Electronic Supporting Information

Towards accurate and precise positions of hydrogen atoms bonded to heavy metals atoms

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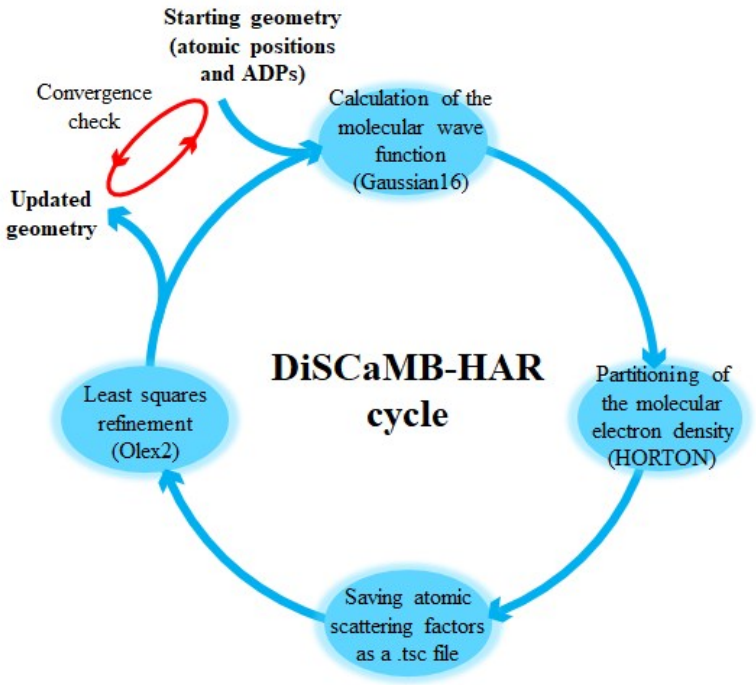
The DiSCaMB-HAR procedure for computationally demanding structures – general description



Scheme S1. Schematic representation of a DiSCaMB-HAR cycle. The detailed description of the method can be found in the ESI.

The cycle of the DiSCaMB-HAR procedure which was applied to the structures of heavy metal compounds is presented in Scheme S1. Starting with the initial geometry, DiSCaMB employs Gaussian16[1] to calculate the molecular wavefunction for the crystal asymmetric unit (or a larger molecular cluster, according to the user's preferences). The effects of interactions with the crystal environment are included via surrounding the central molecule with a cluster of atomic charges and dipoles centered on atoms of

surrounding molecules having at least one atom within a selected radius. Calculations of the atomic multipoles and the molecular wavefunction are performed in a self-consistent procedure. Various quantum chemical methods, such as HF, DFT, MP2 and CCSD) and basis sets can be used to calculate the molecular wave function. Subsequently, DiSCaMB employs the HORTON program[2] to perform Hirshfeld partition (or another selected partition) of molecular electron density into atomic contributions, based on which DiSCaMB calculates aspherical atomic scattering factors and saves them in a .tsc format file.[3] The aspherical atomic scattering factors are then used in a standard least squares refinement carried out in Olex2 in order to obtain the improved positional and thermal parameters of the atoms in the analyzed crystal structure. Therefore, unlike in the case of traditional HAR performed with the Tonto program, refinement is carried out against F^2. Finally, convergence of structural parameters is assessed based on the value of maximum parameter shift divided by the estimated error is checked. The described DiSCaMB-HAR cycles should be repeated until the desired convergence is reached. In the case of computationally demanding structures, such as the systems studied here, to carry out the DiSCaMB-controlled phases, especially the self-consistent procedure leading to the molecular wave function in the crystal, using high performance computing is indispensable.

The details of the DiSCaMB-HAR procedure

For the 5 considered structures the basis sets used to obtain the atomic scattering factors of all the atoms present in the structure was determined by the heavy atom: cc-pVDZ or cc-pVTZ for the Fe complex, cc-pVTZ-DK for Ru and Rh, and jorge-DZP for Os. The method applied for molecular wave function calculations in each case was DFT/B3LYP and the radius of the cluster of charges and dipoles was the standard radius of 8 Å. The "insane" grid provided by HORTON was used to partition molecular electron density. The refinement was started from the IAM structure retrieved from the CSD. Positions of all hydrogen atoms were freely refined with HAR. All the reflections were used in the refinement. The weighting scheme varied between the structures and the adjustment of weighting scheme was a crucial factor allowing to obtain the best quality of the final structure and in some cases to successfully complete the refinement (details below). For the majority of the structures, 5 DiSCaMB-HAR cycles were performed, since this number was sufficient to achieve acceptable values of the parameter shift/σ between the structural parameters from the succeeding cycles (see Table S1). The only exception was XAXMEP, for which during the first 3 DiSCaMB-HAR cycles positions of all H atoms except those bonded to the transition metal had to be determined according to the riding model. Only starting from the 4th DiSCaMB-HAR cycle was unconstrained refinement of all hydrogen positions possible and consequently, it took 6 cycles to achieve convergence. Starting from the 4th DiSCaMB-HAR cycle in XAXMEP, the isotropic thermal parameter of the hydrogen atom H31 had to be fixed at its value from the previous cycle, in order to assure convergence. Anisotropic refinement of hydrogen thermal motions could be achieved for 3 structures (QOSZON, NOBBOX, SITKUB). However, in the case of QOSZON for the two hydrogen atoms bonded to Fe their thermal ellipsoids were non-positive definite (N.P.D.). Therefore, the 5th DiSCaMB-HAR cycle was repeated with those two H atoms refined isotropically and the 6th cycle was performed in order to achieve convergence. This procedure contributed to the improvement of agreement between the DiSCaMB-HAR and neutron Fe-H bond lengths. Moreover, in order to investigate the benefits of using a triple zeta basis set, a B3LYP/cc-pVTZ version of HAR was performed for QOSZON. In the 1st DiSCaMB-HAR cycle after obtaining convergence of isotropic refinement, full anisotropic refinement was performed. Since refinement of ADPs of the Fe-bonded H atoms was not successful (one very flat thermal ellipsoid and one N.P.D.), those two H atoms were kept isotropic in the following refinement cycles. The total number of 3 DiSCaMB-HAR cycles was necessary to achieve the desired shift/σ and the improvement obtained in terms of the Fe-H bond lengths was the best in this case. A triple zeta basis set (jorge-TZP) was also utilized in the case of XAXMEP, however no improvement was achieved in the 1st DiSCaMB-HAR cycle and the procedure was not continued.

