A Study of the Bonding in Some Five- and Six-co-ordinate Compounds of Silicon Based on Si $K\beta_{1,3}$ X-Ray Emission Spectra

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The silicon $K\beta_{1,3}$ X-ray emission spectra of a series of β-diketone and catechol complexes of silicon have been measured. The results are compared with the corresponding X-ray emission spectra from silicon and silica and are interpreted using a simple molecular orbital model. With unsaturated ligands the main $K\beta_{1,3}$ peak is split into two, showing the presence of both σ- and π-character in the Si–ligand bond. Neither the overall charge of the complex nor the co-ordination number of the silicon had any discernible effect upon the spectra.

X-RAY emission spectra are generated by the relaxation of excited ions which have vacancies in tightly bound inner orbitals.[1] The energy of the emitted X-ray is the difference between the initial and final states of the ion. The number of these states will be determined by j–j coupling and the probability of emission of radiation (electric dipole) will be controlled by the selection rules $\Delta l = \pm 1$ and $\Delta j = 0, \pm 1$. In a singly ionised atom or a molecule with otherwise closed shells and for light elements (*i.e.* $Z < 20$) where spin-orbit coupling is small (*i.e.* 1 eV or less) these rules give rise to very simple spectra. For example, a 1s vacancy in silicon can only be filled by an electron from a 2p- or a 3p-orbital, and the j–j splitting associated with a vacancy in either of these orbitals is such that only one $K\alpha_{1,2}(2p \rightarrow 1s)$ and only one $K\beta_{1,3}(3p \rightarrow 1s)$ peak is observed. When chemical compounds are formed the valence-shell orbitals will participate in chemical bond formation; in the specific case of silicon 3p-character could then be found in a variety of orbitals with different ionisation energies.[2] The $K\beta_{1,3}$

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[1] A. H. Compton and S. K. Allison, '*X-Rays in Theory and Experiment*,' Van Nostrand, New York, 1935.

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

peak would then exhibit a structure which would faithfully reflect this distribution of silicon $3p$-character amongst various molecular orbitals. Indeed it can be shown [3] that the intensities of the various component peaks of the $K\beta_{1.3}$ spectrum should be related to the squares of the atomic orbital coefficients, a_{ri}, in the LCAO approximation for a molecular orbital, $\psi_i = \Sigma a_{ri}\phi_r$. It is for this reason that a study of X-ray emission spectra is of especial interest to chemists. In this paper some six- and five-co-ordinate compounds of silicon have been selected in order to investigate the effect of co-ordination number upon the position of X-ray emission peaks [4] and also to study the structure of the Si $K\beta_{1.3} - K\beta'$ peaks to deduce the involvement of the silicon $3p$-orbitals in covalent bond formation with saturated and unsaturated ligands. Previous work with magnesium [5] and aluminium [6] complexes has shown that considerable information can be obtained even with instruments of modest resolving power.

EXPERIMENTAL

The compounds studied (I)—(VI) were prepared as follows.

Compound (I).—Acetylacetone (0.15 mol) was added to tetrachlorosilane (0.05 mol) in dry chloroform and the product was precipitated from diethyl ether.[7] The pale yellow product was purified by repeated dissolution in chloroform and precipitation with ether.

Compound (II).—A concentrated aqueous solution of sodium perchlorate (0.03 mol) was added to (I) (0.02 mol) in water.[8] The precipitate was dissolved in chloroform, separated from the aqueous layer and the chloroform solution dried. Compound (II) was precipitated from solution by addition of diethyl ether. This process was repeated to purify the white solid which was then dried under vacuum.

Compound (III).—This compound was made in the same way as compound (I) but with dibenzoylmethane in place of acetylacetone.[7]

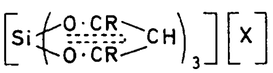
Compound (IV).—A solution of tetraethylsilane (0.05 mol) in dry triethylamine (50 ml) was added to catechol (0.15 mol), dissolved in triethylamine (50 ml).[9] A precipitate of (IV) formed during ½ h and was purified in the same way as (I).

