The Metal–Ligand Bond in Tropolone † Complexes of Aluminium and Silicon. A Study Based on *X*-Ray Emission and *X*-Ray Photoelectron Spectra

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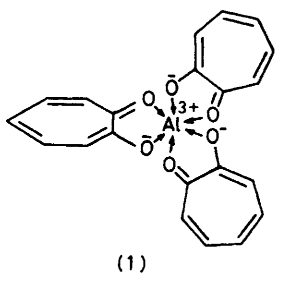
X-Ray photoelectron and *X*-ray emission (Al-$K_{\beta_{1,3}}$, Si-$K_{\beta_{1,3}}$, O-K_α) spectra from the tris('tropolonate') complexes [$Al(C_7H_5O_2)_3$] and [$Si(C_7H_5O_2)_3$][PF_6] have been measured. These spectra show that the bond between the ligand and aluminium or silicon has both σ and π components. This observation is rationalised using simple molecular orbital theory.

A study of the *X*-ray emission spectra of organometallic complexes of magnesium,[1] aluminium,[2] and silicon[3] has shown that the involvement of metal 3*p* character in bonds to the ligands can be discerned from the fine structure of the metal $K_{\beta_{1,3}}$ peak. This is because $K_{\beta_{1,3}}$ *X*-ray emission arises from the electronic transition $3p \rightarrow 1s$. If 3*p* character is present to varying degrees in different molecular orbitals (m.o.s), each of which has a different ionisation energy, then $3p \rightarrow 1s$ relaxation from these m.o.s will generate a set of *X*-ray peaks of different energies and with intensities that reflect the varying amounts of 3*p* character in each m.o.[4] In particular it has been established[3] that if extensive π-bonding is present in the ligand (*e.g.* acetylacetonate, catecholate) then two intense peaks are found in the metal $K_{\beta_{1,3}}$ spectrum whereas if no π-bonding is present in the ligand (*e.g.* oxide, glycol) then only one principal peak is observed. It seems reasonable to conclude that in the former case the delocalised π-bonding system in the ligand can be extended to encompass the metal atom giving rise to metal–ligand bonds with both σ and π character whilst for the latter only σ bonds are formed. In order to test the generality of this conclusion and to determine the factors which might determine the relative intensities of the two component peaks of $K_{\beta_{1,3}}$ the tropolone ($C_7H_5O_2H$) complexes of both aluminium (1) and silicon (2) were investigated by *X*-ray emission (x.e.) and by *X*-ray photoelectron (x.p.) spectroscopy.



(1)

Experimental

Preparation of Compounds.—Tropolone. The method of Stevens *et al.*[5] was found to be the most efficient. The addition of triethylamine (2 °C) to a solution of cyclopentadiene and dichloroacetyl chloride in dry hexane gave 17.7 g of a liquid phase to which was added, after the removal of the solid hydrochloride, acetic acid (300 cm^3), potassium hydroxide (25 g), and water (10 cm^3). This mixture was refluxed overnight (16 h). Copper sulphate solution and solid sodium carbonate were then added to yield, when extracted with methylene chloride, the crude copper complex of tropolone. The complex was purified by recrystallisation from chloroform and decomposed using hydrogen sulphide[6] to give free tropolone. Filtration and distillation left solid tropolone which was recrystallised from hexane.

[$Al(C_7H_5O_2)_3$] (1).[7] This complex precipitated from a mixture of tropolone (0.083 mol) in methanol (250 cm^3) and aluminium trichloride (0.015 mol) in methanol (100 cm^3) and was purified by recrystallisation from a hot acetonitrile–methanol (1 : 1) mixture.

[$Si(C_7H_5O_2)_3$][PF_6] (2). A mixture of silicon tetrachloride (10 mmol) in benzene (10 cm^3) and tropolone (40 mmol) in 50% aqueous methanol (80 cm^3) was refluxed for 1 h. The complex precipitated out when a concentrated solution of ammonium hexafluorophosphate was added.

Spectroscopic Methods.—X-Ray photoelectron spectroscopy. Core and valence band spectra were measured using a Vacuum Generators ESCA 3 Mk1 spectrometer (unmonochromated Al-$K_{\alpha_{1,2}}$ radiation; *X*-ray power 10 mA, 20 kV) operated at a pressure of *ca.* 2×10^{-9} Torr. Powdered samples were mounted by pressing into a gold mesh. Spectra were calibrated with respect to gold lines (Au-*N*6, 86.4 eV; Au-*N*7, 82.8 eV) and were recorded in analog mode on a chart recorder–ratemeter, reading *versus* electron kinetic energy.

