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Opinion

What is supramolecular?

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The popular adjective 'supramolecular' has conflicting meanings in the current literature. It can mean intermolecular, as originally intended, which specifies weak and long interactions. It commonly describes elaborate coordination chemistry, which involves strong and short intramolecular interactions. Supramolecular chemistry is also a philosophy and strategy for the controlled assembly of complex matter. In my opinion we should re-establish terminology that embodies the integrity of fundamental chemical principles, describing intermolecular interactions as such, coordination chemistry as such, and restrict use of the adjective 'supramolecular' to the philosophies and strategies of grand assembly.

The adjective 'supramolecular', immensely popular in the current literature of chemistry, can be traced back at least to 1925.[1] The meaning of 'supramolecular' is 'beyond the molecule', and early uses reflected this, describing the interactions between macromolecules,[2] and the organization of enzyme and membrane systems.[3]

The 'extramolecular' interactions involved in this supramolecular chemistry are the same as intermolecular interactions, which also have a long scientific history. Intermolecular interactions are weak and long relative to intramolecular interactions: specifically, intermolecular energies are normally $< 10\%$ of corresponding bond energies, and interatomic contact distances between molecules are about double the corresponding bond distances. The contrast and distinction between weak and long intermolecular interactions and strong and short intramolecular bonds is unambiguous for almost all types of molecules.[4]

In the mid 1960s, research on macrocyclic and macropolycyclic ligands and their variable and controllable association with metals in solution, initiated a link between coordination chemistry and supramolecular chemistry. This supramolecular coordination chemistry developed slowly, but has flourished: now all of the major journals are replete with reports of quite sophisticated coordination chemistry involving elaborate ligands and multiple metals, and this chemistry is almost invariably labelled as supramolecular chemistry.

But, the metal ligand interaction — the core of coordination chemistry—is not weak and long, but *strong and short*. The shortness is obvious, with M–L bond distances normally in the range 1.8 to 2.5 Å, depending on M and L.[5] M–L bond energy data are less abundant, and diverse: some representative mean bond energies are 170–250 kJ mol^{-1} for M–O in acetylacetonate complexes,[6] 160–290 kJ mol^{-1} for Pd/Pt–N/P/Cl in amine and phosphine complexes L_2MCl_2,[7] 180–230 kJ mol^{-1} for M–S in complexes of $^{-}S_2CNEt_2$,[6] 139 kJ mol^{-1} for Ag^+–OH_2,[8] 216 kJ mol^{-1} for H_3NCu^+–NH_3,[8] and 517 kJ mol^{-1} for Zr–O in $Zr(OPr^i)_4$.[9] These are well beyond the magnitudes of normal intermolecular interactions.

So, 'supramolecular' appears to have two conflicting meanings. It can intend to describe the weak long interactions between molecules, or it can refer to the short strong bonds between metals and ligands. In current usage 'supramolecular' can mean either 'extramolecular' or 'intramolecular'. Occasionally, although rarely, 'supramolecular' is applied to both intra- and extra-molecular aspects of the one chemical system.

This dichotomy is unfortunate. The adjective is indefinite, and our language is diminished.

Another confusion exists in current terminology. There is now common usage of the descriptor 'non-covalent interactions', apparently in many cases to encompass intermolecular interactions and the ligation of metal ions, that is the two parts of 'supramolecular' chemistry. This use of 'non-covalent' to describe interactions is unhelpful because it mixes interactions that are energetically different.[10] Further, the covalency of M–L bonds[11] is substantial and often quite large. This misrepresentation of M–L bonds probably arises in an assumption that the usually fast M–L exchange processes imply bond weakness: this is confusion of chemical kinetics and thermodynamics. In my opinion, use of the phrase 'non-covalent interactions' to invoke supramolecular effects is unfortunate because it is negative, of dubious validity in some cases, and mixes low- and high-energy phenomena.

A grander view of supramolecular chemistry, expounded eloquently by Lehn,[12] focuses on the controlled assembly of multiple chemical components. The assembly can involve standard intermolecular interactions, and/or metal coordination. Historically and logically this follows from the notion that metal ligation equilibria and intermolecular recognition processes are kinetically fast. For multi-component assembly to be feasible, timely, and controlled, exchanges of individual entities must be rapid in order to achieve the required thermodynamic control of the system. One broad goal is to have the ability to mimic the structure and the function of the magnificent assemblies of molecular biology, and to generate complex clever matter: the assembly of so many components to reproduce the equilibrium array requires sampling of innumerable possibilities in fluid media, which is possible only if individual processes are extremely fast.

So, 'supramolecular' currently has three different meanings:

(a) intermolecular interactions;
(b) applied coordination chemistry;
(c) a strategy of controlled organisation of multiple separate components.

There are fundamental chemical differences between (a) and (b), and (c) includes (a) or (b) or both. I think our language should recognise and disentangle this confusion, because fundamental chemical concepts of bonding, energy and dynamics are in danger of being compromised.

To re-establish meaning we can use 'intermolecular' as the adjective for the well-known weak and long interactions between molecules, and we can describe elaborate coordination

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complexes and polymers simply, clearly, and unambiguously with the terminology of coordination chemistry. We can restrict use of the adjective 'supramolecular' to the philosophies and strategies of grand assembly.

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