

Marvellous Molecular Shapes

Santiago Alvarez

Departament de Química Inorgànica and Institut de Química Teòrica i Computacional

Universitat de Barcelona

Martí i Franquès 1-11, 08028 Barcelona, Spain

Dedicated to Michel Verdaguer

Abstract

A survey of a variety of interesting molecular shapes characterized mostly in the last two decades is presented. The selection of molecules shown is made based on their attractive three-dimensional structures (so often concealed by their usual two-dimensional structural formulae), the unusual coordination geometries of metal atoms, the subjective appreciation of how beautiful, funny or interesting a molecular shape is, or the sticky nature of arene rings at terphenyl groups and their effects on the molecular shapes of metal complexes.

Introduction

In an inspired essay, Roald Hoffmann reflected on how chemists perceive "molecular beauty".¹ According to Hoffmann, beauty may arise from novelty, epitomized at the time by metal clusters containing six-coordinated carbon atoms. Beauty may also be associated to molecular shape, and some examples given by him are "simple, symmetrical and devilishly hard to make", but other forms of molecular beauty have to do with the perception of the chemist of what is unique about its composition, structure or bonding. Finally, what we may consider beautiful is the way a molecule behaves in front of some external stimulus, as exemplified by haemoglobin, a porphyrin-bearing protein that experiences important changes in response to the binding of oxygen.

In this paper, I wish to present more recent examples of beautiful molecules. In some of them I find beauty in the way they surprise us by adopting a structure in space that is hard to anticipate from a structural scheme. Conversely, in some cases it is the two-dimensional scheme of a molecule that excites our imagination. The choice of structures to be discussed is completely subjective, based on my perception of what is interesting, beautiful, or just funny in the molecular shapes displayed by them.

Deceiving structural drawings

An example of how a structural drawing may give us a poor information of a remarkable three-dimensional molecule is provided by hexadecaphenyl-dodecabenzene.² Although it is drawn on paper as a square molecule (Figure 1a), its structure in space is that of a tetrahedron such that chains of four phenyl groups occupy four out of the six edges of the tetrahedron (Figure 1b). Continuous shape measures³ of the centres of the four phenyl groups at the corners indicate a nearly perfect tetrahedron, with just a slight (9%) distortion toward a square. The shapes of the 2D scheme and the real molecular structure can hardly be more different!

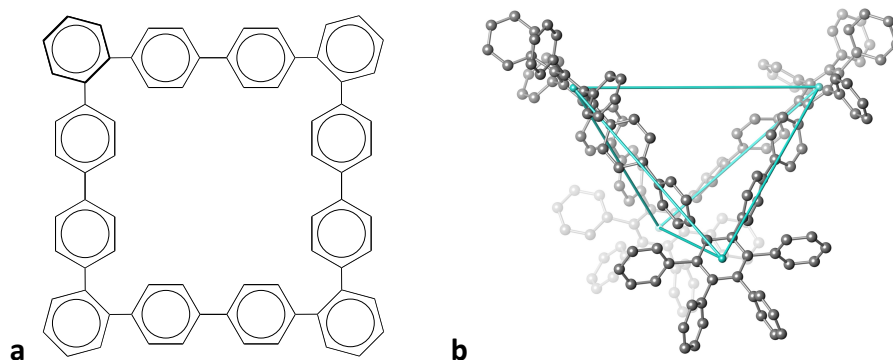


Figure 1. Schematic drawing of a dodecabenzene skeleton (a) and its three-dimensional tetrahedral structure (b).

To the variety of molecules that have the shape of daily live objects,⁴ I choose two cases that also stress the inability of two-dimensional schemes to suggest their three dimensional structures. Both are fully aromatic molecules composed of fused phenyl rings around a central five- or seven-member ring (Figures 2a and 2b, respectively), that look quite similar when represented as a 2D scheme. However, their three-dimensional structures are non-planar and very different: while the former has the shape (Figure 2c) of a bowl⁵ –and is often referred to as a "buckybowl"–, the latter is non planar as well, but bent in such a way as to form a sawhorse⁶ (Figure 2d).