X-*Ray emission spectroscopy.* Aluminium and silicon $K_{\beta_{1,3}}$–$K_{\beta'}$ spectra were excited by irradiation with a sealed chromium anode *X*-ray tube (50 mA, 50 kV) and measured in a Philips PW 1410 spectrometer operated at *ca.* 10^{-1} Torr. Fine collimation [150 μm, angular divergence ±0.14 (2θ)°] was used in conjunction with an ethylenediaminedium tartrate crystal (2*d* = 881 pm; *d* = interplane separation in crystal) to give an overall resolving power, *E*/Δ*E*, of *ca.* 800. The characteristic *X*-rays were detected in a proportional counter (P-10 counting gas, atmospheric pressure, 1-μm window) the output from which was amplified using Harwell 2000 series electronics. The *X*-ray peaks were automatically step scanned in steps of 0.02(2θ)°, 360 s per step. The oxygen K_α spectrum from the silicon complex was measured using exactly the same method but with a rubidium acid phthalate, *o*-($RbO_2C)C_6H_4$-CO_2H, diffracting crystal (2*d* = 2 601 pm).

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† 2-Hydroxy-2,4,6-cycloheptatrien-1-one.

Non-S.I. units employed: 1 Torr = (101 325/760) Pa; 1 eV ≈ 1.60×10^{-19} J.

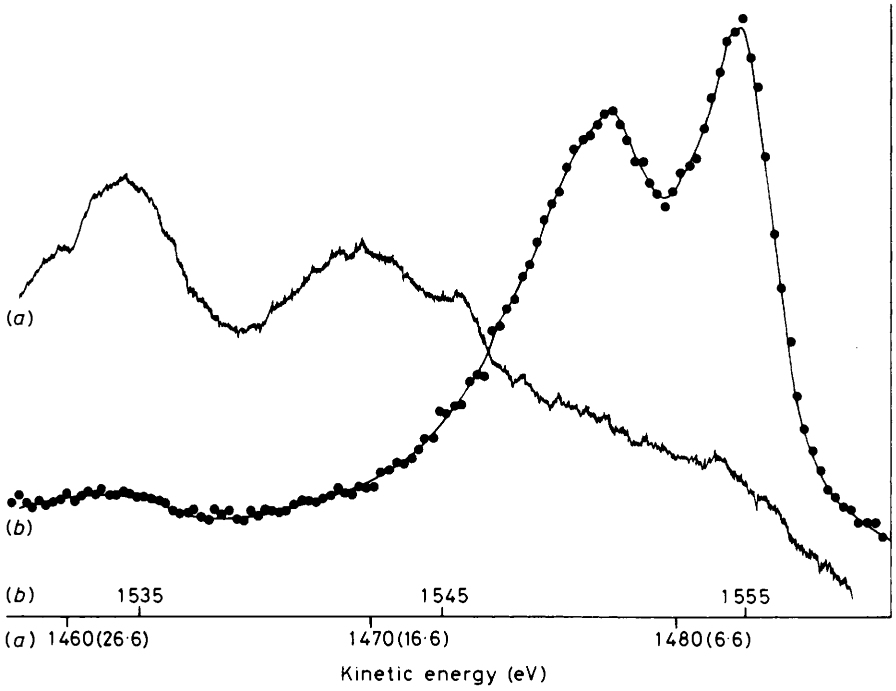


Figure 1. (*a*) *X*-Ray photoelectron and (*b*) Al-$K_{\beta_{1,3}}$ *X*-ray emission spectra from [Al($C_7H_5O_2$)$_3$] aligned using the Al 2*p* ionisation energy of 72.7 eV and Al-$K_{\alpha_{1,2}}$ = 1 486.6 eV. The dots indicate individual data points. Binding energies (eV) are given in parentheses after the values on the scale for spectrum (*a*)

