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# Different van der Waals radii for organic and inorganic halogen atoms: a significant improvement in IMOMM performance

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**Abstract.** The discrepancies between X-ray and integrated molecular orbital molecular mechanics computed geometries for $Os(H)_2Cl_2(P^iPr_3)_2$ and $Ir(H)_2Cl(P^tBu_2\,Ph)_2$ are explained by the inadequacy of the default molecular mechanics van der Waals radii for halogen elements. A simple procedure is proposed for the calculation of corrected van der Waals radii, and the application of the corrected radius for chloride is shown to improve substantially the results for the systems under test.

**Key words:** Van der Waals radii – Organic and inorganic halogen atoms – Integrated molecular orbital molecular mechanics

## 1 Introduction

Integrated molecular orbital molecular mechanics (IMOMM) is a recently proposed computational scheme [1], that has been already applied successfully to a number of cases [2–5]. It uses two different methodological levels for different parts of the same chemical system, quantum mechanics for the part harder to describe, and molecular mechanics (MM) for the rest, in a way not very different from other proposed schemes [6, 7]. Its accuracy depends on the performance of each one of its two components, the quantum mechanics description must be precise enough to evaluate accurately all interactions within the quantum mechanical region of the system, and the molecular mechanics description must be precise enough to evaluate accurately all the other interactions.

IMOMM implemented with the MM3(92) force field [8] appears to be well suited for the quantification of steric effects in transition metal complexes with bulky ligands [2–4]. There appears to be, however, a systematic error in complexes containing sterically active halide ligands, their steric effects seeming to be underestimated. One of the possible sources of this error is the inadequacy of the default van der Waals radii used in the force field. They are fitted essentially for organic systems, and one may expect that inorganic, more anionic, halogen atoms would have larger radii.

This work proves the validity of this hypothesis and proposes solutions to the problem. In the following sections, the problem is presented, the possible solution is outlined, and its validity is tested on the model systems.

## 2 The $Os(H)_2Cl_2(P^iPr_3)_2$ and $Ir(H)_2Cl(P^tBu_2Ph)_2$ systems

Tests on two different systems are carried out. The first of them is $Os(H)_2Cl_2(P^iPr_3)_2$ (system **1a** Fig. 1). The chemical characteristics of this particular hexacoordinated species have been discussed in detail elsewhere [5]. It suffices to say that the defining parameter of the steric effect is the X-Osl-P2-C14 dihedral angle, roughly defining the angle between the Os1-P2-P3 and Os1-C14-C15 planes. This dihedral angle has a value of 41.9° in the X-ray structure [9, 10] and a value of 0.0° in a geometry optimization at the restricted Hartree-Fock (RHF) level on the model system $Os(H)_2Cl_2(PH_3)_2$ (**1b**) [11].

This result (0.0°) for the $Os(H)_2Cl_2(PH_3)_2$ model system is confirmed by a more sophisticated ab initio calculation at the BECKE3LYP level [12]. In contrast, a geometry optimization of Fig. **1a** at the IMOMM (BECKE3LYP:MM3) computational level using the aforementioned model system for the quantum mechanical part and the default MM3(92) parameters [8], yielded a dihedral angle of 27.2°. This is a remarkable improvement from the 0.0° obtained on the model system, but still lower than the experimental value of 41.9°. At any rate, the previous proposal of a steric origin for the distortion [11] is qualitatively confirmed.

The second test system is $Ir(H)_2Cl(P^tBu_2PH)_2$ (system **2a** Fig. 2). The geometry of this pentacoordinated complex is better seen as derived from a trigonal

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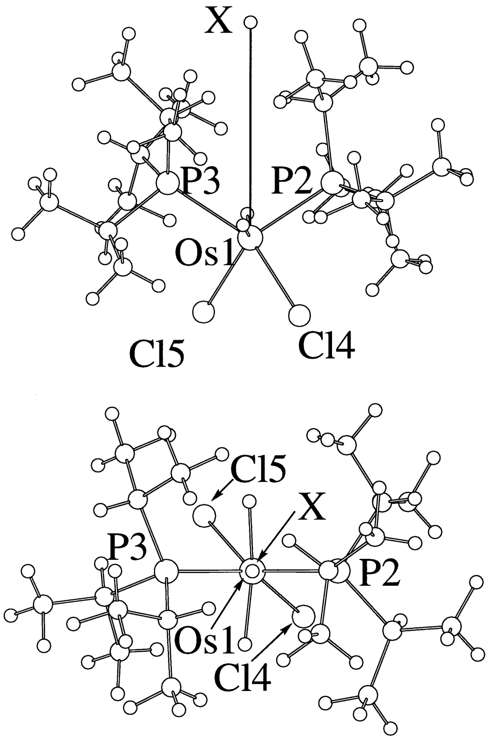

