Hydrogen atoms location in [Re$_4$(μ_3-H)$_4$(CO)$_{12}$] by joint X-ray single-crystal and neutron powder diffraction analysis

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The hydrogen atom locations in [Re$_4$(μ_3-H)$_4$(CO)$_{12}$] are accurately determined by joint X-ray single-crystal and time-of-flight neutron powder diffraction analysis; this new methodology does not require large crystals of several mm dimensions but only a sizeable amount of monophasic microcrystalline sample.

A number of different methodologies are available to solve structural problems, whatever the aggregation state of the sample.[1] Surely single-crystal (SC) X-ray (X) diffraction is the easiest, quickest and most definitive method. However, when (*i*) suitable crystals are unavailable or (*ii*) the relative atomic scattering powers in the sample are too different (hampering, for instance, the location of hydrogens in the presence of heavy atoms) or (*iii*) too similar (inhibiting the distinction of neighbouring elements), the power of XSC weakens and other techniques are better suited. While it has been known for a long time that neutron (N) diffraction on relatively large SCs offers an elegant, although expensive, solution to point (*ii*), only recently powder (P) diffraction has been shown to overcome point (*i*) (at least for moderately complex structures).[2] As large SCs needed for neutron diffraction are often not available, we propose, to tackle point (*ii*) [and (*iii*)], a joint XSC, NP approach which relies, for the burden of the structure determination, on XSC data, while subtle structural details are essentially rescued from NP measurements, the final model being validated by simultaneous refinements on both data sets. A similar approach has been used in studying the cation distribution in doped KTiOPO$_4$[3] and the incommensurately modulated structure of Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$.[4]

The combined use of different radiations as well as of different spectroscopic and computational methods, under the assumption that 'different' biases may cancel out, likely affords results of higher quality than those obtainable from the individual techniques, allowing to refine more complex structures. This approach has been pioneered, within the crystallographic community, by the combined use of X–N data (from either two SC datasets[5] or two P diffraction experiments[6]), by the introduction of steric energy contributions into protein structure refinements[7] or, more frequently, by the sagacious use of stereochemical knowledge (by imposing geometrical restraints) in complex refinements. Combined EXAFS and powder diffraction analyses have been recently reported.[8] The proposed methodology differs from other more conventional complementary X–N studies, in which juxtaposition of individual results leads to a unitary interpretation; moreover, even if it can be exemplified on a high symmetry crystal phase, it may not necessarily require simple systems (like other powder diffraction methods), since XSC data should grant superior convergence properties to the joint least-squares refinement.

Despite the relevance of transition-metal hydrides in modern inorganic chemistry, the ubiquitous hydrido ligand is still the most poorly structurally characterised. Even if its coordination behaviour and/or classical/non-classical nature can be qualitatively retrieved from a number of experimental techniques (X-ray diffraction, IR, NMR, inelastic neutron scattering), the only definitive technique is neutron diffraction. Compounds containing face-bridging (μ_3) hydrides are much less common than those with edge-bridging (μ) or terminal hydrides, with only five NSC crystal structures reported in the literature, [FeHCo$_3$(CO)$_9${P(OMe)$_3$}$_3$],[9] [Ni$_4$H$_3$(C$_5$H$_5$)$_4$],[10] [Rh$_4$H$_4$(C$_5$Me$_5$)$_4$][BF$_4$]$_2$,[11] [HCu{P(*p*-C$_6$H$_4$Me)$_3$}]$_6$[12] and [Cr$_4$(μ-H)$_5$(μ_3-H)$_2$(C$_5$R$_5$)$_4$],[13] none of them regarding third-row transition elements. [Re$_4$(μ_3-H)$_4$(CO)$_{12}$] **1** is unusual among metal cluster compounds, being one of the few known 'unsaturated' carbonyl clusters (56 *vs.* 60 CVEs); its XSC structure has been previously reported and the μ_3-H character inferred from local stereochemical considerations and an 'image enhanced' (*i.e.* symmetry averaged) difference Fourier map (estimated average Re–H 1.77 Å).[14] Here we present the complete structural characterisation, from XSC and TOF NP diffraction data,† of the new **1**·2C$_6$D$_6$ crystal phase which is the major product of the standard synthetic approach to **1**,‡ but has never been recognized before. The availability of sizeable amounts of this phase (but not of large SC) and our experience with XP on coordination and organometallic systems[15] prompted us to attempt the viability of the above mentioned method.

