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► **To cite this version:**

Alessandro Genoni. Elucidating the nature of chemical bonds in a coordination compound through quantum crystallographic techniques. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials* [2014-..], 2023, 79 (4), pp.253-254. 10.1107/S2052520623006364 . hal-04205343

HAL Id: hal-04205343

<https://hal.univ-lorraine.fr/hal-04205343>

Submitted on 12 Sep 2023

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Acta Cryst. (2023). **B79**, 253–254



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Elucidating the nature of chemical bonds in a coordination compound through quantum crystallographic techniques

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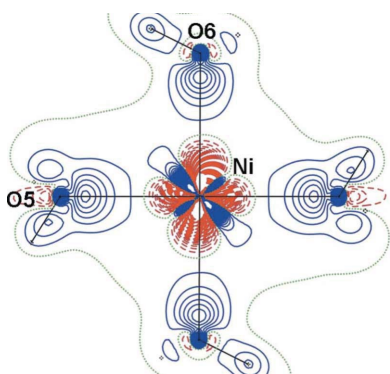
Keywords: quantum crystallography; multipole model; Hirshfeld atom refinement; topological analysis of the electron density; chemical bond.

In recent years, quantum crystallography (Genoni *et al.*, 2018; Genoni & Macchi, 2020; Grabowsky *et al.*, 2017; Macchi, 2020) has emerged as an innovative and vibrant area of research in solid state sciences. It clearly stemmed from the mature field of experimental charge density studies (Koritsanszky & Coppens, 2001; Coppens, 2005), although its roots can already be found in the early days of quantum physics and modern crystallography (Macchi, 2020, 2022). An ultimate definition of quantum crystallography has not been given yet, but researchers working in this area generally agree in presenting it as a multidisciplinary field having as its main purpose the investigation of properties and phenomena that are important for or manifest in the crystalline state, and that can be explained or illustrated by exploiting methods based on the laws of quantum mechanics (Genoni *et al.*, 2018).

To achieve the goal, several techniques have been devised and applied over the years. Among them we can certainly include multipole models (MM) for the determination of experimental electron distributions from high-quality and high-resolution experimental X-ray diffraction data (Stewart, 1976; Hansen & Coppens, 1978). We can encompass the fully periodic *ab initio* methods that are now efficiently implemented in widely used software, such as *CRYSTAL* (Erba *et al.*, 2023), *Quantum Espresso* (Giannozzi *et al.*, 2017) or *Wien2K* (Blaha *et al.*, 2020). Furthermore, in this area, an important role is also played by the so-called quantum chemical topological strategies [*e.g.* the quantum theory of atoms in molecules (QTAIM) (Bader, 1990)], which allow analyses and interpretations of experimental or theoretical electron densities. Finally, a prominent place in the field has been recently occupied by those approaches characterized by a very strict interplay between quantum chemistry methods and X-ray diffraction measurements (Grabowsky *et al.*, 2017, 2020), with two strategies as representative examples: Hirshfeld atom refinement (HAR) (Jayatilaka & Dittrich, 2008) and the X-ray restrained/constrained wavefunction (XRW/XCW) approach (Jayatilaka & Grimwood, 2001; Genoni, 2022).

Although researchers may have their own preferred techniques to study properties and phenomena in the solid state, from the previous paragraph one could also evince that investigations simultaneously involving multiple techniques of quantum crystallography could be very useful to prove the consistency of obtained results or to highlight different facets of the same scientific phenomenon or problem. The paper by Pinto *et al.* (2023) represents a clear example in this direction, where three different techniques (Hansen & Coppens multipole model, QTAIM analysis, and HAR) are exploited to characterize the nature of chemical bonds and of intra/intermolecular interactions in an organometallic compound, namely tetraaquabis(hydrogenmaleato)nickel(II) $[[\text{Ni}(\text{C}_4\text{H}_3\text{O}_4)_2(\text{H}_2\text{O})_4]$, hereinafter referred to simply as NiHmA.