Weighting scheme used in the DiSCaMB-HAR refinements

For all structures the refinement was started with isotropically refined hydrogen thermal motions, for most of the structures with weights refined according to the SHELX weighting scheme, except XAXMEP, for which statistical weights were applied throughout the whole refinement procedure. For XAXMEP, starting from the 4th DiSCaMB-HAR cycle, the isotropic thermal parameter of the hydrogen atom H31 had to be fixed at its value from the previous cycle, in order to assure convergence. For QOSZON, after attaining convergence of isotropic refinement with SHELX weights in the 1st cycle, anisotropic refinement was performed until convergence and then statistical weights were used to continue the anisotropic refinement. In the succeeding DiSCaMB-HAR cycles anisotropic refinement was continued with SHELX weights followed by refinement with statistical weights. The same strategy was applied in the 5th and 6th cycle in which hydrogen atoms H1 and H2 were changed to isotropic. In turn, in the refinement of QOSZON with cc-pVTZ basis set used to calculate the molecular wave function, SHELX weights were applied throughout the whole refinement procedure. For MIGKIY, in each DiSCaMB-HAR cycle only isotropic refinement with SHELX weights was convergent. In the case of NOBBOX, after attaining convergence of isotropic refinement with SHELX weights, anisotropic refinement with SHELX weights was continued in the 1st DiSCaMB-HAR cycle, as well as in all the subsequent cycles. In the case of SITKUB, in the 1st DiSCaMB-HAR cycle, after isotropic refinement with SHELX weights, the weights were switched to statistical ones and isotropic refinement was continued. Subsequently, anisotropic refinement with statistical weights was performed until convergence was reached. The same procedure was applied in the following DiSCaMB-HAR cycles.

Comment of refinement statistics

DiSCaMB-HAR did not necessarily result in improved refinement statistics, compared to IAM. Goodness of fit is often further from 1 (QOSZON, SITKUB, XAXMEP) than in IAM or similarly close to 1 (MIGKIY, NOBBOX). R-factor obtained with DiSCaMB-HAR is minimally worse (MIGKIY, NOBBOX, XAXMEP) or minimally better (QOSZON, SITKUB) than R-factor obtained with IAM. More considerable improvement resulting from using DiSCaMB-HAR is reflected by lower values of wR2 for the majority of the structures. The only structure for which this parameter is improved only slightly compared to IAM is MIGKIY, which might be the consequence of applying SHELX weigths throughout the whole refinement. HAR most of the times results in increasing minima or maxima (or both) of residual density. The only exception for which HAR improved residuals to certain extent is QOSZON.

Comment on data and refinement quality (neutron and X-ray)

Since quality of the experimental data and quality of the model refined against this data is crucial for a sound comparison between hydrogen positions obtained based on HAR of X-ray data and based on neutron data, we ranked the data sets according to the quality of experimental data and the quality of the refined model. The ranking of structures by data quality was based on data completeness, R_{int} and data resolution. Structures were ordered from the "worst" to the "best" according to given quantity. The place in the ranking became the number of points, which were summed for each structure in order to determine the position of

the structure in the final ranking. Since our final goal is a comparison between the neutron and the X-ray results, for each structure the X-ray and the neutron result in the ranking was summed in order to obtain an overall ranking of structures with respect to the quality of the neutron and X-ray data set. Similarly, quality of the refinement was evaluated using statistical values such as goodness of fit, R, wR2 and the range of residual density values (Δρ range). This ranking was done for neutron, IAM and HAR. An overall ranking comparing the neutron-IAM and the neutron-HAR refined models was also made. In every case, if certain quantity taken into account in the ranking procedure was unknown, the structure automatically obtained the lowest position in the ranking with respect to this quantity. The values of all the parameters taken into account are given in Table S1. At the end, the points obtained in the data quality and the refinement quality ranking were summed for each structure in order to obtain the final data-refinement ranking of neutron, X-ray(IAM), X-ray(HAR) and joint neutron-X-ray(IAM) and neutron-X-ray(HAR). The obtained rankings are only tentative since the differences between parameters are in certain cases very small and all the parameters were considered with equal importance, which might not be optimal. There are additional circumstances indicative of refinement quality that are not taken into account by the ranking - e.g. (1) for XAXMEP neutron experiment resulted in the data to parameter ratio insufficient to refine the ADPs of hydrogen atoms [10], (2) in the X-ray structure of MIGKIY unmodeled disorder in the vicinity of one of the CF_3 groups is found (the disorder is separated from the Ru-H bonds and the related residual density is up to 0.4 e/Å^3 for F atoms, however it influences all the reflections and therefore it might also influence the Ru-H bonds region). Nevertheless, the overall ranking of structures correlates with certain trends, such as (1) similarity of TM-H and other X-H bond lengths obtained as a result of neutron and X-ray data refinement (2) the number of electrons in the TM (3) feasibility of anisotropic refinement of H atoms (the overall X-ray(IAM) and X-ray(HAR) ranking).

