chemistry of metallic iodates. In addition to the acentric crystal structure, the molecular or ionic arrangement of the crystal has to contain a periodic system of polarizable free electrons in order to obtain highest non linear susceptibilities. So, the IO_3^- iodate anion with the lone pair of electrons on iodine is an appropriate building block as proposed by Bergman [1]. The coordination of this asymmetrical ligand to cations favours the formation of acentric inorganic crystals. Furthermore, these metallic iodates present high non linear coefficients and high optical damage thresholds on powders and are particularly interesting for infrared applications as they possess a large domain of transparency from visible to the beginning of the far-infrared (12 m) [2-5]. The environment of I(V) in iodate groups is formed by three strong bonds (mean bond length: 1.80 Å) corresponding to an AX_3E conformation. In addition, the environment of iodine is generally filled up by three weak bonds (mean bond lengths in the range 2.45 Å to 3.00 Å) arranged around the lone pair direction. This leads to an octahedron in which the iodine atom is displaced off centre along the ternary axis [6]. In the I_2O_5 iodic anhydride structure we observe intermediate I-O bond lengths (1.94-1.96 Å) and short I…O interactions (2.22 Å) which give a five coordination number of iodine. The discovery of new oxo-iodine (V) anions as IO_4^{3-} and $I_3O_8^-$ brings some questions. Indeed, some interatomic distances between oxygen and iodine from different anions are in the same range as bond lengths. Thus what is the maximal I-O bond length that we have to consider to define a chemical entity? Bond or interaction that is the question.

In order to answer this question, theoretical calculations using the gas-phase geometries for theses species are optimized with several basis sets and computational methods. The optimized geometries are compared with the experimental structures. The bonding in iodates has been investigated from the natural bond orbital and electron localization function analyses.

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MS43 O4

Charge Distribution (CD) of anion-centred structures

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The charge distribution (CD) method [1] gives a description of the connectivity of crystal structures based on a Madelung scheme. The applicability of the method does not depend on the nature of the chemical bonds in the structure, provided that this does not contain polycations or polyanions (groups containing cation-cation or anion-anion bonds). The method computes the Effective Coordination Number (ECoN) on the basis of the experimental geometry of each coordination polyhedra and distributes the result among all the chemical bonds in which are involved atoms of the given polyhedron. The formal oxidation number (charge) is used as weight of this distribution that, after summing up around each atom, should be obtained back. Discrepancies around the corner atoms (**V**-atoms) suggest a certain degree of over- or under-bonding, whereas discrepancies around the **P**olyhedra-**C**entring-Atoms question the structure validity or the applicability of the method. In the computation, no empirical parameter is used, apart from an exponent that is constant and simply determines the decrease rate of the bond strength with the bond length: this is a fundamental difference with respect to other empirical methods like. e.g., the bond-valence method.

In the Madelung scheme, crystal structures are commonly described as packing more or less compact of electronegative atoms (the "anions") with the electropositive atoms (the "cations") occupying the empty sites formed by the packing. A smaller, but not negligible, number of structures have been reported, where the role of the two types of atoms seems be inverted, or at least interchangeable. Recent studies have drawn more attention on this alternative description. We have generalized the software developed for the CD calculation to treat both cases, and now the same structure can be easily analysed in terms of CD both as "cation-centred (CC)" and "anion-centred (AC)". A number of structure previously considered doubtful or significantly over-under-bonded appear correct and well balanced when the AC description is adopted. Apart from cases where the numerical effect of very distorted CC polyhedra vs. more regular AC polyhedra seems to explain the difference, the AC description seems in general more reasonable when the structure contains large cations. In fact, often the relative sizes of the atoms seem to be a key factor, an aspect which determines the (not necessarily close) packing of the structure. In this respect, the effective atomic size needs to be evaluated carefully taking into account the previous critics to the concept of ionic radii [2]. Finally, a comparison of the results in both models (CC and AC) is recommended before making a conclusion about the validity and the bonding balance of the structure.

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MS43 O5

What we can learn from interatomic distances - Some case studies using the bond valence method. Herbert Boller, *Institut für Anorganische Chemie, Universität Linz, A-4040 Linz, Austria.* E-mail: herbert.boller@JKU.at

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The bond valence method [1, 2] relating a bond length to its bond valence by the formula:
$$v_{ij}=\exp[(R0_{ij}-d_{ij})/b_{ij}],$$
$R0_{ij}$, b_{ij} being individual parameters for a pair of bonded atoms, and d_{ij} the actual bond distance, is very useful for the analysis of interatomic distances in general. In this paper some special applications and experiences will be presented.

In complex anions the charge of a ligand can be estimated as the difference between its chemical valence and its

bond valence sum. By this argument very reasonable charge distributions in complex anions of general formulae $[(TX_4)(MCl)_n)]^{2-}$ and $[(TX_4)_mM]^{(2m-1)-}$, (T...Mo, W; X...S, O; M...Cu, Ag), are obtained: Bridging two- or three-bonded sulfur is almost neutral, while a charge of ~ -0.5 is found on terminal O, S or Cl ligands.

The valence (oxidation state) can in principle be determined from the bond valence sum of a cation. This is shown for thioferrates with three-valent or mixed-valent iron. A model for the ordering of Fe(II) and Fe(III) in $Fe_2Mo_4O_7$ could also be suggested from the bond valence sums [3].

In rigid framework structures, e.g. the $KTCuS_4$ compounds (T...Mo, W) [4] or MMo_4O_6 bond valence sums are no good measure for the oxidation state, but they rather indicate the fit of the cations into the holes or channels of the framework. When the bond valence sum is smaller than the chemical valence some rattling or disorder is suggested, when it is larger, the cation is squeezed.

In conclusion the bond valence method can give significant information, especially taking into account the simplicity of the calculations. If the interatomic distances are known, a simple pocket calculator is sufficient. There are, however, some pitfalls, because interatomic distances are influenced by other factors too, e.g. atoms of the second coordination sphere, special bonding conditions or the rigidity of the structure. Of course the right choice of the $R0_{ij}$ and b_{ij} values is also important, although in most cases the values of R0ij presented in reference [2] with a universal $b = 0.37$ give good results. Therefore the bond valence method must be used in the context of additional chemical and crystallographic information. It should be checked, if possible by comparison with compounds where one is sure to know the right outcome or by other measurements, e.g. Moessbauer spectroscopy in the case of iron [5].

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