**Fig. 1.** X-ray structure of $Os(H)_2Cl_2(P^iPr_3)_2$ [9,10]. X is a dummy atom on the bisector of the P2-Os1-P3 angle. Two different views are shown for clarity

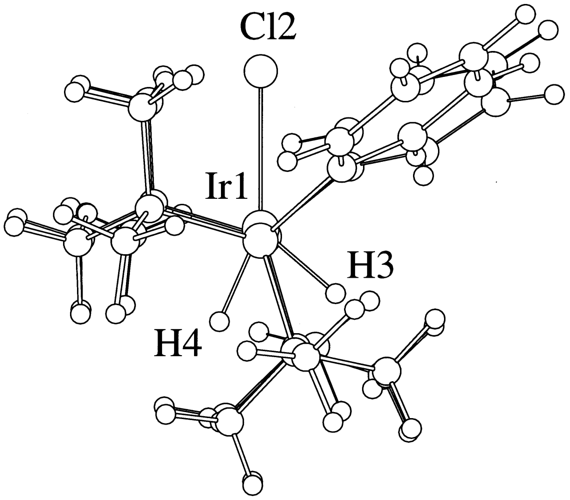

**Fig. 2.** X-ray structure of $Ir(H)_2Cl(P^tBu_2Ph)_2$ [10,13]

bipyramid with the phosphine ligands in the axial positions. The metal centre and the other three ligands (Cl2, H3, H4) lie essentially in a plane. The X-ray structure shows a remarkable asymmetry between the two Cl—Ir—H bond angles: Cl2—Ir1—H3 is 131.1°, while Cl2—Ir1—H4 is 156.2° [13], an asymmetry that is maintained in solution [14]. This asymmetry is not reproduced in the geometry optimization at the RHF level of the model system $Ir(H)_2Cl_2(PH_3)_2$ (**2b**) that gives a $C_{2v}$ structure with two identical Cl—Ir—H values [15].

This unsatisfactory result could not be corrected when calculations on the same $Ir(H)_2Cl(PH_3)_2$ model system were carried out at the more sophisticated BECKE3LYP level [12]. The resulting geometry was again $C_{2v}$, with a Cl—Ir—H angle of 145.3°. A geometry optimization of **2a** at the IMOMM(BECKE3LYP:MM3) level using $Ir(H)_2Cl(PH_3)_2$ for the quantum mechanical part and the default MM3(92) parameters [8] did not produce any significant improvement. The molecule was no longer $C_{2v}$ because of the asymmetry of the $P^tBu_2Ph$ ligand, but the two Cl—Ir—H bond angles were still essentially identical: 147.1° and 146.0°. This result was in contrast to the previous proposal of a steric origin for this distortion [13].

If the discrepancy between calculations on model systems and X-ray structures is related to steric effects, it ought to have been corrected by IMOMM, as has been proven in previous studies [2–4]. The fact that the improvement was only partial for **1** and non-existent for **2** hints at the existence of a methodological problem in these particular systems. One peculiarity of both systems is that the steric repulsion is mostly caused by interactions between the anionic $Cl^-$ and $H^-$ ligands attached to the metal and the organic alkyl substituents of the phosphine ligands. Interactions of this type are essentially controlled by the van der Waals interaction between the atoms. It is hard to argue on the accuracy of MM3 parameters for alkyl substituents, since the force field is especially designed for this kind of atoms [16]. On the other hand, the quality of the van der Waals parametrization of the inorganic ligands $Cl^-$, $H^-$ is much less reliable, since the MM3 force field considers them to be in an organic environment. The accuracy of this parametrization is analysed in detail in the following section. Another well-known limitation of the MM3 force field, the lack of electrostatic interactions, must be discarded as the source of this systematic error. Electrostatic interactions between ionic and neutral fragments must be weakly binding, through the interaction of the charge with dipoles and induced dipoles, and not the repulsive interaction missing in these IMOMM calculations.

## 3 Improved van der Waals radii for halide atoms

In the MM3 force field, the main contribution to the direct interaction between two non-bonded atoms i,j comes from the so-called van der Waals energy, defined in the following way [16c]

$$E_{ij} = \varepsilon\left[184000\exp(-12.0 d_{ij}/D_{ij}) - 2.25(D_{ij}/d_{ij})^6\right]$$

with

$$D_{ij} = r_i + r_j$$

$$\varepsilon = \sqrt{\varepsilon_i \cdot \varepsilon_j}$$

where $d_{ij}$ is the interatomic distance, and $r_i$ and $\varepsilon_i$ correspond to the van der Waals radius and hardness of atom i. Our goal is to determine whether the default parameters, defined for organic substituents, are appropriate for inorganic ligands, and if not, how they should be modified.