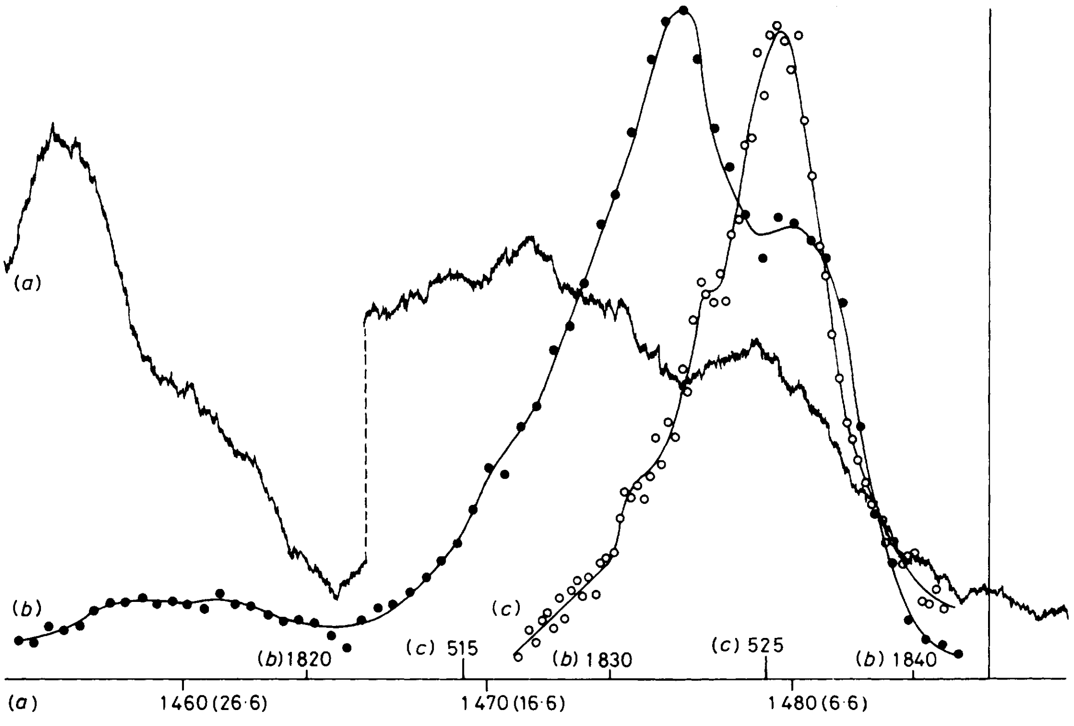


Figure 2. (*a*) *X*-Ray photoelectron spectrum, (*b*) Si-$K_{\beta_{1,3}}$, and (*c*) O-K_{α} *X*-ray emission spectra from [Si($C_7H_5O_2$)$_3$][PF_6] aligned using the Si 2*p* ionisation energy of 102.7 eV, Si-$K_{\alpha_{1,2}}$ = 1 739.8 eV, and O 1*s* ionisation energy of 532.4 eV. Note the change of vertical registration at 1 466 eV in (*a*). Individual data points are indicated by (●) Si-K_{β} and (○) O-K_{α}. Binding energies (eV) are given in parentheses after the values on the scale for spectrum (*a*)

Results and Discussion

The aluminium and silicon $K_{\beta_{1,3}}$–$K_{\beta'}$ *X*-ray emission spectra for the tropolone complexes aligned to their respective x.p. valence band spectra (using Al and Si $2p$ core ionisation energies, and Al-$K_{\alpha_{1,2}}$ = 1 486.6 eV and Si-$K_{\alpha_{1,2}}$ = 1 739.8 eV) are presented together with O-K_α for the silicon complex in Figures 1 and 2. Since the cross-sections for photoelectron emission initiated by Al-K_α *X*-rays are much larger for $2s$ orbitals than for $2p$ orbitals of the light elements the principal features of the aluminium complex x.p. spectrum can be identified as due to O-$2s$ at *ca.* 25 eV and C-$2s$ in the range 14—19 eV. The gentle increase in photoelectron intensity (4—14 eV) must then be due to photoemission from σ and π orbitals in the tropolone ligand that have considerable C-$2p$ character. The overall spread of ionisation energies for all the orbitals with carbon $2p$ and $2s$ character of *ca.* 15 eV is comparable to that which has been observed for benzene.[8]

