellite). The bonding between the aluminium and the ligands will be considered in two stages, first σ- and then π-bonding.

Although the overall symmetry of the molecule is D_3, the local environment of the aluminium atom is at the centre of an octahedron of oxygen atoms. Al–O σ Bonds will be formed between aluminium $3s$, $3p$ (and $3d$?) orbitals and ligand $2p$ orbitals directed towards the central atom along cartesian axes. In the local O_h symmetry these orbitals will belong to irreducible representations a_{1g}, e_g, and t_{1u}. Only the latter has any relevance to this discussion since the aluminium $3p$ orbitals transform as t_{1u}. Depending upon the relative extent of ligand–ligand interactions across the central atom, and between adjacent ligands, so the t_{1u} orbitals will be non- or slightly anti-bonding relative to the original ligand $2p$ orbitals. Unless the symmetry is grossly distorted there seems no reason to believe that

---

[7] W. L. Baun and D. W. Fischer, *Adv. X-ray Analysis*, 1965, **8**, 371.

the t_{1u} orbitals will not remain effectively degenerate. The interaction with the aluminium $3p$ orbitals should therefore give rise to just one set of three degenerate occupied orbitals and so there should be just one peak in the $K\beta_{1,3}$ emission spectrum. The fact that this is not so clearly points to the concomitant presence of π-bonding.

The three lowest lying, and therefore occupied, π orbitals of the acetylacetonate ligand are shown diagrammatically in Figure 3. A consideration of the symmetries of the orbitals presented to the central atom for π-bond formation shows that only $\pi1$ and $\pi3$ could interact with aluminium $3p$ orbitals. This in turn suggests that there might be two π molecular orbitals with some Al $3p$ character.

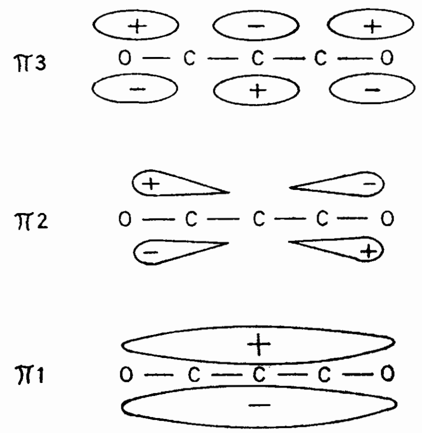


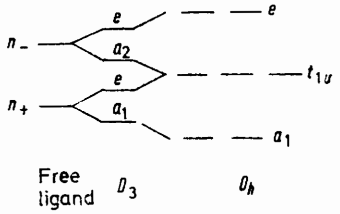
FIGURE 3 Diagrammatic representation of the occupied orbitals of the acetylacetonate ligand

Orchard *et al.*[8] have studied the helium-(I) photoelectron spectrum of acetylacetone, which exists mostly in the enol form in the gas phase. They concluded that the two orbitals of ionisation energies 9·9 and 9·3 eV were most probably $\pi3$ and the antisymmetric combination of oxygen σ lone pair orbitals, but there would seem to be no easy way of telling which orbital was which. Other molecular orbitals had ionisation energies in the range 12·5—16 eV. It therefore follows that the energy separation between $\pi3$ and $\pi1$ must be at least 2·6 eV and molecular orbital calculations suggest[9] that the separation is probably about 4 eV.

Three acetylacetonate ligands can therefore present the following orbitals for interaction with the $3p$ orbitals of a central aluminium atom: (i), an antisymmetric combination of oxygen ligand lone pair σ orbitals; (ii), $\pi3$; (iii), $\pi1$. (i) and (ii) Have comparable ionisation energies, (iii) is more tightly bound. Since three clearly defined features (B, C, D) are observed in the $K\beta_{1,3}$ spectrum it seems reasonable to identify them with interactions brought about by these three sets of ligand orbitals. The problem now arises as to how B, C, and D are to be related to these ligand orbitals.

When σ-type interactions are considered not only must $2p$ ligand orbitals orientated along the axes to the central atom be considered but also the family of ligand $2s$ orbitals. The $2s$ orbitals cannot interact with the π orbitals and so the $K\beta'$ peak is associated exclusively with σ bonding. Thus it ought to be possible to use the $K\beta - K\beta'$ ($= \Delta$) energy difference to identify the σ component of the main $K\beta_{1,3}$ peak. In simple examples (see above) it was found that Δ for oxygen ligands was *ca.* 15 eV. This argument points to peak C as arising from the $3p$ component of the σ bonds whilst D and B would then be associated with $\pi3$ and $\pi1$ respectively. Since (i) and (ii) in the ligand have comparable energy, this result seems quite reasonable. σ Interaction, being stronger than π interaction, makes the σ m.o. more tightly bound and so C has a lower energy than D. The B, D separation is *ca.* 8 eV, which is about twice the $\pi1 - \pi3$ ionisation energy difference suggested by S.C.F. calculations for the free ligand. Hanazaki *et al.*[9] did, however, extend their calculations to study the effect of a point charge placed in an appropriate position relative to the ligand. When this was done the calculated $\pi1 - \pi3$ energy difference increased to 5 eV. The agreement is not good but is probably the best that can be expected in a comparison of rather simple m.o. calculations with imperfectly resolved spectra.