The problem of the assignment of parameters for the description of nonbonding interactions has a long history of its own, with approaches based both on experimental [17] and theoretical methods [18]. It is not the focus of this paper to discuss the validity of the different approaches, but just to apply a reasonable method to obtain a crude estimate of the difference between organic substituents and inorganic ligands. With this idea in mind, we chose to concentrate on the parameters of chloride, that is bulkier and more negatively charged than hydride. Of the two van der Waals parameters corresponding to chloride, the radius seems to be more critical to the steric effects in this type of hindered systems than the hardness. Therefore, our efforts will concentrate on determining what value should be assigned to the van der Waals radius of chloride within the MM3(92) force field.

The van der Waals radius for chlorine atoms in organic and in inorganic environments is computed with a method that has been deemed to be appropriate for the calculation of the van der Waals surface of molecules in a recent publication [19]. It consists of using the helium atom as a probe in geometry optimizations at the Møller-Plesset (MP3) level with a 6-311++G(3*d*, 3*p*) basis set.

One simple model is chosen for each of the two different environments considered. The model organic system is $H_3C—Cl \cdots He$, and the model inorganic system is $Na—Cl \cdots He$. For further simplification, the helium atom is restricted to a head-on approach on the chlorine atom, as shown in Fig. 3. The resulting optimized Cl—He distances for the two systems are significantly different: 3.31 Å for the organic system and 3.71 Å for the inorganic system. The radius for helium is found from a calculation on the helium dimer to be 1.58 Å. According to this, the van der Waals radius for organic chlorine is 1.73 Å, and the van der Waals radius for inorganic chlorine, 2.13 Å. The inorganic chlorine ligand, more negatively charged than the organic chlorine substituent, has a significantly larger radius, as should be expected.

These values are remarkably similar to those that can be obtained through the application of completely different approaches used in the field of solvation models [20]. The following formula has been proposed for the atomic radius (Å) of chlorine [20a]:

$$\rho_{\mathrm{Cl}} = 1.65 + 0.559\{-(1/\pi)\arctan[(q + 0.75)/0.1] + 1/2\}$$

with $q$ corresponding to the partial charge on the chlorine atom. Using a charge of −0.21 a.u. for organic chlorine [20b] and a nominal value of −1.00 a.u. for inorganic chlorine, the corresponding atomic radii would be 1.68 and 2.14 Å, respectively.

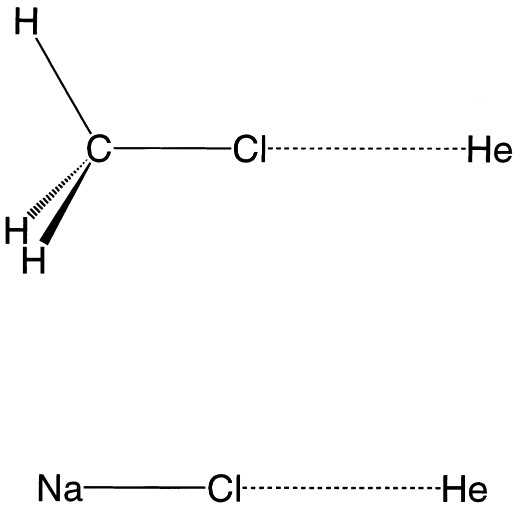

**Fig. 3.** Orientation used in the geometry optimizations of the $H_3C—Cl \cdots$ He and $Na—Cl \cdots He$ systems

In contrast, the agreement of our computed value for organic chlorine with the MM3 van der Waals radius for this element (2.07 Å) is unexpectedly poor. The MM3 value is actually much closer to that of inorganic chlorine! In order to understand this discrepancy, the standard experimental van der Waals radii [21] that can be found in textbooks [22], were examined. The value for chlorine, determined essentially for organic systems, is 1.75 Å [21] . This is in good agreement with our computed value and far from the MM3 standard value. The discrepancy between standard and MM3 van der Waals radii is by no means restricted to chlorine. The standard value for carbon in methane, ethane and ethylene is 1.70 Å [21, 22] while the MM3 value for $sp^3$ carbon is 2.04 Å. This apparent contradiction is simply a problem of terminology. What MM3 calls the van der Waals radius is a parameter inserted in a mathematical expression, the value of which is adjusted to reproduce properly the overall experimental properties, like crystal parameters and heat of sublimation [16c, 23]. It probably incorporates corrections to other errors in the force field. As a result, it does not correspond exactly to the van der Waals radius, although it is directly related to it.