The x.p. spectrum for the silicon complex is very similar to that for the aluminium complex but with the addition of an intense peak centred at 30.5 eV due to fluorine $2s$ and to a broad weak peak at 5—10 eV due to fluorine $2p$ and phosphorus orbitals in the hexafluorophosphate anion. For both complexes the main peaks of the $K_{\beta_{1,3}}$ emission spectra align with that region of the x.p. spectrum that is due to the less tightly bound ' tropolonate ' orbitals, except for $K_{\beta'}$ which lines up with the oxygen $2s$ x.p. peak. In the silicon complex, for which oxygen K_α data are also available, the Si–$K_{\beta_{1,3}}$ and O-K_α spectra overlap showing that the bonds to the metal have considerable oxygen $2p$ character. The high-energy peak in the silicon spectrum at 1 837 eV coincides with the principal oxygen peak and with the π-orbital region of the ' tropolonate ' x.p. spectrum whereas the other main K_β peak aligns with that part of the oxygen spectrum produced by more tightly bound, *i.e.* σ, orbitals. Whilst the form of the oxygen spectrum is mainly determined by the bonds made to the tropolone ring the O-K_α–Si-K_β juxtaposition indicates the types of bond (σ and π) by which silicon is bound to the ' tropolonate ' ligand.

The $K_{\beta_{1,3}}$–$K_{\beta'}$ spectra for both the complexes are very similar: a very weak $K_{\beta'}$ peak and two main peaks separated by *ca.* 4.5 eV. This close similarity suggests that the basic features of the electronic structure of the ligand–metal bond are the same for both silicon and aluminium. Therefore, in the following discussion, ' metal ' refers to both silicon and aluminium.

The weakness of $K_{\beta'}$ shows that, as far as metal $3p$ orbitals are concerned, it is interaction with oxygen $2p$ orbitals that is of primary importance in metal–ligand bonding. The spatial arrangement of oxygen $2p$ orbitals in the ligand will be: two perpendicular to the plane of the ligand, which can participate in π-bonding, and four orbitals in the plane, with σ-bonding potential. The two oxygen $2p$ π orbitals and also the carbon $2p$ π orbitals of the tropolone ring can be classified as symmetric or antisymmetric with respect to the mirror plane which perpendicularly bisects the ' tropolonate ' ligand. As in the case of the isoelectronic catechol the strongest interaction will be between the symmetric oxygen and carbon orbitals so that the least tightly bound occupied orbital will have this symmetry and considerable oxygen character. The local symmetry of the metal atom in the complex is D_3 and the ligand π orbitals classed as symmetric will transform as a_2 or e (x,y) [the antisymmetric are a_1 and e $(x^2 - y^2, xy)$]. Metal $3p$ orbitals a_2 (z) and e (x,y) should therefore be able to interact strongly with the symmetric π orbitals but the other half of the π orbitals should play an insignificant role in bonding since those which transform as e $(x^2 - y^2, xy)$ will have favourable spatial overlap only with metal $3d$ orbitals and the a_1 representation has no $3p$ counterpart.

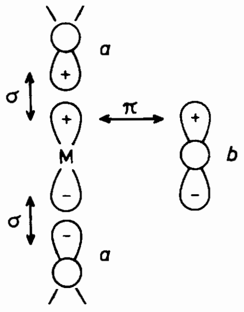
Of the four in-plane $2p$ oxygen orbitals, one from each oxygen can be orientated towards the nearest carbon atom leaving the other ' lone-pair ' orbitals free to bond to the metal atom (M). Since the M–O–C angle is not 90° this is only an approximate picture. Even so it is a useful simplification to think of just six orbitals being directed at the metal atom from the ligands. If the local symmetry, for σ bonding, is assumed to be O_h then the ligand σ orbitals transform as a_{1g}, e_g, and t_{1u}. Thus only half of these orbitals (t_{1u}) can form bonds with metal $3p$ orbitals. If interaction with $3s$ and $3d$ orbitals is discounted half the ' lone-pair ' oxygen orbitals will remain non-bonding, even in the complex, contributing to the intensity of the O-K_α peak at 525.5 eV. To summarise, two sets of orbitals can be identified from the ' tropolonate ' ligands that are well placed by virtue of their oxygen $2p$ character to form bonds with metal $3p$ orbitals; one, the less tightly bound, has π symmetry and the other set is more tightly bound and lies in the plane of the ligand-σ.

The interaction of aluminium $3p$ orbitals with these two trios of ligand orbitals will generate two sets of occupied orbitals with metal $3p$ character which give rise to the two main peaks observed in the metal $K_{\beta_{1,3}}$ *X*-ray emission spectra. The tail to lower energies observed for the lower-energy peak is probably due to lesser amounts of Al $3p$ character in other molecular orbitals that are mostly ligand bonding. This is possible because the M–O–C angle is not 90° and so metal orbitals can interact with both oxygen σ $2p$ orbitals, the ' lone-pair ' orbital (to a greater extent) and the orbital directed to the nearest ligand carbon atom (to a lesser extent).