Ranking of structures by data quality (neutron and X-ray):

Ranking of structures by completeness (from the worst to the best):

Neutron: 1-XAXMEP, 2-SITKUB, 3-QOSZON, 4-MIGKIY, 5-NOBBOX

X-ray: 1-MIGKIY, 2-XAXMEP, 3-QOSZON, 4-SITKUB, 5-NOBBOX

Ranking of structures by R_{int} (from the worst to the best):

Neutron: 1-XAXMEP, 2-MIGKIY, 3-SITKUB, 4-NOBBOX, 5-QOSZON

X-ray: 1-MIGKIY, 2-QOSZON, 3-XAXMEP, 4-SITKUB, 5-NOBBOX

Ranking of structures by resolution (from the worst to the best):

Neutron: 1-XAXMEP, 2-SITKUB, 3-QOSZON, 4-NOBBOX, 5-MIGKIY

X-ray: 1-QOSZON, 2-XAXMEP, 3-SITKUB, 4-MIGKIY, 5-NOBBOX

Overall ranking of structures (from the worst to the best):

Neutron: 3-XAXMEP, 5-SITKUB, 11-MIGKIY, 11-QOSZON, 13-NOBBOX

X-ray: 6-MIGKIY, 6-QOSZON, 7-XAXMEP, 11-SITKUB, 15-NOBBOX

Neutron-X-ray: 10-XAXMEP, 16-SITKUB, 17-MIGKIY, 17-QOSZON, 28-NOBBOX

Ranking of structures by refinement quality (neutron, IAM and HAR):

Ranking of structures by goodness of fit (from the worst to the best):

Neutron: 1-XAXMEP, 2-QOSZON, 3-NOBBOX, 4-SITKUB, 5-MIGKIY

X-ray (IAM): 1-SITKUB, 2-XAXMEP, 3-MIGKIY, 4-NOBBOX, 5-QOSZON

X-ray (HAR): 1-SITKUB, 2-XAXMEP, 3-MIGKIY, 4-NOBBOX, 5-QOSZON (cc-pVTZ, 2Hiso)

Ranking of structures by R (from the worst to the best):

Neutron: 1-XAXMEP, 2-SITKUB, 3-MIGKIY, 4-NOBBOX, 5-QOSZON

X-ray (IAM): 1-MIGKIY, 2-XAXMEP, 3-QOSZON, 4-SITKUB, 5-NOBBOX

X-ray (HAR): 1-MIGKIY, 2-XAXMEP, 3-SITKUB, 4-NOBBOX, 5-QOSZON (cc-pVTZ, 2Hiso)

Ranking of structures by wR2 (from the worst to the best):

Neutron: 1-SITKUB, 2-MIGKIY, 3-NOBBOX, 4-XAXMEP, 5-QOSZON

X-ray (IAM): 1-MIGKIY, 2-XAXMEP, 3-QOSZON, 4-SITKUB, 5-NOBBOX

X-ray (HAR): 1-MIGKIY, 2-XAXMEP, 3-QOSZON (cc-pVTZ, 2Hiso), 4-NOBBOX, 5-SITKUB

Ranking of structures by residual density Δρ range (from the worst to the best):

Neutron: 1-XAXMEP, 2-MIGKIY, 3-NOBBOX, 4-SITKUB, 5-QOSZON

X-ray (IAM): 1-XAXMEP, 2-MIGKIY, 3-SITKUB, 4-NOBBOX, 5-QOSZON

X-ray (HAR): 1-XAXMEP, 2-MIGKIY, 3-SITKUB, 4-NOBBOX, 5-QOSZON (cc-pVTZ, 2Hiso)

Overall ranking of structures (from the worst to the best):

Neutron: 7-XAXMEP, 11-SITKUB, 12-MIGKIY, 13-NOBBOX, 17-QOSZON

X-ray (IAM): 7-XAXMEP, 7-MIGKIY, 12-SITKUB, 16-QOSZON, 18-NOBBOX

X-ray (HAR): 7-XAXMEP, 7-MIGKIY, 12-SITKUB, 16-NOBBOX, 18-QOSZON (cc-pVTZ, 2Hiso)

Neutron-X-ray (IAM): 14-XAXMEP, 19-MIGKIY, 23-SITKUB, 31-NOBBOX, 33-QOSZON

Neutron-X-ray (HAR): 14-XAXMEP, 19-MIGKIY, 23-SITKUB, 29-NOBBOX, 35-QOSZON

Overall ranking of structures by data-refinement quality (neutron, IAM and HAR) (from the worst to the best):

Neutron: 10-XAXMEP, 16-SITKUB, 23-MIGKIY, 26-NOBBOX, 28-QOSZON

X-ray (IAM): 13-MIGKIY, 14-XAXMEP, 22-QOSZON, 23-SITKUB, 33-NOBBOX

X-ray (HAR): 13-MIGKIY, 14-XAXMEP, 23-SITKUB, 24-QOSZON (cc-pVTZ, 2Hiso), 31-NOBBOX

Neutron-X-ray (IAM): 24-XAXMEP, 36-MIGKIY, 39-SITKUB, 50-QOSZON, 59-NOBBOX

Neutron-X-ray (HAR): 24-XAXMEP, 36-MIGKIY, 39-SITKUB, 52-QOSZON, 57-NOBBOX

Comment on various hydrogen ADP models in QOSZON

QOSZON is the only structure for which DiSCaMB-HAR with hydrogen ADPs estimated by SHADE2 was successful. Therefore, there are three models of hydrogen ADPs: full anisotropic refinement (anis), H atoms bonded to Fe refined isotropically and the remaining ones anisotropically (2Hiso) and ADPs of all H atoms estimated with SHADE2 (SHADE). Each of those 3 models was combined with cc-pVDZ and cc-pVTZ wave function. On average, precision of H ADPs obtained with HAR is two orders of magnitude lower than it is in the case of non-H atoms (see averaged values of U_{ij} standard deviations in Table S4). The same orders of magnitude, as in the case of U_{ij} standard deviations calculated separately for H and non-H atoms, can be observed in the case of mean absolute difference and root mean square deviation calculated between the anis/2Hiso models and SHADE (see Table S3). The agreement between the ADPs of non-H atoms is within one combined standard deviation (wRMSD < 1). For the H atoms the agreement is within 2-3 standard deviations (with standard deviations 2 orders of magnitude higher than for the non-H atoms).