In the above-mentioned investigation, the authors started with a traditional Hansen & Coppens MM against experimental X-ray structure factors collected at low temperature (121 K) up to a high resolution of 1.12 \AA^{-1} . A distinctive feature of the examined compound and of its bonding pattern immediately emerged from a first analysis of the obtained crystal structure: the asymmetry of the intramolecular hydrogen bond in the hydrogen maleate ligand compared to the case of the uncoordinated anion (Madsen *et al.*, 1998). This is ascribable to the coordination of the ligand with the metal center, but also to the other hydrogen bonds in which the oxygen atoms of hydrogen maleate are involved, in agreement with an investigation previously conducted by Ruggiero & Korter



(2016). Much deeper insights into the nature of chemical bonds in NiHmA were grasped through the analysis of the refined multipole-based charge density. For example, by inspection of the deformation density maps, the absence of density overlap in the coordination sphere was quite evident, thus indicating the partially electrostatic nature of the interactions between the nickel center and the surrounding ligands. This was confirmed by the MM-based *d*-orbital populations, which also clearly indicated a sort of asymmetry of the deformation density around the metal atom.

The MM electron density was afterwards subjected to the QTAIM analysis, which gave a reasonable molecular graph and values of the electron density at the bond critical points (bcps) completely in line with the observed bond lengths and interaction distances. However, the most interesting results of the topological analysis were obtained by Pinto and co-workers by inspecting the trend of the Laplacian of the electron density along the bond paths and by evaluating kinetic and potential energy densities at the different bcps. As a result of this investigation, the Ni–O bonds were mainly classified as closed-shell interactions with partial covalent character, in full agreement with the results of the analysis simply based on deformation densities and *d*-orbital populations (see previous paragraph). Always making use of the above-mentioned descriptors, the authors also labeled all the detected hydrogen bonds as mainly closed-shell interactions. The only exception was the intramolecular hydrogen bond in the hydrogen maleate ligand, which was classified as open-shell (*i.e.* covalent nature) and correlates quite well with the structural results and the MM descriptors obtained through the multipolar refinement.

Finally, Pinto *et al.* (2023) exploited the increasingly popular Hirshfeld atom refinement approach, which allowed the authors to obtain longer element to hydrogen (E–H) bond lengths than in the MM case. Notably, the determined E–H bond distances were in excellent agreement with those resulting from neutron diffraction measurements performed on the Zn analog of NiHmA. After the HAR, the authors carried out the QTAIM analysis of the underlying final electron density, which, however, is fully theoretical and not experimental. Overall, the results were in quite good agreement with those previously obtained through the topological analysis of the MM charge distribution. The only significant differences were observed for the Laplacian profiles of some E–H bond lengths, as one should have preliminarily expected due to the different hydrogen-atom positions.

The most important feature of the highlighted investigation is certainly the consistency of results obtained by applying different methods of modern quantum crystallography, which strengthens the main conclusions on the nature of chemical bonds in the examined coordination compound. Nevertheless, to fully complete the study, it would also have been desirable to determine an experimental electron density through an XRW/XCW calculation on the HAR geometry, in analogy to the recently proposed X-ray wavefunction refinement

(Woińska *et al.*, 2017) and Hirshfeld atom-based X-ray constrained wavefunction fitting (Davidson *et al.*, 2022) procedures. This would have allowed a more significant comparison of two experimental electron distributions (*i.e.* the MM and XRW/XCW ones). Unfortunately, some preliminary XRW/XCW computations did not fully converge, so far preventing this further analysis. However, we expect a follow-up study of the investigation, where the bonding patterns of other coordination compounds will be analyzed through a full spectrum of quantum crystallographic techniques (obviously including the XRW/XCW approach).

In conclusion, the study carried out by Pinto and co-workers can be considered as an example of modern investigations in quantum crystallography, where different and complementary strategies are used to obtain consistent and robust results about properties and phenomena in the solid state. More such investigations are envisaged in the near future.

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