INTRODUCTION

In the last five years there has been a growing interest and development of the ab-initio crystal structure determination technique [1], that afforded a few hundreds of new structures solved, and refined, from powder diffraction (PD) data only [2]. The vast majority of the species studied are ionic, inorganic compounds, although more recently the methodology has been successfully used to study molecular species (such as organics and metal complexes) and polymeric coordination compounds [3].

However, the number of organometallic compounds (containing at least one metal-to-carbon bond) which have been characterized by PD is surprisingly low (see Table 1) and can be in principle ascribed to the following reasons:

i) while solution of the phase problem is simplified by the presence of heavy scatterers [the metal(s)], completion of the structural model is hampered by the minor contribution to the whole scattering power of light atoms which can be easily missed in difference Fourier maps.

ii) as for organic compounds, packing of organometallics is mostly dictated by weak(er) intermolecular forces, affording large a.d.p.'s and a rapid fall-off of the scattering power at high angles. The absence of significant reflections above $\sin(\theta)/\lambda = 0.4 \text{ Å}^{-1}$ dramatically decreases the resolution and, for light atoms linked by short bonds (<1.5 Å), causes, again, uninterpretable Fourier maps and instability in the Rietveld refinement (RR).

iii) most organometallic species contain ligands with a wide conformational flexibility which hampers, or makes very difficult, structure solution, model completion and/or theoretical crystal structure predictions.

iv) culturally speaking, powder diffractionists have often been linked to material science, metallurgy and mineralogy, but not to the world of molecular solids; differently, because a large number of crystal growth techniques are available for (soluble) coordination compounds,
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

Sponsored by the International Centre for Diffraction Data (ICDD).

This document is provided by ICDD in cooperation with the authors and presenters of the DXC for the express purpose of educating the scientific community.

All copyrights for the document are retained by ICDD.

Usage is restricted for the purposes of education and scientific research.

DXC Website — www.dxcicdd.com  
ICDD Website - www.icdd.com
structural organometallic chemists have mainly employed conventional single-crystal diffractometry.

Table 1. Summary of Organometallic Species characterized by \textit{ab-initio} XRPD.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Author(s)</th>
<th>Reference</th>
</tr>
</thead>
</table>

This paper is intended to briefly review some applications of PD to moderately complex organometallic systems, with particular emphasis on the active use of ancillary computational techniques.

RESULTS AND DISCUSSION

Since 1992, we have started a project on the structural characterization of coordination compounds from PD data measured on conventional equipment [4], and soon realized the necessity of adding 'external' (\textit{i.e. not} present in the diffraction pattern) information in order to improve the quality of the results, because independent atom models often converge to unphysical bonding values. Typically, the detailed knowledge of the most common stereochemistries (available from large databases) and the hidden assumption that harmonic wells (of arbitrary curvature) about 'reference' values can be added in a \textit{generalized} cost function, allow to include geometrical restraints in the refinement procedure.

While these approximations hold for intramolecular bond distances (and angles), parametrization of nonbonding (\textit{intra-} and \textit{inter-}molecular) interactions by this technique is not
viable, because the flatness of their potential energy wells and their asymptotic behaviour for large separations can hardly be reproduced by restraining a number of interatomic distances. Notwithstanding, the true structural model should correspond to a packing energy minimum and be consistent with the experimental diffraction data; therefore, as briefly described in the following, joint (energy + Rietveld), or even uncoupled (iterated), refinements may act as a valuable tool for obtaining and/or validating \textit{ab-initio} XRPD crystal structures.

The methodology described hereafter is based on standard Rietveld refinements and Molecular Mechanics (MM) Steric Energy minimizations, \textit{performed in an alternate and iterative way}; this is only a short-cut to the real problem, which, however, grants successful results at the expenses of longer computing times. The ultimate goal, however, resides in a unique, joint minimization, for which no software is presently available.

\begin{center}
\textbf{CASE 1: Molecular Mechanics in the Crystal Lattice as a Tool for Solving Structures:}

\[ [(\text{CO})_2\text{Rh(\mu-Cl)}_2\text{Rh(C}_8\text{H}_8)] \ 1 \ [5] \]
\end{center}

While solving the crystal structure of 1, location of two independent Rh atoms (Patterson) and two bridging Cl ions (difference Fourier) was easily achieved. At this point, no easily distinguishable C and O atoms could be found in the difference map. However, packing considerations, \textit{i.e.} the qualitative analysis of the empty volumes about the \text{Rh}_2\text{Cl}_2 core, clearly indicated which metal was bound to cyclooctadiene and which to carbonyls.