Compound (V).—This compound was prepared [9] in the same way as for (IV) but using 0.1 mole of phenyltrimethylsilane in place of tetraethylsilane and with 0.2 mole of catechol.

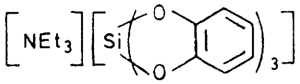
Compound (VI).—Tetraethoxysilane (0.1 mol), ethylene glycol (0.25 mol), hexamethylenediamine (0.05 mol), and methyl cyanide (35 ml) were heated under reflux for 1 h.[10] The precipitate of (VI) was filtered off and washed with methyl cyanide.

Compounds (I)—(V) all gave satisfactory analyses for C, H, and N (and Cl where needed) to within ±3% of the requirements of the molecular formulae. The silica sample (VII) was of natural quartz supplied by the Geology Department of Queen Mary College: silicon powder (VIII) was obtained from Koch-Light Limited.

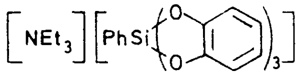
The X-ray emission spectra were obtained by subjecting these compounds to the radiation from a chromium anode X-ray tube operated at 50 kV, 50 mA, in a Philips PW 1410 X-ray fluorescence spectrometer. Samples were presented to the spectrometer in the form of pressed discs backed with terephthalic acid. Gypsum ($2d = 1.515$ nm) was chosen as the diffracting crystal since the silicon $K\beta_{1.3}$ spectrum occurs in 2nd order at a high 2θ angle (124—129°) which gives good resolution. The X-rays were detected using a proportional counter fitted with a thin window (1 μm Mylar); P-10 (90% argon, 10% methane) was used as the counting gas. Pulses from the detector were amplified using Harwell 2000 series equipment. All the spectra were obtained by a stepping technique in which counts were collected at a particular angular position for 3 min; the range 124—128.5° (2θ) was covered in steps of 0.1°. The results are presented graphically in the Figure. An indication of the statistical counting error is given by the vertical bars of length $\pm\sqrt{N}$ for a count of N (*i.e.* one standard deviation). A rather more important factor which affects the quality of the spectra is the resolution of the spectrometer. This is primarily determined by the degree of collimation used and the mosaic structure of the diffracting crystal. The main Soller slit collimator has a length of 12.5 cm: 'fine' (150 μm) collimation was used in these experiments which gives an angular dispersion of ±0.1° (2θ) width of peak at half height. For the silicon spectra recorded here this corresponds to a width of ±0.8 eV. The energy scale was calibrated by means of the known $K\beta_{1.3}$ emission energy of silicon, 1 835.9 eV.[11]



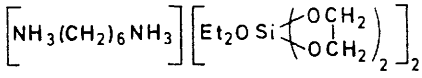
	R	X
(I)	Me	HCl_2
(II)	Me	ClO_4
(III)	Ph	HCl_2



(IV)



V



$[NH_3(CH_2)_6NH_3][Et_2OSi(OCH_2OCH_2)_2]_2$

(VI)

SiO_2 (VII) Si (VIII)

RESULTS AND DISCUSSION

The $K\beta_{1.3}$ X-ray emission spectra of silicon in the compounds (I)—(VI) are shown in the Figure. Spectra for silica (VII) and silicon (VIII) are included for comparison. It is interesting to note the differences between the $K\beta_{1.3}$ peak for elemental silicon and for silicon in a chemical compound. From the element there is but one peak which has a pronounced asymmetry. This is in contrast to the other spectra which, whilst more complex, appear to be composed of numerous more symmetrically shaped peaks. This fundamental difference in peak shape is due to the involvement of silicon $3p$ orbitals in a band of molecular orbitals spreading over many electron-

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[3] D. S. Urch, *J. Phys.* (*C*), 1970, **3**, 1275.

[4] D. E. Day, *Nature*, 1963, **200**, 649.