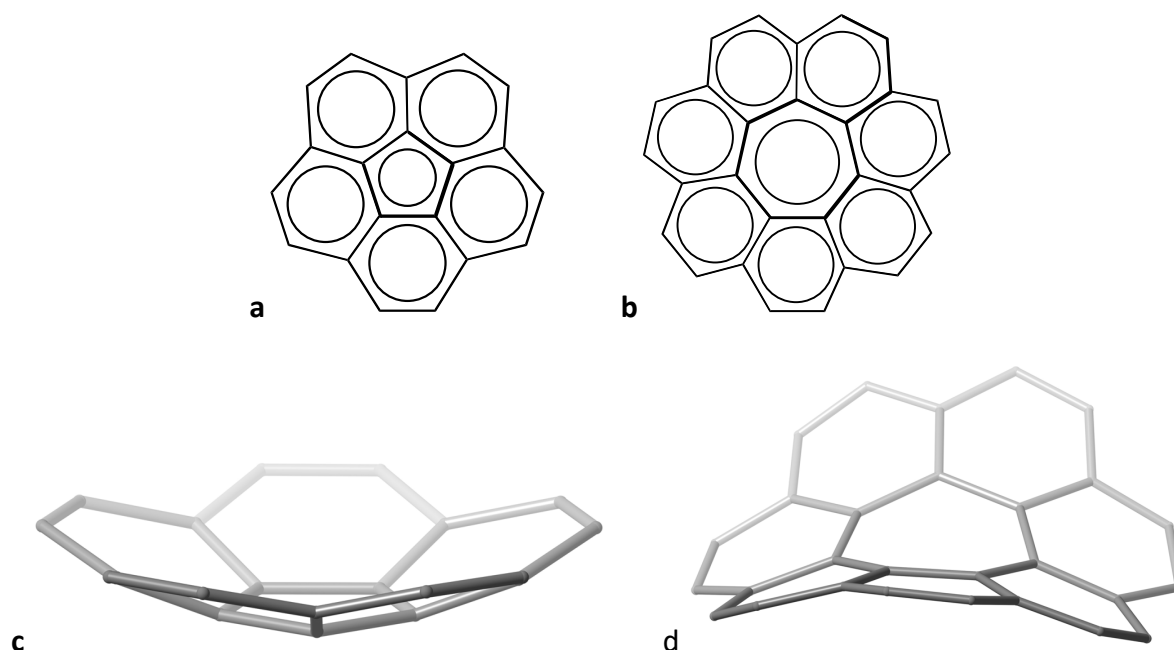


Figure 2. Two-dimensional representation of corannulene (a) and [7]circulene (b), and their three-dimensional structures (c and d, respectively).

Impossible structural drawings

When we try to draw a sequence of fused phenyl rings everything seems to work right for up to five rings (Figure 3a). However, our drawing suggests a planar molecule, far from what we find in its crystal structure,⁷ that shows a helical geometry in keeping with its name "pentahelicene" (Figure 3b). If we wish to add one more phenyl ring, with all the rings being regular hexagons, we end up (Figure 3c) with a representation of coronene, $C_{24}H_{12}$, instead of hexahelicene, $C_{26}H_{16}$. To

make a two-dimensional representation of the latter, we must make use of irregular hexagons (e.g., Figure 3d), but we still misrepresent the helical shape of the molecule. The situation worsens as we go to higher helicenes, requiring highly distorted hexagons. An alternative is to use hexagons of increasing size, in order to avoid the rings to overlap and additionally providing some sense of perspective that transmits better the idea of helicity, as shown in Figure 3e for heptahelicene. But, regardless of how we represent them in two dimensions, the 3D structures of the helicenes look highly attractive and reminiscent of the spiral staircase of the entrance Hall of the Louvre museum, as illustrated by undecahelicene⁸ and hexadecahelicene⁹ (Figure 4).

