**d Orbitals in s-Block Chemistry**

The question of whether d orbitals have any rôle in bonding in p-block element compounds, particularly in those compounds which are often described as hypervalent, is covered in Chapters 6 and 8 on pages 110-111 and 133-135, and a summary of the history of this topic can be found in ref. 1. It may be that vacant 7d orbitals turn out to be important in the chemistry of the 7p elements such as Flerovium and Moscovium mentioned on page 62, but this addendum will highlight some recent (2021) studies which have proposed that d orbitals are involved in the bonding in certain compounds of the heavier s-block elements.

As noted on page 124, s-d hybridisation has been advanced as one possible explanation to account for the bent geometries of species such as BaF2 in the gas phase, as well as in metallocenes such as [Ba(h-C5Me5)2]. In the former example, the F–Ba–F angle has been determined to be about 110˚,2 whilst in the latter, the angle at barium between the two barium to ring centroid vectors is 131˚ in the solid state [148(6)˚ in the gas phase].3,4



The involvement of d orbitals in bonding has also been proposed, based on computational studies, for the species CsN7Ba, in which the barium centre is bonded to a planar N7 ring, and also in the experimentally observed gas phase ion [Ba(CO)]+. More recently (2021), however, the carbonyl complexes [M(CO)8] (M = Ca, Sr, Ba) have been prepared and characterised spectroscopically in low temperature solid matrices and shown to adopt cubic geometries of O*h* symmetry.5 All three of these Group 2 element complexes exhibit CO stretching vibrations typical of transition metal carbonyls in which there is significant p back-donation from filled metal d orbitals into the CO p\* orbitals and this same bonding model for the Group 2 complexes is supported by detailed quantum chemical calculations. Specifically, the calculations are in accord with a model in which the Group 2 element adopts a valence state electronic configuration of (*n*–1)d2*n*s0*n*p0 in which the electrons of the CO ligands donate into vacant s, p and d orbitals accompanied by back-donation of the M d2 pair into the CO p\* orbitals. It should be noted, however, that others have challenged this interpretation and argue for a more ionic description which can be represented as M2+[(CO)8]2– all of which is covered and considered in detail in ref. 5 and refs. therein.



As an aside, it is interesting to note that these Group 2 complexes [M(CO)8] (M = Ca, Sr, Ba) are isostructural with the Group 4 species [M(CO)8] (M = Zr, Hf) which at first sight appear to be 20-electron compounds (4 electrons from the Group 4 element and 8 x 2 from the 8 CO ligands). In fact, a ligand combination of a*2u* symmetry finds no symmetry match on the metal so the total electron count at the Group 4 element centre is only 18. Likewise, the apparently 18-electron count for the Group 2 examples is reduced to 16 for the same symmetry reasons, the two highest energy electrons occupying a degenerate pair of orbitals of e*g* symmetry thus rendering these Group 2 compounds paramagnetic with a triplet ground state.

Other matrix-isolated compounds of a similar nature have also been prepared including the homoleptic dinitrogen and benzene complexes [M(N2)8] and [M(h6-C6H6)3] (M = Ca, Sr, Ba) in which similar back-bonding involving metal d orbitals is invoked.5 Indeed, it has even been argued that the extent of d orbital involvement for calcium, strontium and barium (and likely radium) is sufficient to warrant these elements being granted the status of transition elements following the earlier description of both barium and caesium as ‘honorary d elements’ in the paper which described the study on CsN7Ba noted above.6 Whether or not periodic tables are amended to accommodate this suggestion remains to be seen but as discussed on pages 19-20, the precise format of a proposed periodic table depends on what particular properties that table has been constructed to illustrate.

In conclusion, as the authors of some of the studies highlighted here have suggested,5 d orbital involvement in s-block element chemistry is of more than purely academic interest since some of the newly discovered chemistry of these elements, particularly involving catalysis, has parallels with d-block element chemistry.

***References***

1. *Hypervalence: A Useful Concept or One That Should Be Gracefully Retired?* N. C. Norman and P. G. Pringle, *Chemistry*, 2022, **4**, 1226-1249.

2. The experimental uncertainty is likely due to the computed very low-energy bending potential of the F–Ba–F angle but the molecule is certainly not linear as would be expected based on VSEPR arguments.

3. The explanations for these bent geometries outlined on page 124 are the s-d hybridisation and ionic or core polarization models. Kaupp argues in ref. 4 that a complete explanation likely involves some admixture of both. A third possible explanation in the case of bent metallocenes such as [Ba(h-C5Me5)2] centres on a van der Waals attraction between the C5Me5 ligands, see: *Why are Bis(pentamethylcyclopentadienyl) Complexes, [MCp\*2], of Calcium, Strontium, Barium, Samarium, Europium and Ytterbium Bent?* T. K. Hollis, J. K. Burdett and B. Bosnich, *Organometallics*, 1993, **12**, 3385-3386.

4. *“Non-VSEPR” Structures and Bonding in d0 Systems*. M. Kaupp, *Angew. Chem. Int. Ed*., 2001, **40**, 3534-3565.

5. See, *Transition-Metal Chemistry of the Heavier Alkaline Earth Atoms, Ca, Sr, and Ba*. M. Zhou and G. Frenking, *Acc. Chem. Res*., 2021, **54**, 3071-3082 and refs. therein.

6. *Cesium and Barium as Honorary d Elements: CsN7Ba as an Example*. L. Gagliardi and P. Pyykko, *Theor. Chem. Acc*., 2003, **110**, 205-210.