TOF neutron scattering measurements (Fig. 1) easily afford powder patterns with good counting statistics (if compared to the constant wavelength mode); however, their analysis in conjunction with conventional laboratory X-ray diffraction data needs some extra care. Since the very same structural model (coordinates and U_{ij} values) is being refined simultaneously on X and N diffraction data, but there are intrinsic differences in physical interactions, size of the samples and experimental geometries, one must ensure that systematic errors have been properly corrected. In particular, since absorption effects may lead to fake, incongruent thermal parameters, a θ-dependent
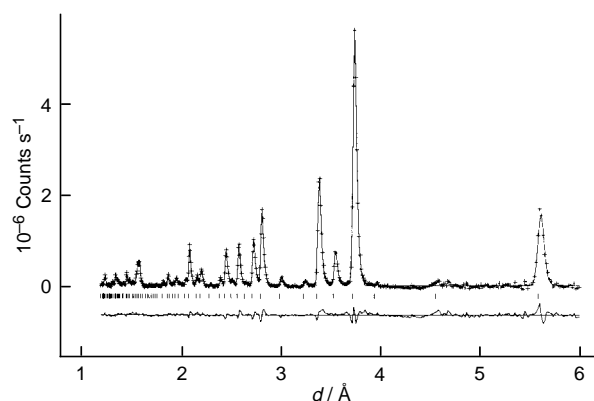

Fig. 1 Final Rietveld refinement plot for TOF neutron data, in the range 1.2 < *d* < 6.0 Å. Peak markers and difference plot at the bottom. For sake of clarity, the high *d*-values section (6.0 < *d* < 9.0 Å, with only two reflections) has been omitted from the plot.
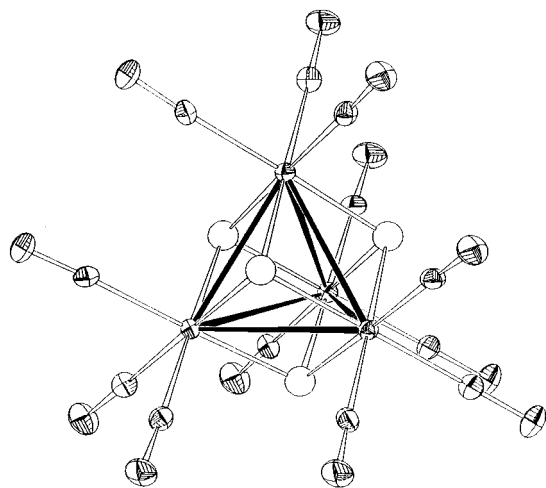
Fig. 2 An ORTEP drawing of the $[Re_4H_4(CO)_{12}]$ molecule, showing the H_n atom position at 1.99(2) Å from the rhenium atoms. Selected bond distances (Å) and angles (°): Re–Re 2.924(2), Re–C 1.912(8), C–O 1.14(1), Re–H_x 1.88(12), Re–H_n 1.99(2); Re–C–O 178(1), C–Re–C 86.9(4), H_n–Re–H_n 85.(1), C–Re–H_n 93.8(6) and 179.0(9), Re–H_n–Re 94.(1), Re–Re–C 92.2(3) and 136.5(2).

(spherical—on top of ψ-scans, XSC) and a d-dependent (NP) corrections have been carefully applied. In addition, in order to deal with the different interactions of X and N beams (with electrons and nuclei, respectively) and the off-centre polarisation of H-valence electron(s) due to the metal–H bond(s), a split-atom H refinement has been performed, defining two pseudoelements [H_x and H_n] with null contribution to the N and X structure factors, respectively. This makes, *inter alia*, the H_n location substantially insensitive to the intrinsic 'overweightness' of the X data set (in terms of quality and, perhaps, number of observations).

Our results show that $[Re_4(\mu_3$-$H)_4(CO)_{12}]$ in **1**·$2C_6D_6$ has a crystallographically imposed T_d symmetry (see Fig. 2), with a $Re_4(CO)_{12}$ core virtually identical to that found in **1**, and confirm the μ_3-nature of the hydrido ligands as originally proposed by Wilson and Bau;[14] however, significant differences are observed in the H-bonding parameters [Re–H_x 1.88(12) *vs.* 1.77 Å, Re–H_n 1.993(17) Å]. As for the precision of our results, our study shows that the (room temp.) esd values related to the H_n atoms are about three to five times poorer than those from conventional NSC data (mostly collected at temperatures below 90 K), but one order of magnitude smaller than those concerning H_x. Unfortunately, in assessing the accuracy of this work we lack the internal consistency check with the C–D distance because the clathrated C_6D_6 molecules are rotationally disordered; however, since the observed Δ(Re–H_x, Re–H_n) value (0.11 Å) is within the range found in most structural comparisons between X- and N-SC results, we think that the actual Re–H_n bond distance should not be affected by severe systematic errors. The observed M–H value might look slightly longer than that in $[Rh_4H_4(C_5Me_5)_4][BF_4]_2$[11] (58 CVEs, av. Rh–H and Rh–Rh 1.86 and 2.76 Å, respectively); however, a much larger apparent metal radius [Re–Re 2.924(2) Å] partially accounts for the observed difference.

Footnotes and References

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