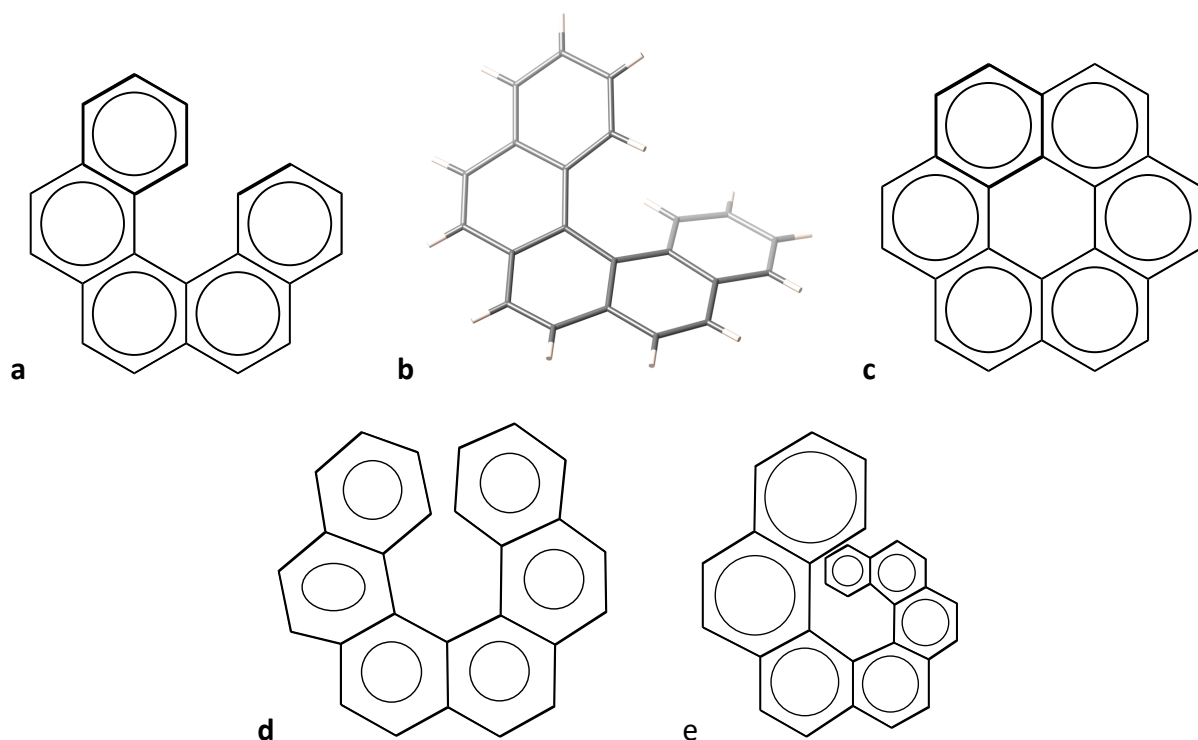


Figure 3. Two-dimensional representation of pentahelicene (**a**) and its 3D molecular structure (**b**), an arrangement of six regular hexagons that corresponds to the formula of coronene (**c**), a set of six distorted hexagons representing the molecular formula of hexahelicene (**d**), and fused six-member rings of different sizes that give some sense of the helical nature of heptahelicene (**e**).

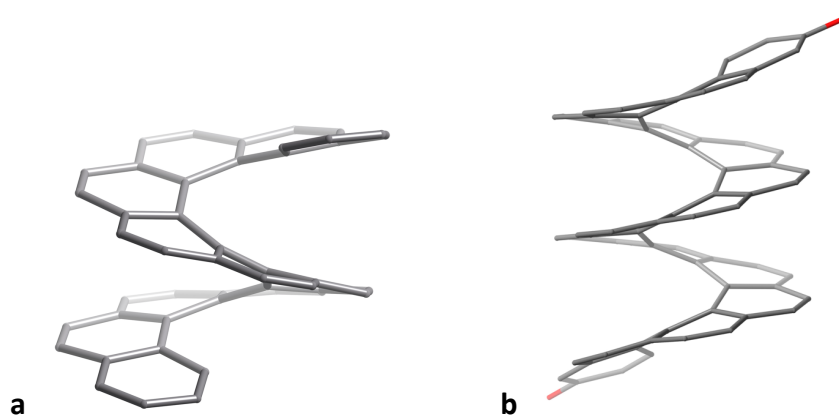


Figure 4. Helical structures of the skeletons of undecahelicene (**a**) and 3,34-bis(triisopropylsilyloxy)hexadecahelicene (**b**, the two terminal triisopropylsilyl groups are omitted for clarity).

Unusual coordination geometries

In the past years we have extensively studied polyhedral molecular structures and their symmetry properties.¹⁰⁻¹⁴ A number of supposedly uncoordinated or monocoordinated transition metal compounds were also recently analysed and showed the existence of hidden beautiful molecular shapes.¹⁵ But the ability of chemists to design and synthesize molecules with new shapes gives me the opportunity to call the attention to some interesting new polyhedral shapes.