[5] D. E. Fenton, C. J. Nicholls, and D. S. Urch, *Chem. Phys. Letters*, 1973, **23**, 211.

[6] C. J. Nicholls and D. S. Urch, *J.C.S. Dalton*, 1974, 901.

[7] W. Dilthey, *Chem. Ber.*, 1903, **36**, 932 and 1595.

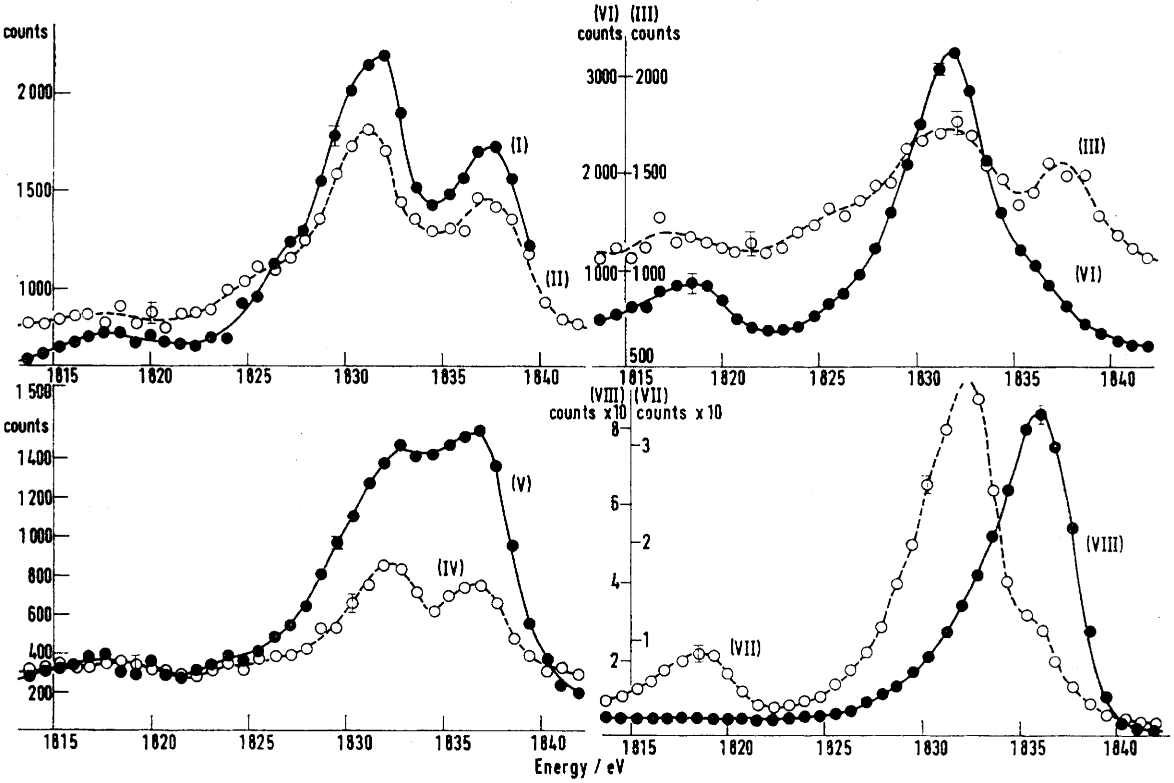
[8] E. Larsen, S. F. Mason, and G. H. Searle, *Acta Chem. Scand.*, 1966, **20**, 191.

[9] A. Rosenheim, B. Raibmann, and G. Schendel, *Z. anorg. Chem.*, 1931, **196**, 160.

[10] C. L. Frye, *J. Amer. Chem. Soc.*, 1964, **86**, 1205 and 3170.