Geometry optimization

Geometry optimizations in the gas phase were performed using Gaussian16[1], the DFT/B3LYP method with GD3 dispersion correction.[4] The IAM geometry was used as the starting point. Only for 3 of the analyzed compounds were the calculations convergent with the following basis sets: QOSZON (cc-pVDZ), SITKUB (jorge-DZP) and XAXMEP (jorge-DZP). For the remaining compounds, the older values from the literature are used as a benchmark (see Table S1).

Discussion of the results obtained for MIGKIY and XAXMEP

In MIGKIY, the Ru-HB bond length obtained with DiSCaMB-HAR and IAM is exactly the same and is severely underestimated, compared to the neutron value. However, DiSCaMB-HAR locates the position of the HA atom more accurately than IAM. The Ru-HA bond length obtained with DiSCaMB-HAR is shorter by 0.02 Å from the neutron bond length (still within 3 neutron esds and on the standard level of HAR X-H bonds in crystals of organic compounds [12]), whereas for IAM the difference amounts to 0.05 Å (within 7 neutron esds). However, the superiority of the DiSCaMB-HAR approach manifests itself in the SiA-HA bond length, which is underestimated compared to the neutron length only by 0.017 Å (within 2 neutron esds), whereas IAM results in a bond length shorter by 0.117 Å (12 neutron esds). In the case of XAXMEP, DiSCaMB-HAR significantly elongates the Os-H bonds, however, for 3 bonds this elongation results in bond lengths further from the neutron ones and only for one – slightly closer to the neutron result than for IAM. For the Os-H2 and Os-H4 bonds the DiSCaMB-HAR bond lengths are overestimated compared to their neutron values (still within 2 neutron esds – the neutron precision is decreased) with the differences equal to 0.028 Å and 0.034 Å, respectively. IAM underestimates the Os-H2 bond length by 0.032 Å and

overestimated the Os-H4 bond lengths by only 0.006 Å. The Os-H1 bond length is underestimated by IAM by 0.006 Å and Os-H3 is overestimated by only 0.001 Å. However, these bond lengths are considerably overestimated by DiSCaMB-HAR by 0.074 Å and 0.081 Å, respectively. The values of Os-H1 and Os-H3 bond lengths obtained in the course of geometry optimization differ from the neutron values whereas usually the neutron bond lengths are reproduced with higher accuracy by theoretical results. They suggest that the neutron values might be underestimated. Given the poor quality of the neutron data for this structure, it cannot be ruled out that the optimized values might be a better reference. Residual density maps both for IAM and HAR reveal volumes of negative density (magnitude > 1 e/Å^3) in the vicinity of Os, also in the region of Os-H bonds. As it turns out, when the divergence between the model and the experimental electron density is so high, aspherical scattering factors might not provide better results than IAM. A triple zeta basis set (jorge-TZP) in the case of XAXMEP did not bring any improvement therefore the results are not presented.

General evaluation of quality of all X-H bond lengths

The general quality of all hydrogen positions obtained with the DiSCaMB-HAR method is evaluated in comparison with IAM based on the mean difference (MD), mean absolute difference (MAD) and mean ratio (MR) calculated between the X–H bond lengths obtained with these refinement methods and the ones obtained with neutron diffraction (the calculated values are presented in Table S2 in the ESI†). IAM in all the analyzed cases leads to shortened bond lengths, the average shortening for all structures amounts to 0.113 Å. For DiSCaMB-HAR, MAD for all X–H bonds averaged over all structures amounts to 0.027 Å. MAD for all X–H bonds in the case of DiSCaMB-HAR displays certain variability which corresponds well with the data-refinement quality ranking (see Table S2 in the ESI†). For the highest quality data sets NOBBOX and QOSZON it amounts to 0.014 Å, which is the level of the average difference between HAR and neutron lengths of typical bonds in crystals of organic compounds [13]. MAD is almost twice as high for SITKUB (0.020 Å) and 3–4 times as high for the structures for which hydrogen atoms could be refined only isotropically (0.039 Å for MIGKIY and 0.046 Å for XAXMEP). Whereas, compared to the neutron values, IAM yields only underestimated X–H bond lengths, for DiSCaMB-HAR on average the effect of shortening is similar in magnitude to the effect of lengthening (MD for all structures is close to zero, MR very close to one). The MAD for TM–H bonds obtained with IAM and averaged over all structures is equal to 0.061 Å and DiSCaMB-HAR allows to decrease it to 0.053 Å. DiSCaMB-HAR results in the best improvement for the two structures from the top of the data-refinement quality ranking – NOBBOX (MAD(HAR) = 0.005 Å and MAD(IAM) = 0.048 Å) and QOSZON (MAD(HAR) = 0.013 Å and MAD(IAM) = 0.095 Å). The improvement in TM–H bond lengths for SITKUB (MAD(HAR) = 0.098 Å and MAD(IAM) = 0.131 Å) and MIGKIY (MAD(HAR) = 0.069 Å and MAD(IAM) = 0.084 Å) is lower. Better agreement with the neutron values in terms of the TM–H bond lengths is obtained for the last structure in the ranking, XAXMEP. For HAR MAD = 0.054 Å (close to average HAR MAD for all TM–H bonds) and for IAM agreement is surprisingly high (MAD = 0.018 Å). Apparently, with residual density as high as in the case of the X-ray structure of XAXMEP the benefits of using aspherical scattering factors might be very limited, especially when determining positions of Os-bonded H atoms is concerned.

