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The van der Waals Radius of Mercury

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It has long been recognized that the coordiation sphere of Hg(II) usually contains both close and distant bonded atoms [1]. This was given more precise definition by Grdenić [2], who formulated dual coordination behaviour for mercury, *viz.* characteristic coordination where the mercury–donor atom bond distance is near the sum of the appropriate covalent radii, and effective coordination where the mercury–donor atom distance is within the sum of the van der Waals radii. Thus, one of the most common situations is characteristic two coordination and effective six coordination giving distorted octahedral stereochemistry [2]. This approach has generally been followed in subsequent interpretations of crystal structures of mercury derivatives [*e.g.* 3, 4]. In deciding the effective coordination number, the value of the van der Waals radius of mercury is of crucial importance. On the basis of mercury··· mercury distances in metallic mercury (3.000 and 3.466 Å), Grdenić proposed 1.50 Å as the van der Waals radius, but also suggested that distances less than 1.73 Å plus the van der Waals radius of the potential donor atom are indicative of some form of bonding [2]. A value of 1.55 Å has been estimated from the critical volume of the metal [5], and 1.75 Å has been suggested from Hg···Hg contacts in $(Et_4N)_2Hg_3MCl_{10}$ (M = Pt or Pd) [6]. Generally, Grdenić [7] and most other workers [*e.g.* 4, 8] have stressed 1.50 Å in assessing the coordination number of mercury (for noteworthy recent exceptions see [9, 10]). Mainly from consideration of recent crystallographic data we now propose that 1.73 Å be taken as the van der Waals radius of mercury and that the value may be higher in some cases.

Initially, the close similarity between the van der Waals radius of 1.50 Å and the tetrahedral covalent radius of mercury (1.48 Å) [2] suggested to us that the former is too low. Moreover, even if the Pauling generalisation [11] that the van der Waals radius is ca. 0.80 Å plus the single bond covalent radius (giving 2.1–2.3 Å for mercury) is not *strictly* applicable to a heavy metal, it certainly points to a value higher than 1.50 Å for mercury. This view is reinforced by the value (1.71–1.76 Å) proposed [12, 13] for the intramolecular non-bonded atomic radius of mercury. Further evidence comes from consideration of Hg···Hg, Hg···aromatic ring, and Hg···other ligand distances.

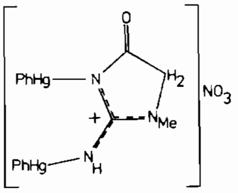
1. Mercury···Mercury Contacts

Between Mercury Atoms Bound to the Same Atom

An intramolecular non-bonded atomic radius of 1.76 Å was proposed [12] for mercury on the basis of structures containing $(XHg)_nY$ (n = 2 or 3) moieties, *e.g.* $(ClHg)_3O^+Cl^-$. This has been subsequently revised [13] to 1.71 Å on consideration of the structure of $(MeCO)_2C(HgCl)_2$, and now needs to be lowered to 1.64 Å in the light of Hg··· Hg distances (3.280(4)–3.398(3) Å) in $C(HgCN)_4$ [14]. This value is definitely too small for a van der Waals radius, since the distance between two atoms bound to the same atom can be significantly less than the sum of the van der Waals radii [11], *e.g.* the Cl···Cl distance in CCl_4 (2.87 Å) is much shorter than the van der Waals sum (3.6 Å) [11]. Pauling concluded that the non-bonded radius in directions close to the bonded direction is *ca.* 0.5 Å less than the van der Waals radius [11]. Accordingly, when compared with a minimum intramolecular nonbonded radius of 1.64 Å, a van der Waals radius of *at least* 1.75–1.80 Å is readily justifiable.

Other Inter- and Intra-molecular Hg···Hg Contacts

In $(Et_4N)_2Hg_3MCl_{10}$ (M = Pt or Pd), the closest non-bonded intermolecular contacts (3.51(1) and 3.48(1) Å respectively) are indicative of a van der Waals radius of 1.75 Å [6]. The structure of A has a non-bonding Hg···Hg contact of 3.407(2) Å [15]. Although this is consistent with a van der Waals radius of 1.70 Å, the Hg···Hg distance may be less than the van der Waals diameter because the geometry is constrained by the structure of the planar guanidinium moiety.