[11] J. A. Bearden, *Rev. Mod. Phys.*, 1967, **39**, 86.

volts in silicon metal and is in contrast to the more localised bond made between silicon and neighbouring atoms in compounds and complexes. In going from silicon to silica not only does the main peak change shape but other new features and peaks become apparent,[12] *i.e.* the formation of the new $K\beta'$ peak at 1 819 eV, the shift of the main peak from 1 835.9 to 1 832.3 eV, and the presence of a shoulder at *ca.* 1 836 eV. A closer look at the spectra in the Figure shows that general differences in peak shape are also to be found within the compounds themselves. Compounds (I)—(V) give a broad $K\beta_{1,3}$ feature, usually with two distinct peaks whilst from (VI) and (VII) narrower peaks are observed. This division also corresponds to the presence of unsaturated or saturated ligands. The subsequent discussion will be facilitated if the simpler spectra (VI) and (VII) are dealt with first.



Si $K\beta_{1,3}$–Si $K\beta'$ X-ray emission spectra for a series of silicon compounds. Typical standard deviations are indicated thus Φ

Saturated Ligands.—Si–O *Bonding in silica* (VII). A simple molecular orbital rationalisation[13] of this spectrum is based on the SiO_4 unit (assumed to be tetrahedral) for which silicon $3p$-character will be found in the t_2 orbitals. From the four ligand atoms there are three sets of symmetry orbitals belonging to this irreducible representation: (a) from oxygen $2s$-orbitals (which transform as $a_1 + t_2$); (b) from oxygen $2p$-orbitals orientated along Si–O bonds (which transform as $a_1 + t_2$); and (c) from oxygen $2p$-orbitals perpendicular to the Si–O bonds (which transform as $e + t_1 + t_2$). Interaction between Si $3p$ and set (b) will be greatest, giving rise to molecular orbitals with considerable silicon $3p$-character. The interaction with set (a) will be much less since the oxygen $2s$-electrons are much more tightly bound than $2p$-electrons, by *ca.* 15 eV. Molecular orbitals derived from Si $3p$–(a) overlap will therefore have preponderantly oxygen $2s$-character with only a small Si $3p$-component. These two interactions thus provide a qualitative explanation for the relative intensities and energies of the main $K\beta_{1,3}$ at 1 832.3 eV and for the less intense $K\beta'$ peak at 1 819 eV. But lone-pair orbitals on the oxygen ligand atoms, (c), can also interact with these bonding orbitals. This overlap will have π-symmetry relative to the Si–O σ-bonds and will presumably be weaker than the primary Si $3p$–(b) σ-interaction. The mixing between Si $3p$–(b) molecular orbitals and (c) lone-pair oxygen orbitals will therefore be slight and only a small amount of Si $3p$-character will enter (c) orbitals, which would not then be greatly perturbed in their ionisation energy. The shoulder at *ca.* 1 836 eV can be understood as arising from this interaction. This in turn provides some indication of the strength of the Si–O bond. The difference in ionisation energies between non-bonding and bonding electrons is 1 836 — 1 832.3, *i.e.* 3.7 eV. Whilst this very simple molecular orbital picture gives a reasonable qualitative picture of the bonding and also provides a rationalisation of the observed X-ray spectra more sophisticated calculations have also been reported. Cruickshank[14]

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[12] W. L. Baun and D. W. Fisher, *Spectrochim. Acta*, 1965, **21**, 1471.

[13] D. S. Urch, *Adv. X-ray Analysis*, 1971, **14**, 250.

[14] G. A. D. Collins, D. W. J. Cruickshank, and A. Breeze, *J.C.S. Faraday II*, 1972, 1189.

has considered the relationship between X-ray emission spectra and *ab initio* calculations based on SiO_4 and also H_2SiO_4 units. Prins[15] has discussed SiO_4 along with other tetrahedral oxy-anions using INDO methods, whilst Breeze[16] has considered the electronic structure of silica using three-dimensional Hückel techniques. Apart from the possible involvement of d-orbitals in the interpretation of L-spectra the more sophisticated calculations are in agreement with the general ideas suggested by the simplest m.o. approach. This method would therefore seem to be both suitable and adequate for the discussion of the electronic structure and Si $K\beta$ emission spectra of the complexes to be considered in this paper.