Table S1. Experimental and computational details of the neutron, X-ray IAM and X-ray HAR crystal structures considered in the study. QOSZON: [a] cc-pVDZ, all H anisotropic; [b] cc-pVDZ, H1 and H2 – isotropic; [c] cc-pVDZ, H ADPs from SHADE2; [d] cc-pVDZ, all H anisotropic; [e] cc-pVDZ, H1 and H2 – isotropic; [f] cc-pVDZ, H ADPs from SHADE2. The IAM structures were re-refined with *Olex2.refine* based on the original structures.

	QOSZON			MIGKIY			NOBBOX			SITKUB			XAXMEP		
	neutron	IAM	HAR	neutron	IAM	HAR	neutron	IAM	HAR	neutron	IAM	HAR	neutron	IAM	HAR
REFCODE [literature reference]	QOSZON01[5]	QOSZON[6]		MIGKIY01[7]	MIGKIY[7]		NOBBOX01[8]	NOBBOX[8]		SITKUB02[9]	SITKUB01[9]		XAXMEP[10]	XAXMEP01[11]	
Chemical formula	$C_{38}H_{32}FeO_8P_2$			$C_{32}H_{12}BF_{24}$, $C_{24}H_{41}N_6RuSi_3$			$C_{27}H_{55}N_9RuSi_3$			$C_{24}H_{47}BClO_2P_2Rh$			$C_{28}H_{52}OsP$, BF_4		
Space group	P -1			P n			P 2_1/c			P 2_1/c			P -1		
Temperature (K)	20(2)	293(2)		20(1)	100(2)		20(2)	100(2)		20(2)	120.15		20	199(2)	
Wavelength	1.315 Å	0.71073 Å		1.1708 Å	0.71073 Å		1.17 Å	0.71073 Å		1.5453 Å	0.71073 Å		0.7-4.2 Å	0.71073 Å	
Theta range (deg)	2.14-61.68	2.11-26.09		4.82-61.29	2.94-29.40		4.94-60.30	1.54-36.39		3.9-66.94	1.78-29.06		N/A	2.14-28.28	
sin(θ)/ λ Å^{-1}	0.67	0.62		0.75	0.69		0.74	0.83		0.60	0.68		N/A	0.67	
Completeness	0.761	0.919		0.88	0.89		0.884	1		0.474	0.998		N/A	0.918	
R_{int}	0.0217	0.0344		0.1253	0.0429		0.0517	0.0222		0.0574	0.0293		N/A	0.0325	
Year of publication	2003	2001		2013	2013		2014	2014		2003	2003		2005	2007	
Parameters	733	570	730 [a] 720 [b] 538 [c] 730 [d] 720 [e] 538 [f]	1297	828	1032	856	365	856	473	354	703	308	332	523
Goodness of fit	1.409	0.9963	1.208 [a] 1.219 [b] 1.257 [c] 0.9641 [d] 0.9683 [e] 1.2298 [f]	1.063	1.0579	1.065	1.119	1.0120	0.967	1.074	1.0595	1.728	1.72	1.0734	1.652
R[%]	2.64	2.68	1.96 [a] 1.97 [b] 2.04 [c] 1.86 [d] 1.87 [e] 2.00 [f]	6.17	3.82	3.56	4.39	2.61	2.08	6.49	2.56	2.15	12.9	3.35	3.33
(reflections)	(6301)	(5084)	(5084)	(7647)	(13569)	(13569)	(9100)	(11599)	(11599)	(1908)	(7021)	(7021)	(2197)	(5953)	(5952)
wR2[%]	5.44	6.92	3.29 [a] 3.32 [b] 3.48 [c] 3.86 [d] 3.89 [e] 3.42 [f]	13.10	9.24	8.39	8.39	5.10	3.40	16.62	5.77	2.86	7.5	8.08	6.81
(reflections)	(6402)	(6202)	(6202)	(9494)	(15166)	(15166)	(15166)	(14045)	(14045)	(2356)	(7624)	(7624)	(6629)	(6629)	(6629)
$\Delta\rho_{min/max}$ (eÅ^{-3})	-0.36/0.37	-0.34/0.34	-0.24/0.26 [a] -0.24/0.25 [b] -0.24/0.25 [c] -0.24/0.22 [d] -0.24/0.23 [e] -0.24/0.24 [f]	-1.30/1.30	-0.47/0.93	-0.47/0.95	-1.08/1.25	-0.47/0.67	-0.41/0.48	-0.73/0.56	-0.79/0.47	-0.76/0.42	N/A	-1.52/1.32	-1.54/1.00
Refined H positions	all	all	all	all	Ru-H, Si-H	all	all	Ru-H	all	all	Rh-H	all	all	Os-H	all
H thermal motions	aniso	iso	aniso [a,d] iso(H1, H2) + aniso (other) [b,e]	aniso	iso	iso	aniso	iso	aniso	iso	iso	aniso	iso	iso	iso