Therefore, it would not be appropriate to input directly the van der Waals radius that we have computed for inorganic chlorine into the MM3 force field. On the other hand, the sophisticated fitting procedure used in the definition of the MM3 force field is out of reach because of the scarceness of experimental data and the prohibitive computing effort. Instead, we make the assumption that the relationship between the "real" and the MM3 van der Waals radius for organic chlorine is conserved for inorganic chlorine. That is, since the difference between the two values for the organic molecule is 0.34 Å, we will assume that the MM3 radius for inorganic chlorine is 2.13 + 0.34 = 2.47 Å. The validity of this approximation is tested in the following section.

## 4 Return to the $Os(H)_2Cl_2(P^iPr_3)_2$ and $Ir(H)_2Cl(P^tBU_2\ Ph)_2$ systems

The geometry optimization of **1a** is repeated at the same IMOMM(BECKE3LYP:MM3) computational level mentioned above with an MM3 van der Waals radius of 2.47 Å for chlorine. The resulting value for the X-Osl-P2-Cl4 dihedral angle is 35.7°. This is substantially closer to the experimental value of 41.9° than the 27.2° obtained when the default radius of 2.07 Å was used, and much better than the 0.0° obtained in the pure ab initio calculation on the model system. This result proves in the first place that the steric effects in this molecule are primarily related to the chlorine atoms, as could indeed be expected [11]. More to the point of this work, it also proves that modification of the MM3 van der Waals radius in the form proposed in the previous section improves significantly agreement with the experiment.

The geometry optimization of **2a** is also repeated at the same IMOMM(BECKE3LYP:MM3) level with the modified van der Waals radius for chlorine. As a result, the symmetry of the two Cl—Ir—H bond angles is broken, with resulting values of 122.0° and 162.6°. Again, this is in much better agreement with experiment (131.1° and 156.2°) than the results obtained with the standard MM3 radius for chlorine (147.1° and 146.0°). In this case, however, the relationship of the increase in the steric effects of chlorine with the distortion is not so obvious. There is no van der Waals interaction between the chlorine and the hydride ligands. Furthermore, the direct interaction with a single chlorine atom could hardly break the equivalence between two hydride ligands in principle equivalent. The answer is in the steric interactions of chlorine with the phosphine ligands. The bulkier chlorine produces a larger repulsion with the phosphine ligands, as exemplified by the Cl—Ir—P angles. Their average is 89.4° in the BECKE3LYP calculation on model system **1b**, 89.4° in the IMOMM calculation with the standard van der Waals radius for chlorine, 92.3° in the IMOMM calculation with the corrected van der Waals radius for chlorine, and 93.8° in the X-ray structure. The introduction of the corrected van der Waals radius forces an increase of the Cl—Ir—P angle, pushing the phosphines towards the hydride ligands, and increasing the phosphine–hydride repulsions, which are direct responsible of the asymmetry of the complex [13].

Therefore, the use of a corrected van der Waals radius for chloride improves dramatically the agreement of IMOMM computed structures with experimental data. Finer tuning of the van der Waals radii for chloride and hydride and of the hardness of both elements would probably account for most of the remaining discrepancies.

## 5 Computational details

IMOMM calculations on systems **1** and **2** are performed with a program built from modified versions of two standard programs: GAUSSIAN 92/DFT [24] for the quantum mechanics part and MM3(92) [8] for the molecular mechanics part. Ab initio calculations use the BECKE3LYP method [12], with a valence double-$\zeta$ basis set [25] supplemented with a polarization *d* shell on P and Cl [25d]. The molecular mechanics part uses the MM3(92) force field [8]. Van der Waals parameters for osmium and iridium atoms are taken from the UFF force field [26], and torsional contributions involving dihedral angles with the metal atom in terminal position are set to zero. Geometry optimizations are full except for the P—H (1.42 Å) distances in the ab initio part and the P—$C_{sp^2}$ (1.843 Å), P—$C_{sp^3}$ (1.828 Å) distances in the MM part.

Calculations for the determination of the van der Waals radii on the NaCl···He and $CH_3Cl$···He systems were carried out with the GAUSSIAN 94 package [27] at the MP3 level [28] with a 6-311++G(3*d*, 3*p*) basis set [29].

## 6 Conclusions

MP3/6-311++G(3*d*, 3*p*) calculations on simple models with helium probes demonstrate that the van der Waals radius for organic, essentially neutral, chloro substituents, is significantly different from that of inorganic, essentially anionic, chloride ligands. Use of a corrected van der Waals radius for inorganic chlorine in the MM part of IMOMM(BECKE3LYP:MM3) calculations leads to significant improvements in the agreement with experimental X-ray structures for the $Os(H)_2Cl_2(P^iPr_3)_2$ and $Ir(H)_2Cl(P^tBu_2Ph)_2$ systems. Further development of specific parameters for the MM description of non-bonded interactions involving inorganic ligands appears as a major venue of improvement for the performance of the IMOMM method.

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