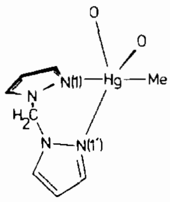
A

2. Mercury···Aromatic Ring Contacts

The shortest mercury···aromatic ring distances in $CoHg_2(SCN)_6 \cdot C_6H_6$ [16] and $HgCl_2(Ph_2SO)_2$ [17] (3.52 and 3.51(1) Å respectively) may involve [16, 17] very weak π interactions between the rings and mercury. Any such interactions must be close to the bonding limit, and can reasonably be considered van der Waals contacts. Subtraction of the van der Waals radius of a benzene ring [11] from the mercury··· ring distance gives a radius of 1.80 Å for mercury. In cases where significant mercury···aromatic ring bonding occurs, *e.g.* in $p\text{-}MeOC_6H_4CH_2CMe(OMe)\text{-}CH_2HgCl$ [18], $p\text{-}HOC_6H_4CH_2CH(CO_2^-)^+NH_2HgMe$ [19], and $MeHg(2\text{-benzylpyridine})NO_3$ [20], the mercury···ring distances are somewhat shorter 3.05–3.33 Å).

3. Other Significant Systems

In the coordination sphere (B) of the bis(pyrazolyl)methane complex of methylmercuric nitrate,



B

the Hg–N(1′) contact [2.96(2) Å] is definitely bonding [21], but is equal to the sum of the van der Waals radius of nitrogen [11] and the radius of 1.50 Å for mercury, indicating the latter value is significantly underestimated. Even more striking is the case of phenyl(quinolin-8-olato)mercury(II), in which the molecules are stacked in columns (from methanol) or have a helical array (from carbon tetrachloride) [22]. There is clear evidence for partial dimerization in benzene and carbon tetrachloride implying intermolecular association in the solid state [23], in which the shortest intermolecular Hg···O contacts (3.3–3.4 Å) link the molecules into columns or helices [22]. Taking these as bonding, a van der Waals radius of 1.9–2.0 Å is indicated. In phenyl mercury(II) dithizonate there is an Hg···S intermolecular contact of 3.69 Å [24], which is 0.34 Å longer than the sum of the van der Waals radii of sulphur [11] and mercury (taken as 1.50 Å), and which nevertheless is considered to be a weak secondary interaction [24]. If this interaction is meaningful (and a molecular weight in solution might be revealing), it implies a van der Waals radius of at least 1.85 Å.

Conclusion

The foregoing structures (Sections 1–3) provide definite evidence that the van der Waals radius of mercury is in the range 1.7–2.0 Å. Apart from variations with direction (Section 1), some imprecision is to be expected with an empirically derived value and there may indeed be slight variations between compounds. Accordingly, a general value for the radius should lie at the conservative end of the range, hence 1.73 Å, conveniently corresponding to Grdenić's largely neglected upper limit for any form of bonding* [2], is proposed. Interestingly, the mercury–ligand bonding in two recent structures [9, 10] was interpreted using a radius of 1.73 Å, not 1.50 Å, *e.g.* a Hg···Br contact of 3.548(4) Å (*cf.* 3.45 Å for the bonding limit using 1.50 Å) was considered to be within the coordination sphere [10]. Because of the relationship between the general radius now proposed (1.73 Å) and the possible range (1.70–2.00 Å), some significant interactions at distances corresponding to a slightly larger radius cannot be excluded.

These conclusions have implications for interpretaion of some previoulsy reported structures, in that a number of contacts previously on the possible bonding borderline should now be viewed as significant interactions. For example, the crystal structure of $[(C_6F_5)_2HgAsPh_2]_2CH_2$ has a long Hg···As contact of 3.40(5) Å [CHgC angle 173(1.4)°] [25, 26], which is just within the former van der Waals radius sum. Some doubt has been expressed as to whether this is a bonding interaction [26], but with the new mercury van der Waals radius coordination of arsenic to give a T-shape arrangement is assured. Thus, this complex provides an example of the T-shape stereochemistry expected for weak interaction of a single donor atom with a diorganomercurial.

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*Surely consistent with the concept of a van der Waals radius.

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