			SHADE [c,f]												
HAR param/σ shift			0.166667 [a] 0.5 [b] 0.333333 [c] 0.5 [d] 0.5 [e] 0.285714 [f]			0.5			0.25			0.166667			0.5
HAR wfn cycles			5[a] 6[b] 3[c] 3[d] 3[e] 3[f]			5			5			5			6
HAR comp. method	B3LYP/cc-pVDZ, $R_{cluster}$ = 8 Å [a-c] B3LYP/cc-pVTZ, $R_{cluster}$ = 8 Å [d-f]			B3LYP/cc-pVTZ-DK, $R_{cluster}$ = 8 Å			B3LYP/cc-pVTZ-DK, $R_{cluster}$ = 8 Å			B3LYP/cc-pVTZ-DK, $R_{cluster}$ = 8 Å			B3LYP/jorge-DZP, $R_{cluster}$ = 8 Å		
Optimized geometry	B3LYP/cc-pVDZ, GD3			[7]			[8]			B3LYP/jorge-DZP, GD3			B3LYP/jorge-DZP, GD3		

Table S2. Mean difference (MD, units: Å), mean absolute difference (MAD, units: Å) and mean ratio (MR) calculated between all the X-H/TM-H bond lengths obtained with DiSCaMB-HAR or IAM and the neutron bond lengths. Since all X-H bond lengths obtained with IAM are too short compared to neutron diffraction, MD for IAM is left out.

			MD=mean(d(X)-d(N))		MAD=mean(|d(X)-d(N)|)				MR=mean(d(X)/d(N))			
			HAR-neutron		IAM-neutron		HAR-neutron		IAM-neutron		HAR-neutron	
			all X-H	metal-H	all X-H	metal-H	all X-H	metal-H	all X-H	metal-H	all X-H	metal-H
NOBBOX		1 Ru-H	-0.012	-0.005	0.106	0.048	0.014	0.005	0.904	0.970	0.989	0.997
QOSZON[a]	cc-pVDZ	2 Fe-H	0.002	-0.034	0.135	0.095	0.014	0.034	0.878	0.938	1.002	0.978
QOSZON[b]	cc-pVDZ		0.003	-0.022			0.013	0.022			1.003	0.985
QOSZON[c]	cc-pVDZ		-0.004	-0.026			0.015	0.026			0.997	0.983
QOSZON[d]	cc-pVTZ		0.005	-0.021			0.011	0.021			1.005	0.986
QOSZON[e]	cc-pVTZ		0.006	-0.012			0.011	0.013			1.006	0.992
QOSZON[f]	cc-pVTZ		-0.002	-0.022			0.014	0.022			0.998	0.985
SITKUB		1 Rh-H	-0.003	-0.098	0.116	0.131	0.020	0.098	0.894	0.914	0.998	0.936
MIGKIY		2 Ru-H	0.000	-0.069	0.118	0.084	0.039	0.069	0.893	0.948	1.001	0.957
XAXMEP		4 Os-H	0.028	0.054	0.100	0.018	0.046	0.054	0.909	0.997	1.025	1.034
XAXMEP[g]			0.018	0.040	0.110	0.022	0.041	0.040	0.901	0.988	1.016	1.024
all structures[a]			0.003	-0.009	0.113	0.061	0.028	0.053	0.897	0.964	1.003	0.994
all structures[b]			0.003	-0.007			0.028	0.050			1.003	0.995
all structures[c]			0.002	-0.008			0.028	0.051			1.002	0.995
all structures[d]			0.003	-0.007			0.027	0.050			1.003	0.995
all structures[e]			0.004	-0.005			0.027	0.048			1.003	0.997
all structures[f]			0.003	-0.007			0.028	0.050			1.002	0.995

Results obtained for QOSZON refined with the following strategy: [a] cc-pVDZ, all H anisotropic; [b] cc-pVDZ, H1 and H2 – isotropic; [c] cc-pVDZ, H ADPs from SHADE2; [d] cc-pVTZ, all H anisotropic; [e] cc-pVTZ, H1 and H2 – isotropic; [f] cc-pVTZ, H ADPs from SHADE2; [g] MD, MAD and MR calculated between IAM or HAR bond lengths and the optimized bond lengths.

Table S3. Mean difference (MD, units: Å^2), mean absolute difference (MAD, units: Å^2), mean ratio (MR), root mean square difference (RMSD, units: Å^2) and weighted root mean square difference (wRMSD) calculated between ADPs obtained in various versions of refinement of the QOSZON structure (excluding the Fe-bonded hydrogen atoms H1 and H2). anis – all H atoms refined anisotropically, 2Hiso – the Fe-bonded H1 and H2 refined isotropically and the remaining H anisotropically, SHADE – ADPs of all H atoms estimated with SHADE2.

compared structures	atoms	MD	MAD	MR	RMSD	wRMSD
cc-pVDZ, anis - cc-pVDZ, SHADE	non-H	0.000034	0.000233	0.988530	0.000319	0.352429
cc-pVTZ, anis - cc-pVTZ, SHADE		0.000072	0.000331	0.974464	0.000442	0.539203
cc-pVDZ, 2Hiso - cc-pVDZ, SHADE		0.000022	0.000224	0.988530	0.000306	0.337661
cc-pVTZ, 2Hiso - cc-pVTZ, SHADE		0.000061	0.000331	1.017960	0.000440	0.548659
cc-pVDZ, anis - cc-pVDZ, SHADE	H	0.012210	0.015799	1.663877	0.020909	1.545381
cc-pVTZ, anis - cc-pVTZ, SHADE		0.011823	0.021406	1.035084	0.027844	2.234603
cc-pVDZ, 2Hiso - cc-pVDZ, SHADE		0.011944	0.015645	1.035535	0.020842	1.542164
cc-pVTZ, 2Hiso - cc-pVTZ, SHADE		0.012262	0.015142	1.151115	0.020016	1.508948

Table S4. Averaged standard deviation of ADPs of non-H and H atoms in QOSZON resulting from various types of refinement (excluding the Fe-bonded hydrogen atoms H1 and H2). Units: Å. anis – all H atoms refined anisotropically, 2Hiso – the Fe-bonded H1 and H2 refined isotropically and the remaining H anisotropically, SHADE – ADPs of all H atoms estimated with SHADE.

structure	non-H	H
cc-pVDZ, anis	0.00059	0.012
cc-pVDZ, 2Hiso	0.00060	0.056
cc-pVDZ, SHADE	0.00059	
cc-pVTZ, anis	0.00056	0.012
cc-pVTZ, 2Hiso	0.00056	0.012
cc-pVTZ, SHADE	0.00059	

Table S5. TM-H bond lengths (units: Å) obtained with various methods for QOSZON. Color coding: green - HAR closer to neutron than IAM. anis – all H atoms refined anisotropically, 2Hiso – the Fe-bonded H1 and H2 refined isotropically and the remaining H anisotropically, SHADE – ADPs of all H atoms estimated with SHADE2.