It is of interest to see how this proposed orbital assignment compares with that of Orchard *et al.* for the hexafluoroacetylacetonate complex of aluminium. These authors concluded that the least tightly bound molecular orbital (A, Figure 5, ref. 8) was the ligand $\pi3$. This corresponds to D in Figure 1(c), since as argued above $\pi3$ will interact with Al $3p$ orbitals. Peak B in the helium photoelectron spectrum is associated with ligand σ orbitals designated n_-. If the octahedral ligand arrangement is assumed then the following correlations can be made:



Peak B would then correspond to the least tightly bound of these orbitals and be either wholly ligand in character or ligand with an admixture of Al $3d$ character. It would therefore not be present in the aluminium $K\beta$ spectrum. The next ligand σ orbital, derived from n_-a_2 and n_+e, can, however, interact with Al $3p$ orbitals and gives rise to C in Figure 1(c). The same molecular orbital probably gives rise to peak C in Figure 5 of ref. 8, as suggested by the authors. The energy separation of photoelectron peaks A and C, and X-ray emission peaks, is in both cases about 3 eV. Since different molecules are being compared and the resolution of the X-ray

---

[8] S. Evans, A. Hamnett, A. F. Orchard, and D. R. Lloyd, *Faraday Discuss. Chem. Soc.*, 1972, **54**, 227.

[9] I. Hanazaki, F. Hanasaki, and S. Nagakura, *J. Chem. Phys.*, 1969, **50**, 265.

emission spectrum is inferior to that of the He PS this correlation is very satisfactory indeed.

Tris-(8-hydroxyquinolinato)aluminium.— 8-Hydroxyquinoline has a complex delocalised π electron system and acts as a bidentate ligand using both nitrogen and oxygen orbitals to form σ-bonds. A discussion of the bonding between such a ligand and aluminium therefore combines the complexities of both the previous sections.

If the ligands are arranged symmetrically about the central atom then the σ bonds along each cartesian axis would involve the atoms N–Al–O. In this case the antisymmetric orbital derived from the nitrogen and oxygen $2p$ orbitals would be of the correct symmetry to interact with the aluminium $3p$ orbital. This type of interaction would therefore lead to three degenerate σ bonds between aluminium and the ligands and give rise to just one peak in the *X*-ray emission spectrum.

The interaction of the ligand π-systems with the central atom must be much more complex since the presence of the heteroatoms in the ligand itself destroys any symmetry other than the most trivial. The orbitals which have the potential of forming π bonds with the aluminium $3p$ orbitals cannot easily be selected. It can, however, be asserted that due to the lack of symmetry in the ligand all six occupied π orbitals will have the possibility of π-bonding with the aluminium. The simplest explanation of the observed emission spectrum is therefore that in the feature *C*, *D*, one peak is due to σ bond formation and the other is derived from π-interactions with ' non-bonding ' orbitals with much nitrogen or oxygen lone pair character. The rather broad low energy tail, possibly concealing peaks *B* and *B'* (but probably more), is then due to the interaction of aluminium $3p$ orbitals with the various occupied π-orbitals of the hydroxyquinolinate anion. Although the ' nitrogen ' $K\beta'$ satellite peak should be observed *ca.* 1545 eV, there would seem to be no way of telling from spectra of this type whether *B* is this satellite or is due to π-interactions, or both. The ' oxygen ' $K\beta'$ satellite *A* appears curiously broadened. This might be due to the presence of some weak low energy peaks derived from Al $3p$ interactions with tightly bound aromatic π-orbitals. These peaks might have an energy comparable with the satellite peak and if they were not completely resolved from it the impression would be created of a broad structureless peak, as is observed.

CONCLUSIONS

A study of the aluminium $K\beta_{1,3}$ emission peaks from a variety of compounds and complexes enables those molecular orbitals with some Al $3p$ character to be identified. Since ligand *s* orbitals cannot participate in π-bond formation the position of the $K\beta'$ low energy satellite permits σ- and thus π-orbital components of the $K\beta_{1,3}$ peak to be distinguished. It is hoped, in future work, to correlate *X*-ray emission spectra with He(I) photoelectron spectra and so to aid in orbital characterisation.

The authors wish to thank the Royal Society, The University of London Central Research Fund, and Queen Mary College for their generous help in the purchase of equipment. One of us (C. J. N.) thanks the S.R.C. for a research studentship.

[3/1789 *Received, 29th August,* 1973]