Multicomponent titanium(IV)-based helicates incorporating the ortho-phenylenediamine ligand: a structural and a computational investigation

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Figure 1: DOSY map analysis of the L²H₄ + Ti(OPr)₄ + opda reaction performed in situ (CD₂Cl₂).
Figure 2: Enlargement at m/z = 1393.335 of the Ti$_2$(L$^2$)$_2$(opda)$_2$ mass spectrum (top). The simulated isotopic profile (down) corresponds to [ Ti$_2$(L$^2$)$_2$(opda) + H]$^+$. 

Figure 3: Enlargement at m/z = 1605.447 of the Ti$_2$(L$^2$)$_2$(opda)$_2$ mass spectrum (top). The simulated isotopic profile (down) corresponds to [ Ti$_2$(L$^2$)$_2$(opda)(bqdi) + H]$^+$. 

Figure 4: DOSY map analysis of the Ti$_2$(L$^2$)$_2$(opda)$_2$ crystals dissolved in CD$_2$Cl$_2$. 
Figure 5: $^1$H NMR spectrum at 260 K (from 3 ppm to 9 ppm) of the Ti$_2$(L$_2$)$_2$(opda)$_2$ crystals dissolved in CD$_2$Cl$_2$. 

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Figure 5: $^1$H NMR spectrum at 260 K (from 3 ppm to 9 ppm) of the Ti$_2$(L$_2$)$_2$(opda)$_2$ crystals dissolved in CD$_2$Cl$_2$. 

The Partial Charges Model (PCM)

The partial charges model is based on a functional approach of chemical bonding using atomic charges \(q\) and their associated potentials \(v\), which are both first derivatives of the total energy of the system \(E\):

\[
q \propto \frac{\partial E}{\partial \nu} \quad \text{and} \quad v \propto \frac{\partial E}{\partial q}
\]

For a chemical system, \(q = Z - N\), with \(Z\) atomic number and \(N\) non-integral number of electrons around the nucleus, while \(v\) becomes a measure of its electronegativity. This may be readily understood by looking at a diatomic molecule \(A-B\) constrained to have \(N = Z_A + Z_B = N_A + N_B\) [1]. For any electron transfer \(dN\) from \(B\) to \(A\) (\(dN_A = -dN_B = dN > 0\)) at the internuclear distance \(R\), the change in the total energy should be:

\[
E = f(N_A, N_B, Z_A, Z_B, R) \Rightarrow dE = \left[ \frac{\partial E}{\partial N_A}_{N_A} - \frac{\partial E}{\partial N_B}_{N_B} \right] dN + \left( \frac{\partial E}{\partial R} \right)_{N_A, N_B} dR \quad (1)
\]

For a given \(R\) distance (\(dR = 0\)) a spontaneous transfer will occur if \(dE < 0\):

\[
\Rightarrow \left( \frac{\partial E}{\partial N_A}_{N_A} \right) < \left( \frac{\partial E}{\partial N_B}_{N_B} \right) \quad \Leftrightarrow \quad \chi_A > \chi_B \quad \text{if} \quad \chi = -\frac{\partial E}{\partial N} = \left( \frac{\partial E}{\partial q} \right) = -\mu_e \quad (2)
\]

The last equalities coming from the fact that electronegativity measures the affinity of atoms for electrons [2]. Another consequence of (1) is that if \(R = R_e\), internuclear equilibrium distance, then \(dE = dR = 0\) i.e. \(\chi_A = \chi_B\). This is the electronegativity equalization principle of R.T. Sanderson [3] meaning that electronegativity should be considered as the opposite of an electronic chemical potential \(\mu_e = \partial E/\partial N\) [4]. The relation between this electronic chemical potential and the empirical electronegativity introduce by L. Pauling in the thirties is immediate if we introduce the chemical hardness \(\eta = \partial^2 E/\partial N^2\) of the system (its chemical softness being \(\sigma = 1/\eta\)):

\[
E(N) = E^0(Z) + (N - Z) \left( \frac{\partial E}{\partial N} \right)_{N=Z} + \frac{(N - Z)^2}{2!} \left( \frac{\partial^2 E}{\partial N^2} \right)_{N=Z} = E^0(Z) + q\chi^0 + \frac{q^2}{2}\eta \quad (3)
\]