The coordination of a cyclodimethylsiloxane with an O₆ donor set to a Ag(I) ion¹⁶ produced a complex with three short Ag-O distances of about 2.42 Å, which would correspond to a canonical trigonal planar coordination of a d¹⁰ ion, but the three remaining oxygen atoms are held at not much longer distances of about 2.67 Å, thus making this molecule a reasonable example of an unusual hexagonal planar coordination of a metal ion (Figure 5a). In a related compound the counter ion establishes a coordination bond to Ag at an axial position, thereby forming an also unusual hexagonal pyramidal coordination. A similar situation can be found¹⁷ with the 18-crown-6 ligand that, together with an oxygen atom of the triflate counter ion, forms an apparent heptacoordination around a silver(I) ion, in a rather distorted hexagonal pyramid (Figure 5b).

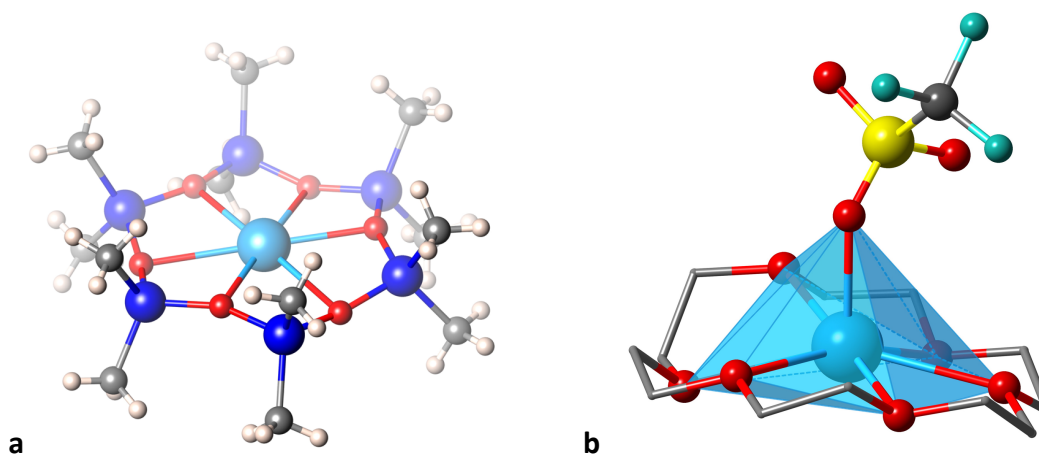


Figure 5. Two cyclic ligands with O₆ donor sets that favour apparent hexagonal planar (a) and hexagonal pyramidal (b) coordinations to silver (I) ions.

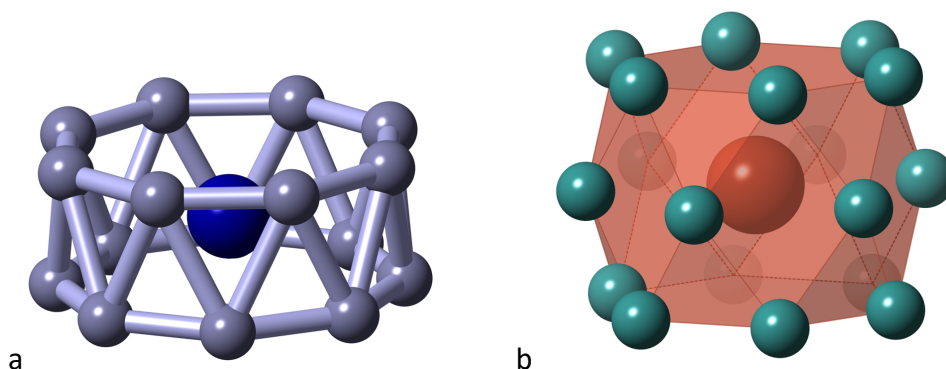


Figure 6. Two drums with very high coordination numbers: the CoB₁₆⁻ anion (a) and the LaNi₁₈ group in LaNi₅ (b).