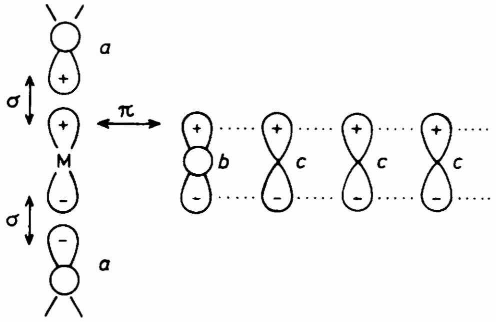
It is interesting to observe that the effect of $3p$ involvement with both ligand σ and ligand π $2p$ orbitals is to reduce the amount of metal $3p$ character present in the oxygen $2s$ orbitals, as measured by the relative intensity of the $K_{\beta'}$ peak. The relative intensity of $K_{\beta'}$ to $K_{\beta_{1,3}}$ is much greater, for example, in silica[4] than in the silicon ' tropolonate ' complex considered here.

Although the twin peaks in the $K_{\beta_{1,3}}$ spectra can be rationalised as due to metal $3p$ orbital interactions with suitable σ and π ligand orbitals it is of interest to enquire why such σ and π features are not observed in the *X*-ray emission spectra from all compounds in which silicon or aluminium atoms are surrounded by oxygen atoms. In other words since, in all complexes, suitable symmetry orbitals can be found for both σ and π interactions, why is it that an intense ' π ' peak is found only when the metal atom is attached to a ligand with an extended π system stretching over many carbon atoms? The systems involved can be represented as shown overleaf by (I) and (II), where a = the two halves of a ligand symmetry orbital which will interact with a metal p orbital to form a σ bond; b = a ligand p orbital orientated for π-bonding with a metal p orbital; c = other p orbitals which interact with b to form a delocalised ligand π system.

In (I), although different resonance intergrals would be appropriate for the σ M–a and π M–b interactions, simple molecular orbital calculations show that, provided the ionisation energies of orbitals a and b are the same, then as well as the expected bonding and antibonding orbitals covering all three orbitals, a non-bonding orbital is formed which is wholly localised on a and b, *i.e.* which has no M character. In such a system then M p character will be found in just one occupied orbital and so only one main K_β peak is observed in systems such as orthosilicate or silicon–glycol complexes where a and b orbitals are very similar. That they do not have identical ionisation energies accounts for the small ' high-energy ' peaks observed in the $K_{\beta_{1,3}}$ spectra of those compounds. As the similarity in energy between a and b type orbitals breaks down, as for example in the case of extended covalent bonding between silicate tetrahedra, in silica or in glasses,[9] so the intensity of the ' high-energy ' peak may in-



(I)



(II)

crease. In (II) however, the interaction of the orbital *b* with the other orbitals *c* ensures that the ionisation energy of the least tightly bound π molecular orbital will be different from and less than that of *a*. In this case therefore it will be possible for considerable M *p* character to be present in many molecular orbitals covering all the orbitals of (II) so that at least two main peaks should be observed in the M-$K_{\beta_{1,3}}$ emission spectra. The relative intensities of the 'σ' and 'π' peaks will, of course, be related to the efficiency with which the M *p* orbital interacts with *a* and *b* . . . *c*(π) orbitals; this in turn, other things being equal as is likely for two so closely related systems as the silicon and aluminium 'tropolonate' complexes, will depend upon the ionisation energy differences M–*a* and M–*b* . . . *c*(π). Since aluminium 3*p* is less tightly bound than silicon 3*p* it is reasonable to expect that the π interaction would be greater for aluminium than for silicon. Thus a relatively greater π : σ peak intensity ratio should be found for aluminium than for silicon, as is in fact observed.

Conclusions

A study of the tropolone complexes of silicon and aluminium shows that their metal–ligand bonding conforms to the general pattern found for other complexes, that if the ligand has a delocalised π system then two intense peaks, 'σ' and 'π', are observed in the M-$K_{\beta_{1,3}}$ *X*-ray emission spectrum. The existence of the strong 'π' peak is due to the relevant ligand σ and π orbitals having different ionisation energies. These results should enable high-resolution *X*-ray emission spectra to be used to establish the existence of σ and π bonding in organometallic complexes.

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