Si–O *Bonding* (VI). The Si $K\beta_{1,3}$ emission spectrum from compound (VI) is almost identical with that from silica indicating that the bonding role of the $3p$ electrons is very similar in the two substances, notwithstanding the difference in co-ordination number. In both cases the silicon atom is surrounded by oxygen atoms which are making further bonds to other atoms (to Si or to C). The orbitals which are available for bonding with silicon are therefore very similar; one orbital from each oxygen for σ-bond formation orientated along these Si–O directions and just one lone-pair orbital which would have π-bonding potential. Five ligand atoms, whether arranged as a trigonal bipyramid or as a square pyramid will give rise to five symmetry orbitals, only three of which will belong to the same irreducible representations as Si $3p$-orbitals. When only four ligand atoms are present (tetrahedrally arranged about silicon) four symmetry orbitals can be derived from the four ligand orbitals orientated along the Si–O bonds; but only three of these four are able to interact with Si $3p$-orbitals. The number of ligand orbitals that can interact with silicon $3p$-orbitals is therefore independent of the co-ordination number of the silicon. (One might expect more dramatic changes in the L-spectra of silicon if $3d$-orbitals were to be involved in bonding.) The other five-co-ordinate compound studied (V) has a very much more complex $K\beta$ spectrum than (VI), which is presumably due to the presence of delocalized π-electrons in the ligand.

Unsaturated Ligands.—Compounds (I)—(V) differ from (VI) in that the oxygen atoms are bound to unsaturated rather than saturated organic groups. In all cases the π lone-pair orbitals are participating in a complex series of delocalised molecular orbitals on the ligand, so that more complex silicon emission spectra are to be expected.

Identification of peaks due to σ-bonds. The Si $K\beta_{1,3}$–$K\beta'$ X-ray emission of compound (I) shows four distinct features, a separate peak at 1 818 eV ($K\beta'$), a shoulder at 1 827 eV, the main peak at 1 831.5 eV, and a relatively intense high-energy peak at 1 837.5 eV. [An identical spectrum is observed from compound (II), but of poorer quality due to a higher background count.] This spectrum is very similar † to $K\beta_{1,3}$ X-ray emission spectra of magnesium[17] and aluminium[6] obtained from their hexafluoroacetylacetonate and acetylacetonate complexes respectively and probably arises from similar ligand–central atom interactions. The approximately octahedral arrangement of oxygen atoms can be used to give a simplified symmetry framework for the immediate ligand environment of the silicon atom in compounds (I) and (II), in much the same way as it can be assumed that silicon is tetrahedrally co-ordinated in silica. Oxygen $2s$-orbitals will give symmetry orbitals ($a_{1g} + t_{1u} + e_g$) [analogous to (a) above] which have only σ-bonding potential to silicon.

Silicon $3p$-character in the t_{1u}-orbitals gives rise to the $K\beta'$ peak at 1 818 eV. In silica and in compound (VI), where only strong σ-interaction by p-orbitals seems reasonable, the $K\beta'$–$K\beta_{1,3}$ energy difference is *ca.* 14 eV. If it is assumed that this energy difference would not be significantly altered by the presence of π-bonding then the position of the $K\beta'$ peak can be used to identify which part of a complex $K\beta_{1,3}$ peak is due to silicon $3p$-character in σ-bonds. This method shows that it is the main peak at 1 831.5 eV in the spectra for compounds (I) and (II) that is associated with silicon–oxygen σ-bonds. The oxygen $2p$-orbitals used in Si–O σ-bond formation will lie in the plane of each acetylacetonate group. However the Si–O–C bond angle is not 90° and so it is not possible to associate this interaction with a single $2p$-orbital on each oxygen: a single t_{1u} symmetry orbital derived from the three ligand groups cannot therefore be envisaged. The ligand $2p$-orbital which interacts with the silicon $3p$-orbitals will be a composite function derived from the many σ-molecular orbitals of the acetylacetonate group. Photoelectron spectra of small alkane molecules reveal[19] two broad bands of orbitals, *ca.* 6 eV apart, associated with C–C bond formation which may be roughly regarded as principally derived from C_s–C_s and from C_p–C_p overlap. $2p$-Orbitals on the oxygen atoms (in the plane of the molecule) in the acetylacetonate ligand will interact with the C_5 σ-molecular orbital system giving rise, on the ligand atoms, to two bands of molecular orbitals, *ca.* 6 eV apart with considerable oxygen $2p$-character. This oxygen character can be donated to the silicon atom when complex formation takes place so that Si $3p$-character will be found in two bands of molecular orbitals *ca.* 6 eV apart; this provides an explanation for