Structure	Bond	Optimized	Neutron	IAM	HAR
cc-pVDZ, anis	Fe-H1	1.530	1.529(2)	1.44(2)	1.513(13)
cc-pVDZ, 2Hiso					1.520(16)
cc-pVDZ, SHADE					1.518(14)
cc-pVTZ, anis					1.520(13)
cc-pVTZ, 2Hiso					1.522(15)
cc-pVTZ, SHADE					1.520(14)
cc-pVDZ, anis	Fe-H2	1.517	1.521(2)	1.42(2)	1.469(11)
cc-pVDZ, 2Hiso					1.485(14)
cc-pVDZ, SHADE					1.480(12)
cc-pVTZ, anis					1.487(12)
cc-pVTZ, 2Hiso					1.505(14)
cc-pVTZ, SHADE					1.485(12)

Table S6. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of QOSZON, cc-pVDZ, anis.

			DiSCaMB-HAR				
	neutron	**IAM**	**cycle 1**	**cycle 2**	**cycle 3**	**cycle 4**	**cycle 5**
Fe1-H1	1.521(2)	1.44(2)	1.466(11)	1.469(11)	1.469(11)	1.469(11)	1.469(11)
Fe1-H2	1.529(2)	1.42(2)	1.514(13)	1.512(13)	1.513(13)	1.513(13)	1.513(13)
max parameter/σ shift				2.28571	0.5	0.181818	0.166667
goodness of fit			1.2104	1.2086	1.2082	1.2083	1.2082
R			0.0197	0.0196	0.0196	0.0196	0.0196
wR2			0.033	0.0329	0.0329	0.0329	0.0329
$\Delta\rho_{min/max}$ (eÅ^{-3})			-0.24/0.26	-0.24/0.25	-0.24/0.26	-0.24/0.26	-0.24/0.26

Table S7. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of QOSZON, cc-pVDZ, 2Hiso.

			DiSCaMB-HAR					
	neutron	**IAM**					**cycle 5a**	**cycle 6a**
Fe1-H1	1.521(2)	1.44(2)					1.485(14)	1.485(14)
Fe1-H2	1.529(2)	1.42(2)					1.520(16)	1.520(16)
max parameter/σ shift							5.4	0.5
goodness of fit							1.2188	1.2186
R							0.0197	0.0197
wR2							0.0332	0.0332
$\Delta\rho_{min/max}$ (eÅ^{-3})							-0.25/0.24	-0.24/0.25

Table S8. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of QOSZON, cc-pVDZ, SHADE.

			DiSCaMB-HAR		
	neutron	**IAM**	**cycle 1**	**cycle 2**	**cycle 3**
Fe1-H1	1.521(2)	1.44(2)	1.476(13)	1.481(12)	1.480(12)
Fe1-H2	1.529(2)	1.42(2)	1.520(15)	1.518(14)	1.518(14)
max parameter/σ shift				2.64286	0.333333
goodness of fit			1.3121	1.2538	1.2567
R			0.0211	0.0203	0.0204
wR2			0.0364	0.0348	0.0348
$\Delta\rho_{min/max}$ (eÅ^{-3})			-0.27/0.28	-0.23/0.25	-0.24/0.25

Table S9. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of QOSZON, cc-pVTZ, anis.

			DiSCaMB-HAR		
	neutron	**IAM**	**cycle 1**	**cycle 2**	**cycle 3**
Fe1-H1	1.521(2)	1.44(2)	1.485(12)	1.487(12)	1.487(12)
Fe1-H2	1.529(2)	1.42(2)	1.519(13)	1.520(13)	1.520(13)
max parameter/σ shift				2.46154	0.5
goodness of fit			0.9686	0.9643	0.9641
R			0.0187	0.0186	0.0186
wR2			0.0389	0.0386	0.0386
$\Delta\rho_{min/max}$ (eÅ^{-3})			-0.24/0.22	-0.24/0.22	-0.24/0.22

Table S10. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of QOSZON, cc-pVTZ, 2Hiso.

			DiSCaMB-HAR		
	neutron	**IAM**	**cycle 1**	**cycle 2**	**cycle 3**
Fe1-H1	1.521(2)	1.44(2)	1.487(14)	1.505(14)	1.505(14)
Fe1-H2	1.529(2)	1.42(2)	1.523(16)	1.522(15)	1.522(15)
max parameter/σ shift				3.23077	0.5
goodness of fit			1.1889	0.9672	0.9683
R			0.0193	0.0187	0.0187
wR2			0.0324	0.0389	0.0389
$\Delta\rho_{min/max}$ (eÅ^{-3})			-0.23/0.24	-0.24/0.22	-0.24/0.23

Table S11. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of QOSZON, cc-pVTZ, SHADE.

