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On the Relationship of Binding Energies and Formal Oxidation States

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The concept of formal oxidation state is useful for categorising compounds with respect to reactivity and structure, and for systematising redox processes. The oxidation state of a metal ion in a complex is assigned by determining the formal charge residing on the metal when the bonding electrons are allocated to the partners in the various bonds according to certain reasonable but arbitrary rules. However, the formal oxidation state does not give the real charge on an atom. On the basis of the electroneutrality principle, the real charges on atoms in molecules are likely to be within the range ± 1.[1]

The determination of charges upon atoms in molecules should enable one to assess, for example, the donor–acceptor properties of various ligands, or the validity of theoretical charge calculations. X.P.S. data have been used to determine metal oxidation states[2] by comparison of binding energies in test compounds with binding energies in 'standard' compounds. In view of the wide range of binding energies associated with a given oxidation state[3] this is of dubious value, and leads to unreliable inferences, *e.g.*, square planar Ni^0.[4] We report here data for a range of related, often isomorphous, tertiary phosphine complexes of known geometry. Some have been used elsewhere for comparing the effects of different ligands,[5] and they enable us to establish correlations between charge, binding energy and formal oxidation state.

The metal $(4f_{7/2})$ electron binding energies of a series of crystalline, six-coordinate complexes $[MCl_x(PMe_2Ph)_y]$ (M = Ir, Os, Re or W; x + y = 6; x = 2, 3 or 4) have been measured by X.P.S. relative to C(1*s*) = 285 eV as standard;[6] they are plotted as a function of formal oxidation state in the Figure. There is seen to be an approximately linear relationship between formal oxidation and electron binding energy for these heavy transition elements, at least in the oxidation state range (II) - (IV). There is only one suitable platinum complex available and the line for platinum has been drawn through the single data point with the slope common to all the other elements.

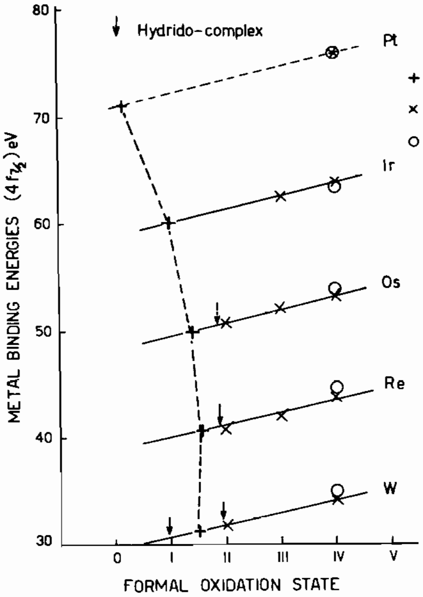

Fig. 1. The relationship of formal metal oxidation state to $(4f_{7/2})$ electron binding energies for $[MCl_x(PMe_2Ph)_y]$ (M = Pt, Ir, Os, Re or W; x = 2, 3 or 4; x + y = 6). Sources of data: for $[MCL_x(PMe_2Ph)_y]$ generally from reference 6; for $K_2[MCl_6]$, from reference 6; for W, C. R. Brundle, personal communication; for Pt, D. T. Clark, D. B. Adams and D. Briggs, *Chem. Comm.*, 1971, 602; for Re, B. Folkesson, *Acta Chem. Scand.*, *27*, 287 (1973); for Os and Ir, ref. 7; all other data, hitherto unpublished, obtained by courtesy of Dr. J. A. Connor, University of Manchester.

The relationship of formal oxidation state to binding energy is not a simple one. The electron binding energy reflects directly the potential field experienced by the 4*f* electrons, and it is generally assumed that changes in the potential are linearly related to changes in the charge on the specific atom in an otherwise constant environment. This is the rationalisation behind the linear correlations of binding energy and calculated charge for atoms such as nitrogen and sulphur.[7] Thus Siegbahn,[7] using a CNDO approximation, writes:

$$\Delta E = q_A k_{AC} + \sum_{B \neq A} \frac{q_B}{R_{AB}}$$

where ΔE is the difference in the binding energy of an electron on the uncombined atom and on the atom in a compound, k_{AC} is the average interaction between a core electron on A and a valence electron on A, q_A is the charge between A in the molecule and uncombined A, and q_B/R_{AB} is the interatomic potential. When comparing different compounds, as we do in the Figure, then two such expressions reduce to

$$\Delta E' = (q_A - q'_A)k_{AC} + \sum_{B \neq A} \frac{q_B}{R_{AB}} - \sum \frac{q'_B}{R_{AB}}$$

The first term involves a difference in charges and also a difference in oxidation states. The observed slopes (1.4 eV/unit oxidation state) are very much less than one would expect for a change in charge of one unit on the basis of Coulombic interactions (perhaps 10 eV). Hence ignoring any effects due to changes in interatomic terms (Madelung contribution), we infer that the real charges on the metal atoms in the complexes are considerably less than the formal oxidation states would suggest. This accords with general chemical experience.