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† Spectra of compounds (I) and (II) differ from the first published[18] Si $K\beta_{1,3}$ spectrum which purported to come from the $[Si(acac)_3]^+$ cation. This spectrum showed a very intense peak at 1 845 eV and weaker peaks at lower energies. It has not been possible to reproduce this spectrum and the most reasonable explanation is that it is due to 2nd order calcium $K\alpha_{1,2}$. Traces of calcium may have been introduced during the preparation of the complex. X-Irradiation from a chromium anode tube favours the emission of characteristic radiation from calcium and if, unfortunately, the pulse-height selector had been set for 2nd order Ca $K\alpha_{1,2}$ and not 1st order Si $K\beta_{1,3}$ then the form of the spectrum could be understood.

[15] R. Prins, *J. Chem. Phys.*, 1974, **61**, 2580.

[16] A. Breeze and P. G. Perkins, *J.C.S. Faraday II*, 1973, 1237.

[17] C. J. Nicholls, Ph.D. Thesis, University of London, 1974.

[18] D. S. Urch, '*Proceedings 7th X-Ray Conference: Durham, 1970*,' N. V. Philips Gloeilampenfabriken Eindhoven, Netherlands, 1971, p. 68.

[19] W. C. Price, A. W. Potts, and D. G. Streets, 'International Conference Electron Spectroscopy: Asilomar, 1971,' North Holland Co., Amsterdam, 1972, p. 187.

the two broad peaks at at 1 827 and 1 831.5 eV observed in the Si $K\beta_{1,3}$ spectra.

π-Bonding in compound (I) *and* (II). The π-orbitals in the acetylacetonate ligand form a delocalised system, perpendicular to the plane of the ligand which involves C-2, C-3, C-4, and the two oxygen atoms. Of the three occupied π-orbitals only the most tightly bound (π_1) and the least tightly bound (π_3) will have the correct symmetry to interact with silicon 3*p*-orbitals. Very simple m.o. calculations indicate that relative to atomic oxygen 2*p*-orbitals, π_1 is more tightly bound and π_3 is less tightly bound.

The energy of a Si $K\beta$ peak from orbitals that are mostly oxygen 2*p* lone-pair in character can be found from the spectrum of (VII); it is 1 836 eV. The peak at 1 837.5 eV in (I) and (II) can, therefore, be reasonably ascribed to silicon–ligand π-orbitals derived from Si 3*p*-acetylacetonate π_3-interactions. Calculations suggest that π_1 is probably *ca.* 5—6 eV more tightly bound than π_3 so that *X*-ray emission features derived from molecular orbitals due to π_1–Si 3*p*-interaction would lie beneath the main $K\beta_{1,3}$ peak at 1 832 eV.

Si–Ligand Bonding in (III).—The presence of the phenyl groups in the ligand in compound (III) has remarkably little effect upon the silicon *X*-ray emission spectrum, except to broaden it slightly and to extend the low-energy 'tail'. Presumably the oxygen orbitals participate in more molecular orbitals, with a greater range of ionisation energies, but the overall effect, given the limited resolution of these experiments, is very much as in the simpler acetylacetonate system itself.