Therefore, location and orientation of the diolefin were initially determined by \textit{rough} standard molecular building (SMILE [6]); later, a steric energy minimization of the whole \textit{flexible} molecule within its crystal lattice (performed by a locally developed program [7]) afforded a good starting point for the final (restrained) RR (\(R_p\) and \(R_F = 0.116\) and 0.085, respectively).
In addition, the roof-shape of the Rh$_2$Cl$_2$ fragment and the overall feasibility of a joint, or split, RR/MM refinement were checked by comparing (see Figure 1) the (two) one-dimensional cuts of $R_{wp}$ (along the Rh...Rh and Cl...Cl directions, respectively) with the two-dimensional section (Rh...Rh/Cl...Cl) of the potential energy hypersurface (PES). Interestingly, but not exceptionally, even if the minima of the two independent cost functions are close (which is not always true), $R_{wp}$ is much more sensible to high $Z$ atoms (Rh vs. Cl) displacements, while the PES is softer along the Rh...Rh direction than along Cl...Cl. As a direct consequence, joint refinements should face the non-trivial problem of relative scaling of different 'observations', which, at present, is not uniquely defined.
CASE 2: Molecular Mechanics in the Crystal Lattice as a Tool for Validating Structures solved by PD data: \[\{(\text{phen})\text{Pd}[\text{C(=O)ON(-CH}_3\text{)C(=O)}]\}\ 2 \ [8]\]

A 'standard' *ab-initio* XRPD structure determination of 2 was undertaken to determine the controversial [9] connectivity pattern of this complex organometallic species. Briefly: i) peak search and indexing of data collected on a conventional powder diffractometer with graphite monochromatized Cu-Kα radiation afforded an orthorhombic unit cell of approximate dimensions \(a = 7.09; b = 10.66\) and \(c = 17.27\) Å, space group \(Pna2_1\), \(Z = 4\), \(M(24) = 17, F(24) = 33 (0.013, 57)\); ii) interpretation of the Patterson map allowed location of the unique Pd atom; iii) the lack of a centre of symmetry and what was later interpreted as remarkable texture determined a noisy and not easily interpretable difference Fourier map; iv) the orientation of a planar \((\text{phen})\text{PdC}_2\) fragment was determined by a rotational grid search about the (refinable) Pd atom position, using P-RISCON [10] and optimized by a rigid-body RR, using a Z-matrix formalism implemented by us into a local version of the program PREFIN [11] (now incorporated into DEBV1N [12]); v) completion of the structure with the few missing light atoms was possible by a surprisingly informative difference Fourier map (see Figure 2) obtained on newly collected data free of texture effects: vi) the correct stereoisomer (2a in Scheme I) was clearly identified by the position of the missing substituent in the metallacycle.

![Image](image_url)

**Figure 2**

**Scheme I**
The relevant stereochemical task of this structural study was to discriminate between two different stereoisomers of 2, each one possibly occurring in the crystal in two different orientations (see Scheme I); therefore, a cross-validation of the XRPD results (structure 2a) was achieved by MM [7]. Given the significantly different energy values reported in Table 2, our computations differentiated among the four plausible structures depicted in Scheme I, reinforced the RR results and showed that subtle information of the molecular shape, hidden in the lattice metrics, symmetry operations and heavy atom locations (obtained from XRPD without a priori information), can successfully be retrieved by MM. Note that, given the quality of the Fourier map in Figure 2, this validation may appear redundant. However, because the original textured data did not allow the successful completion of steps vi) and viii), we actually employed MM well before resynthesizing our product. It was indeed this computational evidence which forced us to attempt such difficult synthesis again, in search for a less textured sample.

Table 2. Results of the Steric Energy Computations (kcal mol\(^{-1}\)) for Molecules 2a-2d (Scheme I)

<table>
<thead>
<tr>
<th>Fragment</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
<th>2d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Steric Energy, (SE_i)</td>
<td>-24.0</td>
<td>-17.4</td>
<td>+26.6</td>
<td>+7.1</td>
</tr>
<tr>
<td>Intramolecular Energy, (IE_i)</td>
<td>+25.2</td>
<td>+25.4</td>
<td>+38.5</td>
<td>+35.0</td>
</tr>
<tr>
<td>Packing Energy, (PE_i)</td>
<td>-49.2</td>
<td>-42.8</td>
<td>-11.9</td>
<td>-27.9</td>
</tr>
<tr>
<td>(SE_i - SE_{2a})</td>
<td>0.0</td>
<td>+6.6</td>
<td>+50.6</td>
<td>+31.1</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Validation of structural results of low quality on adding external observations is a customary behaviour in protein crystallography, where interatomic constraints are typically taken from multidimensional NMR data or steric energy contributions; analogously, combination of EXAFS with PD data has also been reported. [13] All these approaches are ultimately based on the assumption that, if the structural model is optimized vs. data of different origins (diffraction, theory, spectroscopy, database frequencies, etc.), it is likely that instrumental biases (systematic errors) are cancelled. In agreement with such expectations, we recently demonstrated that a joint refinement of the crystal structure of the organometallic cluster \(\text{H}_2\text{Re}_4(\text{CO})_{12}2\text{C}_6\text{H}_6\) [14] from single-crystal X-ray and powder neutron (TOF) data could lead to the correct hydrogen atom location for a species containing third row transition elements.
The proposed methodology significantly increases the confidence in commonly attainable XRPD results; such coupling of experimental diffraction data with steric energy computations in the crystal lattice can successfully discriminate between a few alternative models by actively using experimental, i.e. accessible, information on lattice metrics, space group symmetry operations and heavy atom location derived from XRPD data. This further step in the ab-initio XRPD process, once a proper force field is available, is thought to increase the resolution inherent in the diffraction method and, therefore, to act as a lens capable to rescue subtle structural details which XRPD data alone cannot afford.

REFERENCES