With \(\chi = -\partial E/\partial N = \chi^0 + \eta \times q\), and \(\chi_A = \chi_B = <\chi>\) for a diatomic molecule, it comes:

\[
\chi_A = \chi_A^0 - \eta_A q = \chi_B^0 + \eta_B q = <\chi> \quad \Leftrightarrow \quad q = \frac{\chi_A^0 - \chi_B^0}{\eta_A + \eta_B} \quad (4)
\]

leading to a stabilization energy \(\Delta = (E_A - E_A^0) + (E_B - E_B^0) = q(\chi_B^0 - \chi_A^0) + q^2(\eta_A + \eta_B)/2:\)

\[
\Delta = -\frac{(\chi_A^0 - \chi_B^0)^2}{\eta_A + \eta_B} + \frac{1}{2} \frac{(\chi_A^0 - \chi_B^0)^2}{\eta_A + \eta_B} = -\frac{1}{2} \frac{(\chi_A^0 - \chi_B^0)^2}{\eta_A + \eta_B} < 0 \quad (5)
\]

in full agreement with the original Pauling definition [2] assuming that \(\eta_A + \eta_B = \text{cste.}\). Relation (5) provides also a firm theoretical justification of the empirical HSAB principle (Hard and Soft Acids and Bases) introduced empirically by R.G Pearson [5]:

\[
\]
The other part of the HSAB principle \([\Delta \text{hard-hard}) < \Delta \text{hard-soft})]\) comes rather from the contraction of atomic orbitals in response to an increase in the nuclear effective charge \(Z^*\) [6], as with \(dZ^* > 0\) and \((\partial E/\partial Z^*) < 0 \Rightarrow \Delta E = (\partial E/\partial Z^*_A)dZ^*_A + (\partial E/\partial Z^*_B)dZ^*_B < 0\).

The problem of the quantitative evaluation of the hardness parameter may be solved by treating an atom as a sphere having a uniformly distributed electric charge \(q\). If this sphere has a characteristic radius \(r\), then:

\[
E(q) = \frac{\varepsilon^2 q^2}{8\pi\varepsilon_0 r} \Leftrightarrow \chi = \frac{(\partial E_0)}{(\partial q)} = \frac{\varepsilon^2 q}{4\pi\varepsilon_0 r} \quad \text{et} \quad \eta = \frac{(\partial^2 E_0)}{(\partial q^2)} = \frac{\varepsilon^2}{4\pi\varepsilon_0 r} \quad (6)
\]

The chemical hardness is then known as soon as some atomic radius has been defined [7].

The link between this functional approach of chemical bonding and the more conventional molecular orbital theory is as follows:

where we have used the Koopmans theorem \(I \sim -E_{\text{HOMO}}\) and \(A \sim -E_{\text{LUMO}}\). For a sphere of charge \(q\) and characteristic radius \(r\), we have \(I = E(q+1) - E(q)\) and \(A = E(q) - E(q-1)\):

\[
I = \frac{\varepsilon^2 (2q + 1)}{8\pi\varepsilon_0 r} \quad ; \quad A = \frac{\varepsilon^2 (2q - 1)}{8\pi\varepsilon_0 r} \quad \Rightarrow \chi = \frac{1}{2}; \quad \eta = I - A
\]

in full agreement with Mulliken’s definition of orbital electronegativity [8]. Consequently, if electronegativity corresponds to the Fermi level of the electrons in a given chemical system [9][10], its chemical hardness \(\eta\) measures its HOMO-LUMO gap [11].

From a practical point of view, given any system resulting from the association of \(n\) atoms and carrying a total electrical charge \(z\), it is possible to write its electronegativity as [12-16]:

\[
\chi_i = \langle \chi \rangle = \chi_i^0 + \frac{e}{4\pi\varepsilon_0 f_i} q_i + \frac{1}{4\pi\varepsilon_0} \sum_{j=1}^{n} M_{ij} e q_j \quad \forall i = 1, ..., n \quad \text{et} \quad \sum_{i=1}^{n} q_i = z \quad (7)
\]
where $\chi_i^v$ are Mulliken-type electronegativities, $r_i$ atomic radii modelling the spatial extent of valence orbitals and $M_{ij}$ Madelung contributions which are readily evaluated as $1/R_{ij}$ for a molecular compound or computed with an Ewald summation for a crystalline network [17]:

$$M_{ij} = \frac{\pi}{V} \sum_{h-k^+i+k^*+h^c \neq 0} \frac{\exp \left[ 2\pi \hbar (\tilde{x}_j - \tilde{x}_i) \right]}{h^2} \exp \left( \frac{\pi^2 |h|^2}{K^2} \right) + \sum_{l=1}^{n} \frac{\text{erfc}(K|\tilde{l} + \tilde{x}_j - \tilde{x}_i|)}{|\tilde{l} + \tilde{x}_j - \tilde{x}_i|} - \frac{2K}{\sqrt{\pi}} \delta_{ij}$$

with $\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(-t^2) \, dt$

Here $V$ is the unit-cell volume and $K$ is an adjustable parameter ruling the convergence speed of this double summation process.