			DiSCaMB-HAR		
	neutron	**IAM**	**cycle 1**	**cycle 2**	**cycle 3**
Fe1-H1	1.521(2)	1.44(2)	1.480(13)	1.485(12)	1.485(12)
Fe1-H2	1.529(2)	1.42(2)	1.522(15)	1.520(14)	1.520(14)
max parameter/σ shift				2.92857	0.285714
goodness of fit			1.3038	1.2262	1.2298
R			0.0211	0.0199	0.02
wR2			0.0361	0.034	0.0341
$\Delta\rho_{min/max}$ (eÅ^{-3})			-0.29/0.27	-0.24/0.23	-0.24/0.24

Table S12. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of MIGKIY, cc-pVTZ-DK, iso.

			DiSCaMB-HAR				
	neutron	**IAM**	**round1**	**round2**	**round3**	**round4**	**round5**
Ru1-HA	1.600(8)	1.55(5)	1.59(6)	1.58(6)	1.58(6)	1.58(6)	1.58(6)
Ru1-HB	1.587(7)	1.47(4)	1.47(5)	1.47(4)	1.47(4)	1.47(4)	1.47(4)
SiA-HA	1.737(10)	1.62(4)	1.74(6)	1.72(6)	1.72(6)	1.72(6)	1.72(6)
max parameter/σ shift				1.5	0.5	0.5	0.5
goodness of fit			1.0834	1.064	1.0646	1.0646	1.0648
R			0.0358	0.0356	0.0356	0.0356	0.0356
wR2			0.0844	0.0838	0.0839	0.0839	0.0839
$\Delta\rho_{min/max}$ (eÅ^{-3})			-0.47/0.95	-0.47/0.95	-0.47/0.95	-0.47/0.95	-0.47/0.95

Table S13. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of NOBBOX, cc-pVTZ-DK, anis.

			DiSCaMB-HAR				
	neutron	**IAM**	**round1**	**round2**	**round3**	**round4**	**round5**
Ru-HA	1.598(3)	1.56(2)	1.592(11)	1.593(11)	1.593(11)	1.593(11)	1.593(11)
SiA-HA	1.874(3)	1.81(2)		1.868(13)	1.868(13)	1.868(13)	1.868(13)
max parameter/σ shift				2	0.333333	0.25	0.25
goodness of fit			0.9769	0.9656	0.9669	0.9667	0.9668
R			0.0212	0.0208	0.0208	0.0208	0.0208
wR2			0.0348	0.0339	0.034	0.034	0.034
$\Delta\rho_{min/max}$ (eÅ^{-3})			-0.42/0.48	-0.41/0.48	-0.41/0.48	-0.41/0.48	-0.41/0.48

Table S14. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of SITKUB, cc-pVTZ-DK, anis.

			DiSCaMB-HAR				
	neutron	**IAM**	**round1**	**round2**	**round3**	**round4**	**round5**
Rh-H1	1.531(11)	1.40(2)	1.431(13)	1.433(13)	1.432(13)	1.433(13)	1.433(13)
max parameter/σ shift				2.28571	0.428571	0.25	0.166667
goodness of fit			1.7636	1.7262	1.7283	1.7281	1.7281
R			0.0219	0.0215	0.0215	0.0215	0.0215
wR2			0.0291	0.0285	0.0286	0.0286	0.0286
$\Delta\rho_{min/max}$ (eÅ^{-3})			-0.76/0.42	-0.75/0.41	-0.76/0.42	-0.76/0.42	-0.76/0.42

Table S15. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of XAXMEP, jorge-DZP, iso.

			DiSCaMB-HAR					
	neutron	**IAM**	**round1**	**round2**	**round3**	**round4**	**round5**	**round6**
Os-H4	1.626(19)	1.53(6)	1.64(6)	1.64(6)	1.64(6)	1.66(5)	1.66(5)	1.66(5)
Os-H3	1.599(21)	1.56(6)	1.62(5)	1.61(5)	1.61(5)	1.67(5)	1.68(5)	1.68(5)
Os-H2	1.632(15)	1.59(5)	1.62(6)	1.62(6)	1.62(6)	1.66(5)	1.66(5)	1.66(5)
Os-H1	1.606(17)	1.59(5)	1.68(3)	1.68(3)	1.68(3)	1.67(3)	1.67(3)	1.68(3)
max parameter/σ shift				0.5	0.333333	4.65	1.0625	0.5
goodness of fit			1.7403	1.7402	1.7402	1.6585	1.6516	1.6518
R			0.0349	0.0349	0.0349	0.0334	0.0333	0.0333
wR2			0.0728	0.0728	0.0728	0.0683	0.068	0.0681
$\Delta\rho_{min/max}$ (eÅ^{-3})			-1.56/1.36	-1.54/1.37	-1.54/1.37	-1.55/0.95	-1.54/1.00	-1.54/1.00
			shortHX*	shortHX*	shortHX*			

* The remaining X-H bond lengths were determined by the riding model in 3 initial DiSCaMB-HAR cycles

Table S16. The table presents the values of various parameters characterizing refinement in each DiSCaMB-HAR cycle for the structure of XAXMEP, jorge-TZP, iso.

			DiSCaMB-HAR		
	neutron	**IAM**	**round1**	**round2**	**round3**
Os-H4	1.626(19)	1.53(6)	1.65(5)	1.65(5)	1.65(5)
Os-H3	1.599(21)	1.56(6)	1.67(5)	1.68(5)	1.68(5)
Os-H2	1.632(15)	1.59(5)	1.66(5)	1.65(5)	1.66(5)
Os-H1	1.606(17)	1.59(5)	1.67(3)	1.67(3)	1.67(3)
max parameter/σ shift				1.13333	0.5
goodness of fit			1.6596	1.6518	1.652
R			0.0335	0.0333	0.0333
wR2			0.0684	0.0681	0.0681
$\Delta\rho_{min/max}$ (eÅ^{-3})			-1.57/0.94	-1.56/0.96	-1.56/0.96

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