On the Relationship between Molecular Core Binding Energies and Atomic Charges

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Summary The linear relationship between molecular core binding energies (as measured by X-ray photoelectron spectroscopy or calculated by an "ab initio" SCF-LCAO method) and the Mulliken gross atomic charges is restored if the interatomic Madelung potential is taken into account.

Recently, Barber and Clark have published communications in which they demonstrated that the simple linear relationship between the binding energies of the molecular core electrons and the atomic charges, as observed earlier, breaks down in several examples. These authors have measured the binding energies of carbon Is and nitrogen Is electrons in acetonitrile and in three nucleic acid bases, adenine, cytosine, and thymine, by X-ray photoelectron spectroscopy. They showed that the experimental core ionization energies are linearly related to the orbital energies calculated by an "ab initio" SCF-LCAO method, as can be expected from Koopmans' theorem. Thus photoelectron peaks can be assigned to ionizations of specific carbon or nitrogen atoms. The authors emphasize, however, that no linear relationship exists between the core electron binding energies and the Mulliken atomic charges on the ionized atoms. In some cases even higher binding energies correspond to more negative atoms.

I report that the linear relation between the core ionization energy of an atom in a molecule and the Mulliken gross charge on this atom is restored if the Madelung potential due to the other atoms in the molecule, considered as point charges, is taken into account. Following Gelius et al., the binding energy of a core electron on atom \( i \), \( E_i \), is given by:

\[
E_i = \alpha + \beta q_i + \sum_{j \neq i} q_j/R_{ij},
\]

where \( \alpha \) and \( \beta \) are constants for the inner shell studied (\( \alpha \) should be corrected for the work function of the sample), \( q_i \) is the Mulliken gross charge on atom \( i \) and \( R_{ij} \) is the distance between the nuclei \( i \) and \( j \). Siegbahn et al. introduced this Madelung potential to explain their observation that, generally, the shifts in binding energies with charge are smaller in molecules or solids than in isolated atoms.

With this formula I have tried to correlate the binding energies determined experimentally by Barber and Clark. No charges on nitrogen or hydrogen were indicated for acetonitrile, but it is easily found that the Madelung potentials on the carbon atoms have different sign, counteract the effects of the atomic charges, and can be sufficiently large to explain the very small difference in binding energy measured. The results for the molecules adenine, thymine, and cytosine, the Mulliken gross atomic charges of which were taken from Mely and Pullman and the structures from Spencer and Barker and Marsh, are shown in Figures 1 and 2. The experimental binding energies have been corrected for the effect of the interatomic Madelung potential and plotted against the atomic charges. A least-square fit through all carbon and all nitrogen points yields...
a 1s binding energy of 288·2 and 406·3 ev respectively for the neutral atoms and a charge dependence of 19·0 and 23·1 ev/unit charge respectively for the isolated atoms. This is in reasonable agreement with literature values for the experimental binding energies of 288 and 403 ev (ref. 4, p. 230) and the calculated shifts of 18·8 and 20·7 ev/unit charge (ref. 4, p. 84). Drawing straight lines through the points of different molecules separately, as Barber and Clark have done, would fit the results even more closely. Although I agree with Barber and Clark that a linear relationship between the X-ray photoelectron spectroscopy points of different molecules separately, as Barber and Clark have done, would fit the results even more closely.

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Summary. X-ray studies reveal the diamagnetic complex anion in [Ph₄As]₂[M(mnt)₃]₂ (M = Mo, W; L = S₂C₆F₄) to have a structure midway between octahedral and trigonal-prismatic limiting geometries.

Recent structural work on tris-(1,2-dithiolate) complexes has shown that while the neutral complexes possess trigonal prismatic co-ordination,¹ the dianionic and trianionic complexes of first-row transition elements have octahedral or severely distorted structures.²,³ However, despite the large number of complexes which have been characterized,⁴,⁵ structural evidence on anionic complexes of second- and third-row elements has been lacking. It has been suggested,⁶ however, that the diamagnetism of ML₃²⁻ species (M = Mo, W; L = S₂C₆F₄) favours assigning them the trigonal-prismatic structure. To provide the needed structural information we report the X-ray determined crystal structure of the dianionic complex Mo(mnt)₃₂⁻ in its bis(tetraphenylarsonium) salt.

Crystal data: C₆₀H₄ₐN₆As₂MoS₆ (green crystals from Me₆CO-PrOH) M = 1283·2; orthorhombic, a = 20·10(2), b = 15·30(2), c = 18·73(2) Å, U = 5760 Å³, Dm = 1·479 g/cm³, Z = 4, Dc = 1·479 g/cm³; space group Pbcn (No. 60). Intensities were measured by visual-photographic methods, using Mo-Kα radiation, for 1643 non-zero reflections. The structure was solved by the heavy-atom method and has been refined to R = 0·087 by full-matrix least-squares analysis using anisotropic thermal parameters for Mo, As, and S. The analogous tungsten compound [Ph₄As]₂[W(mnt)₃] crystallizes in the same space group, with a = 20·16(2), b = 15·27(2), c = 18·69(2) Å, and is assumed to be isomorphous.

As seen in the Figure, Mo lies on a two-fold axis which bisects one of the ligands and relates the other two. Six sulphur atoms surround the Mo at an average distance of 2·385 Å and form a polyhedron which is not close to either the trigonal-prismatic or octahedral geometries. Although the molecule in fact possesses only the crystallographically-required C₃ₐ symmetry, we refer to an idealized D₃ₐ geometry for the purpose of description and discussion. In this context the structure consists of two approximately parallel (dihedral angle = 178°), roughly equilateral triangles separated by a distance of 3·00 Å. The triangles are twisted from each other by an averaged angle of 27° from shifts and the atomic charges is not "a priori" obvious, I think it can be concluded that for the examples given such a relation exists if the Madelung potential is added. This is convenient as, at least for the interpretation of an X-ray photoelectron spectrum, an "ab initio" SCF-LCAO calculation including all innershell orbitals need not be carried out, but a semi-empirical MO method applied to the valence electrons might suffice.

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