Si–Ligand Bonding in (IV) *and* (V). Catechol is a more complex ligand than acetylacetone but as can be seen from the Figure (IV), a very similar Si $K\beta_{1,3}$ emission spectrum results. An *X*-ray crystallographic study of (IV) has not been carried out but the presence of the tris(*o*-phenylenedioxy)siliconate dianion has been established for the pyridinium salt.[20] Even in those ammonium salts where deviations from the simple $[Si(O_2C_6H_4)_3]^-$ structure have been found [21] two of the three catechol ligands remain bidentate. As with the β-diketonate complexes the *X*-ray emission spectrum of (IV) would seem to indicate clear σ- and π-type bonding interactions between the silicon atom and the ligands. A broad 'σ' peak at 1 832 eV with a low-energy tail down to *ca.* 1 825 eV can be rationalised, as for the acetylacetonate complexes, as due to the interaction of oxygen 2*p*-orbitals, which are themselves involved in bonding with many carbon–carbon σ-molecular orbitals and which can be very approximately classified as carbon–carbon 2*s* and carbon–carbon 2*p* type, with silicon 3*p*-orbitals. Of the five occupied π molecular orbitals of the catechol anion, three will have the correct symmetry for interaction with silicon 3*p*-orbitals: a more complex spectrum than for (I) or (II) should, therefore, result, and the fact that it does not is presumably due to the lack of high resolution.

It is interesting to compare compound (IV) with the five-co-ordinate compound (V) which contains two catechol groups and a phenyl directly bound to the silicon.[22] A very broad spectrum results with two peaks which can be correlated with the σ- and π-peaks of (IV) but with a reversed intensity ratio. It seems reasonable to suggest that the peak at 1 833 eV is primarily due to silicon–oxygen σ-bonds from the catechol and that some of the intensity of the peak at 1 837 eV is due to π-bonding with catechol. Phenyl as a ligand will have a very different array of orbitals available for interacting with silicon 3*p*-orbitals. The π-orbitals will all be more tightly bound than the carbon lone-pair orbital which has σ-bonding (Si–C) potential. Since σ-interactions are usually stronger than π- the ionisation energies of silicon–carbon σ-orbitals and π-orbitals might well be comparable; also these orbitals will have ionisation energies less than for silicon–oxygen bonds. It is, therefore, anticipated that the orbitals involved in Si–C bonding will be less tightly bound than Si–O bonds and so give rise to higher energy peaks in the Si $K\beta_{1,3}$ emission spectrum. These transitions will also be at higher energies than those from Si–C bonds to Si 1*s* vacancies in compounds such as silicon carbide.[12] This is because the four electronegative oxygen atoms from the two catechol ligands will enhance the silicon 1*s*-orbital ionisation energy. Transitions from the Si–O bond will appear with the 'normal' $K\beta_{1,3}$ emission energy whilst those from the Si–C bond will appear at an abnormally high energy.

Conclusions.—The silicon $K\beta_{1,3}$, $K\beta'$ *X*-ray emission spectrum can be used to identify the bonding role played by Si 3*p*-orbitals in compounds and complexes of silicon. In particular it is possible, by using the $K\beta' - K\beta_{1,3}$ energy difference established for compounds in which only σ-bonds are found, to identify those peaks in a complex $K\beta_{1,3}$ spectrum which are due to transitions from σ-orbitals and those from π-orbitals. The involvement of Si 3*p*-orbitals in both σ- and π-bonding to unsaturated ligands is clearly established. The actual structure of the Si $K\beta_{1,3}$ is a reflection of the electronic structure of the ligand and is not in any detectable way affected either by the co-ordination number of the silicon nor the overall charge of the complex in which the silicon atom is found.

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[20] J. J. Flynn and F. P. Boer, *J. Amer. Chem. Soc.*, 1969, **91**, 5756.

[21] D. W. Barnum, *Inorg. Chem.*, 1972, **11**, 1424.

[22] F. P. Boer, J. J. Flynn, and J. W. Turley, *J. Amer. Chem. Soc.*, 1968, **90**, 6973.