Very high coordination numbers are rare, but once they are achieved, some unexpected coordination polyhedra can be found, such as the octagonal antiprism "drum" of the CoB₁₆⁻ cluster¹⁸ (Figure 6a), or the hexacapped hexagonal prism of the LaNi₁₈ group (Figure 6b) in the

solid state structure of LaNi_5 ,¹⁹ with the so-called CaCu_5 structure found in hundreds of binary intermetallic compounds.

An attractive double decker sandwich structure (Figure 7) combines three slices of "bread", the outer ones formed by two different porphyrin, the inner one by a phthalocyanine ring.²⁰ The metal ions sandwiched by these rings are Ce(III) and Gd(III) . While both metal ions are octacoordinated, Ce is in a cubic environment and Gd in a square antiprismatic one and both polyhedra share a square face.

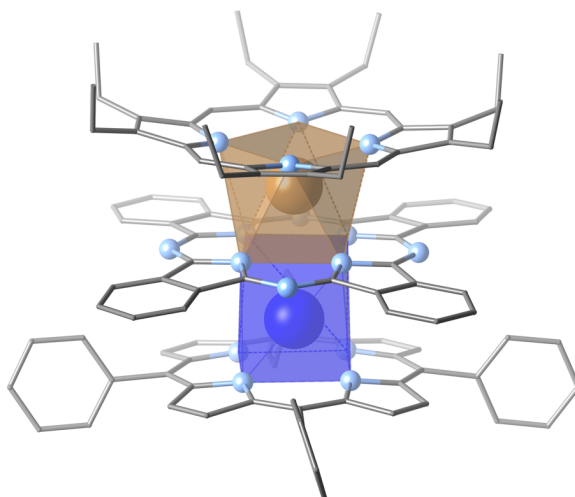


Figure 7. A Gd and Ce double decker sandwich complex with a square antiprismatic and a cubic coordination spheres, respectively, that share a square face.

Stars and planets of several sorts

Some molecules may remind us of planets and stars. For instance, a ring made up of 11 phenyl rings surrounding a C_{70} fullerene,²¹ resembles the planet Saturn (Figure 8a) with its planetary rings. And simple molecules, such as the XeF_5^- anion²² or the well-known tetramethylsilane, SiMe_4 ,²³ appropriately coloured, look like shining stars (Figures 8b and 8c, respectively).

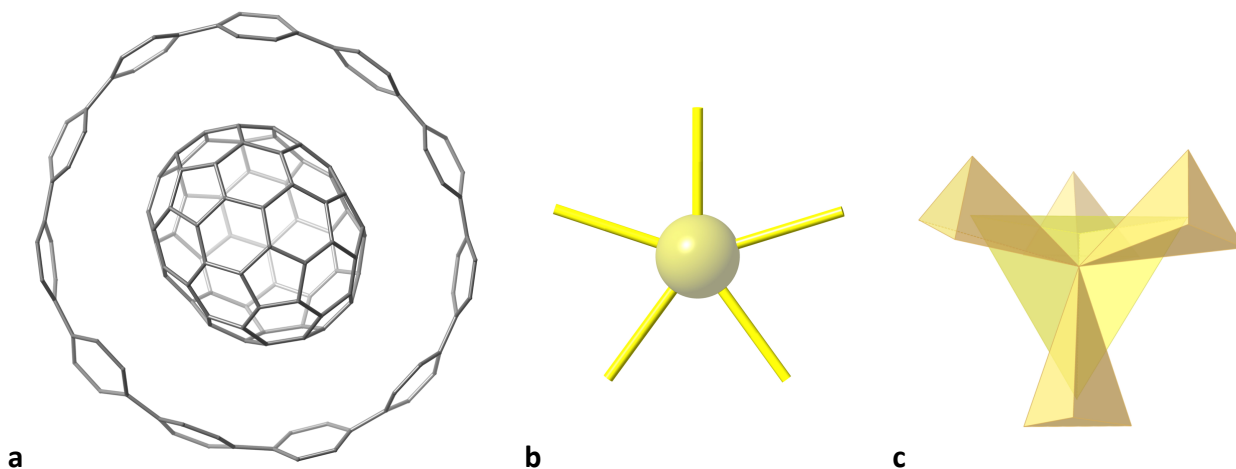


Figure 8. A ring made up of 11 phenyl rings encircling a C_{70} fullerene that reminds the planet Saturn (a), a XeF_5^- star (b), and the tetramethylsilane molecule (c).

