High-resolution *X*-Ray Emission Study of Central Atom–Ligand Bonding in Phosphorus-containing Compounds

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Summary The capability of *X*-ray photon-emission spectroscopy to characterize and distinguish specific central atom–ligand orbital bonding is discussed.

We have investigated the K_β emission spectrum for phosphorus in various environments. Since photon-emission spectra, in contradistinction to photoelectron spectra, are governed by electric-dipole selection rules[1,2] the K_β spectra to be discussed below contain detailed information about the nature of the central P atom $3p$ orbital contribution to specific molecular orbitals.[3]

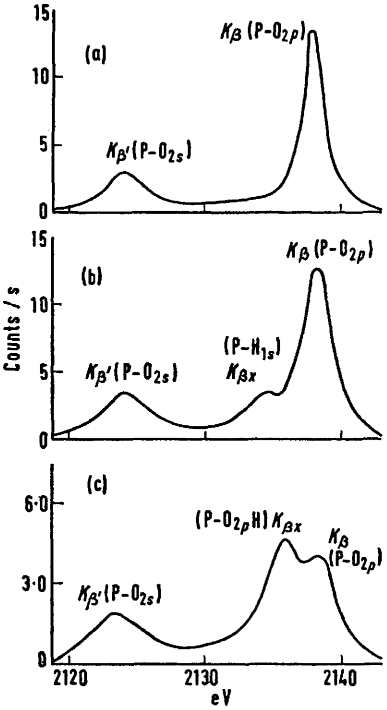

Figure 1. (*a*) $Ca_3(PO_4)_2$; (*b*) $CaHPO_3$; (*c*) H_3PO_4.

For the highly symmetrical phosphate ion, PO_4^{3-} (T_d), the electronic environment was modified by successive replacement of the oxygen ligands with hydrogen to give the phosphite (HPO_3^{2-}, C_{3v}) and hypophosphite ($H_2PO_2^-$, C_{2v}) ions, or with hydroxo-ligands to produce phosphoric acid (H_3PO_4, C_{3v}) and its mono- ($H_2PO_4^-$, C_{2v}) and di- (HPO_4^{2-}, C_{3v}) basic salts. The resultant K_β spectra are shown in Figure 1.

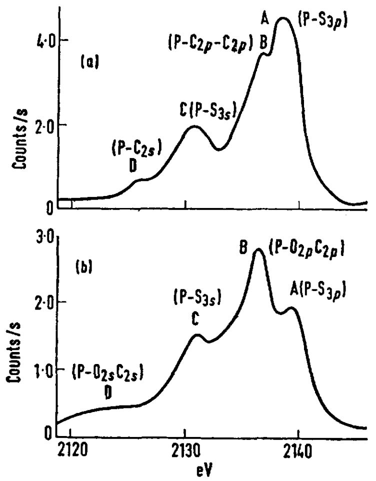

Figure 2. (*a*) $Ni[S_2P(C_2H_5)_2]_2$; (*b*) $Ni[S_2P(OCH_3)_2]_2$.

CNDO/2 Calculations indicate that the K_β band for PO_4^{3-} originates from a molecular orbital composed of phosphorus $3p$ and oxygen $2p$ atomic orbitals, whereas the low energy band, K_β represents a molecular orbital with phosphorus $3p$ and oxygen $2s$ contributions. For HPO_3^{2-}, K_β and $K_{\beta'}$ originate primarily in molecular orbitals describing P_{3p}–O_{2p} and P_{3p}–O_{2s} bonding, respectively.[3] The $K_{\beta x}$ transition, however, arises predominantly from a molecular orbital comprised of phosphorus $3p$ and hydrogen $1s$ atomic orbitals. This band represents P_{3p}–H_{1s} bonding in the HPO_3^{2-} molecule.[3]

For H_3PO_4, K_β is again attributed primarily to P_{3p}–O_{2p} bonding, whereas $K_{\beta x}$ constitutes a set of molecular orbitals formed predominantly from the interactions of the phosphorus $3p$ and hydroxo-oxygen $2p$ atomic orbitals, thus representing P_{3p}–$O_{2p}H_{1s}$ bonding. $K_{\beta'}$ contains mostly contributions from both ligands' $2s$ orbitals (P_{3p}–O_{2s} and P_{3p}–$O_{2s}H_{1s}$ bonding) and is not resolved here. These same effects are observed for the other hydroxo-compounds with the intensity of $K_{\beta x}$ increasing upon successive substitution of hydroxo-ligands for oxygen. Therefore, for the phosphorus oxy-anions each spectral band is associated with the bonding between a specific ligand orbital and the phosphorus $3p$ atomic orbital.

Further evidence of this unique ligand interaction with the central atom was observed in the investigation of a series of compounds of the type, $Ni[Si_2P(R)_2]_2$[4,5] where R is an alkyl or alkoxo-group. Sample spectra for the methoxo- and ethyl compounds are given in Figure 2.

The CNDO/2 results are similar to those for the hydroxo-compounds, indicating several sets of molecular orbitals with differing ligand orbital contributions. Each spectral band is again attributable to specific ligand orbital bonding. For example, the K_β bands for the methoxo-compound, bis(dimethyl dithiophosphinato-*OO′*)nickel(II) may be designated as:

$$K_{\beta A}: P_{3p}\text{–}S_{3p} \qquad K_{\beta C}: P_{3p}\text{–}S_{3s}$$
$$K_{\beta B}: P_{3p}\text{–}O_{2p}C_{2p} \qquad K_{\beta D}: P_{3p}\text{–}O_{2s}C_{2s}$$

An analogous assignment is possible for the ethyl compound.

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