However, we have no *a priori* reason for ignoring the interatomic terms. Even where we restrict our considerations to complexes containing only one kind of phosphine and one kind of halide, as here, and to complexes of similar structure (all $[MCl_2(PMe_2Ph)_4]$ are *trans,* all $[MCl_3(PMe_2Ph)_3]$ are *mer,* and all $[MCl_4(PMe_2Ph)_2]$ are *trans*) there is no reason to expect that all the Madelung contributions are equal. Nevertheless, the approximate linearity of the plot suggests that they are indeed very similar.

The Figure also contains data for $[MCl_6]^{2-}$ ions. We cannot assume that the Madelung contribution in an ionic compound is the same as in a covalent one. However, if we assume that the changes already suggested for rhenium[5] apply generally, *i.e.,* that the addition of a tertiary phosphine to a five-coordinate complex lowers the metal binding energy by 1 - 2 eV, and that the addition of a chloride lowers it by about 1 eV, then one would expect the binding energy changes arising from the replacement of PMe_2Ph by Cl^- alone in the transformation $[MCl_4(PMe_2Ph)_2] \rightarrow [MCl_6]^{2-}$ to be about +1 - 2 eV. In fact, the observed binding energies are from 1 eV more (W and Re) to 1 eV less (Ir) so that variations in the Madelung term must amount to about 1 - 2 eV.

Data for the $(4f_{7/2})$ binding energies measured for the pure metals with respect to the Fermi levels are also shown in the Figure. In this case it is certainly unreasonable to ignore the effects of coordination number changes and so on. If one were to do so, the apparent formal oxidation states for the metals vary from 0 to II; the use of pure metal binding energies as a basis for assigning oxidation state zero by X.P.S. techniques is not easy to justify.

Finally, the data for $[WH_6(PMe_2Ph)_3]$, $[WH_4(PMe_2Ph)_4]$, $[ReH_5(PMe_2Ph)_3]$ and $[OsH_4(PMe_2Ph)_3]$ indicate that, whereas again it is unwise *a priori* to assume that Madelung contributions are comparable, the adoption of that assumption suggests once more that the metal atoms are much less positive than the formal oxidation states would imply. Both ^{1}H n.m.r. and i.r. data suggest that the hydrido-protons in $[WH_6(PMe_2Ph)_3]$ are not very hydridic,[8] and the $P(2p_{3/2})$ binding energies in the hydrides are the same as in the corresponding $[MCl_3(PMe_2Ph)_3]$, which implies that the hydrido-protons are loading charge onto the metal ions, but that this charge is not appreciably delocalised onto the phosphines. This accords with general chemical experience.

These data are thus consistent with the following three conclusions: (i) that the charge on a metal in a complex is considerably less than the formal oxidation state implies; (ii) that the Madelung contributions to measured binding energies in complexes are comparable and do not invalidate comparisons provided halide, phosphine or other ligands are kept invariant; (iii) that solid metal is not a suitable standard for oxidation state zero in comparison with metal complexes.

1 L. Pauling, *The Nature of the Chemical Bond,* Third Edition, Cornell University Press, Ithaca, New York, 1960, p. 270.

2 See, for example. V. I. Nefedov, M. A. Porai-Kishits, I. A. Zakharova, and M. E. Dyatkina, *Doklady Akad. Nauk S.S.S.R., 202,* 605 (1972).

3 There are many examples of this; see, for example, W. E. Moddeman, J. R. Blackburn, G. Kumar, K. A. Morgan, R. G. Alldridge, and M. M. Jones, *Inorg. Chem., 11,* 1715 (1972); R. J. Matienzo, L. I. Yin, S. O. Grim and W. E. Swartz, *Inorg. Chem., 12,* 2762 (1973); C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King and R. C. Wendt, *Inorg. Chem., 12,* 2770 (1973).

4 S. O. Grim, L. J. Matienzo and W. E. Swartz, *J. Am. Chem. Soc., 94,* 5116 (1972).

5 J. Chatt, C. M. Elson, N. E. Hooper and G. J. Leigh, *J. Chem. Soc. (Dalton),* submitted for publication.

6 G. J. Leigh and W. Bremser, *J. Chem. Soc. (Dalton),* 1216 (1972).

7 K. Siegbahn *et al., ESCA Applied to Free Molecules,* North Holland Publishing Company, Amsterdam, 1969, Chapter 5; K. Siegbahn *et al., ESCA: Atomic, Molecular, and Solid State Structure studied by means of Electron Spectroscopy,* Almquist and Wiksells, Uppsala, 1967.

8 J. R. Moss and B. L. Shaw, *J. Chem. Soc. (A),* 1910 (1972).