In the case of the PACHA formalism, great care has been taken to define the atomic $(\chi, \rho)$ parameterization needed for computing partial charges $q$. Concerning atomic electronegativity $\chi$, the Allen scale was selected owing to its clear definition based on the average one-electron energy of the valence-shell electrons in ground state free atoms [18]. This scale is attractive because it can be indifferently based on high-resolution experimental values concerning atomic energy levels or on high accuracy numerical Dirac-Hartree-Fock solutions. This double check both experimental and theoretical is thus a solid guarantee that we are not using in the model arbitrary values. Moreover, as Allen’s electronegativities are given in energy units (eV), it solves also a very troublesome physical unit problem coming from the failure of L. Pauling to recognize that the polarity of a bond was not only a consequence of the difference in electronegativity but also a matter of matching between chemical hardness of both partners. The only problem with the Allen’s scale is that it is defined only for main group and d-block elements, values for the f-block being not yet available. In the PACHA formalism this problem is solved thanks to (6) recalling that energy and size are two perfectly equivalent ways of dealing with the electromagnetic interaction. This particularly means that atomic electronegativity should also correlates with the volume density of the valence electrons, as originally stated by the pioneering work of R.T. Sanderson who was the first to recognize the importance of the electronegativity equalization principle in chemistry [3]. Based on the knowledge of the maxima of the electron density of the electrons of the valence orbitals, it was possible to derive Pauling-type atomic electronegativities for f-elements [19] that may be converted into eV-values after adequate scaling: $\chi(\text{Allen}) = (13.605/2.30016) \times \chi(\text{Pauling})$ [20]. By coherence with (6) the chemical hardness may not arbitrarily defined but approximated by the radius corresponding to the most diffuse principal maxima in the radial distribution function $r^2 \psi^2(r)$, computed using relativistic wavefunctions solutions of the Dirac equations [21]. In order to keep coherence with the chosen units for measuring electronegativities all radii and distances (structure) are scaled by the non empirical factor $k = e^2/(4\pi \varepsilon_0) = 14.4$ eVÅ, where $e$ is the elementary charge $(1.60219 \times 10^{-19} \text{C})$ and $\varepsilon_0$ the permittivity of the vacuum $(8.85419 \times 10^{-12} \text{C.V}^{-1}\text{.m}^{-1})$.

Relation (7) allows us to switch very quickly between a set of chemical parameters (electronegativities, sizes and spatial positions) and the associated partial charge distribution $q_i$. From this distribution, it is possible to define two kinds of self-energies $SE$:

$$SE = \frac{e^2}{8Z \pi \varepsilon_0} \sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij}(K)(q_i)(q_j) = \frac{694.68}{Z} \sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij}(K)[A^{-1}](q_i)(q_j) \text{kJ.mol}^{-1}$$

6
one SE(q) using the partial charge distribution q_i, and the other one SE(z) computed using integral oxidation states z_i. The ratio of these two self-energies defines the global ionicity I of the structure: \( I(\%) = 100\sqrt{SE(q)/SE(z)} \). Moreover, given a characteristic distance \( R_0 \), the Madelung constant \( A \) is readily obtained as:

\[
A = 4\pi \varepsilon_0 R_0 \times \frac{SE(z)}{e^2}.
\]

The Madelung tensor \( M_{ij} \) allows also to get a set of strictly positive numbers \( f_i = \partial^2E/\partial q_i \partial v_i \leftrightarrow \partial^2\text{HOMO-LUMO}/\partial N \), called frontier indexes [22], and showing where the variation of \( \mu_e \) should be the largest [23]:

\[
\eta = \frac{e}{4\pi \varepsilon_0} f_i + \frac{1}{4\pi \varepsilon_0} \sum_{j=1}^{n} M_{ij} f_j \quad \forall i = 1,...,n \text{ et } \sum_{i=1}^{n} f_i = 1
\]

(8)

Where \( \eta \) is the global hardness of the system i.e. its HOMO-LUMO gap.

Here is an example for an input file used for computing partial charges distributions directly from crystalline data. As shown, some atoms (#108-115) are defined using internal coordinates instead of triclinic coordinates allowing performing rotation of a phenyl group as explained in the paper. The following table gather the values used for atomic electronegativities and chemical hardnesses in the paper:

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References