Some time ago Michel Verdaguer suggested me the analogy between the representation made by artist Joan Miró of stars, be them six- or eight-pointed, and the way coordination chemists schematically draw an octahedron. Some reflections on representation in art and chemistry, based on the discussions we had, can be found in a recent book,²⁴ where an outstanding heptanuclear compound²⁵ created by the Jussieu group illustrates a sort of constellation is formed by a central star surrounded by six more six-pointed stars (Figure 9). It corresponds in fact to a central chromium atom connected via cyanide bridges to six nickel atoms.

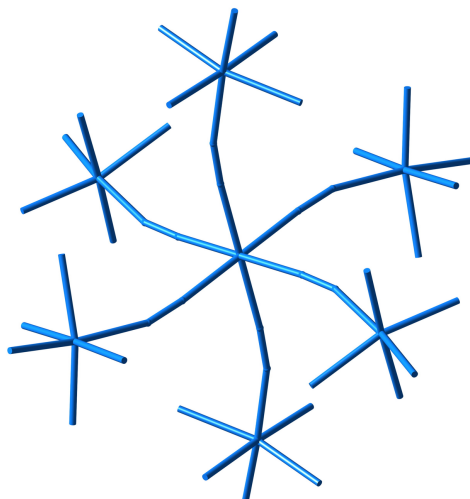


Figure 9. A cyano-bridged heptanuclear CrNi₆ complex as a constellation of six-pointed stars.

Molecules that are just beautiful, funny or curious

Let me show here two examples of polyhedra surrounded by planar ring. One is a Pd₁₃ centred cuboctahedron with its square faces covered by C₇H₇⁺ tropylium ions whose centers form an octahedron²⁶ (Figure 10a). Related structures showcase a tetrahedron of tropylium ions, each on top of a vertex of a tetrahedral Mo₄ cluster.²⁷ In contrast, with the larger COT (C₈H₈²⁻) ligands one can get at most four tetrahedrally arranged rings around the titanium atoms of a Ti₄Cl₄ cubane (Figure 10b).²⁸

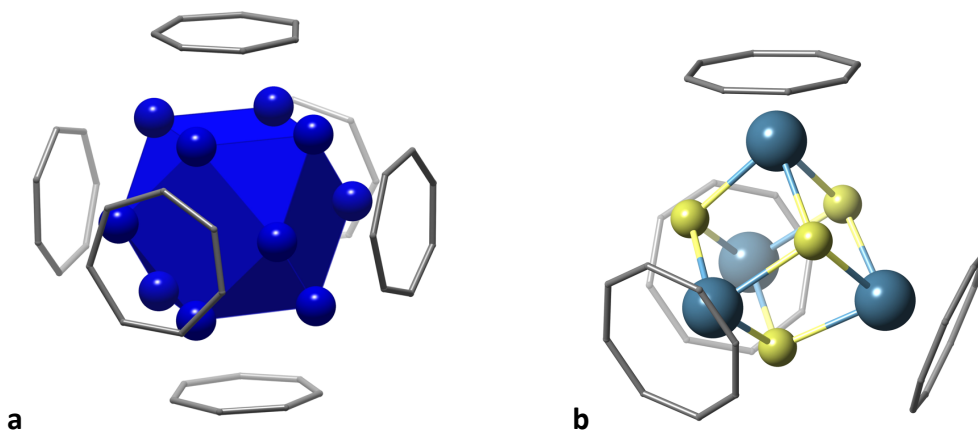


Figure 10. Large aromatic rings covering metal clusters: (a) tropylium ions on a Pd₁₃ cluster, (b) COT²⁻ anions on a Ti₄Cl₄ cubane.

Some molecules that are highly interesting for their architecture and bonding, can also be associated with funny or curious shapes. Let us see three examples. The extensive double bond systems of two β -carotene molecules, which is responsible for the orange colour of carrots, have been coordinated to a Pd_{10}^{2+} chain,²⁹ altogether presenting the aspect of a hot-dog sandwich (Figure 11a). A hamburger sandwich, on the other hand, has a molecular representation in the $\text{Pd}_4(\text{COT})_2^+$ cation³⁰ (Figure 11b).

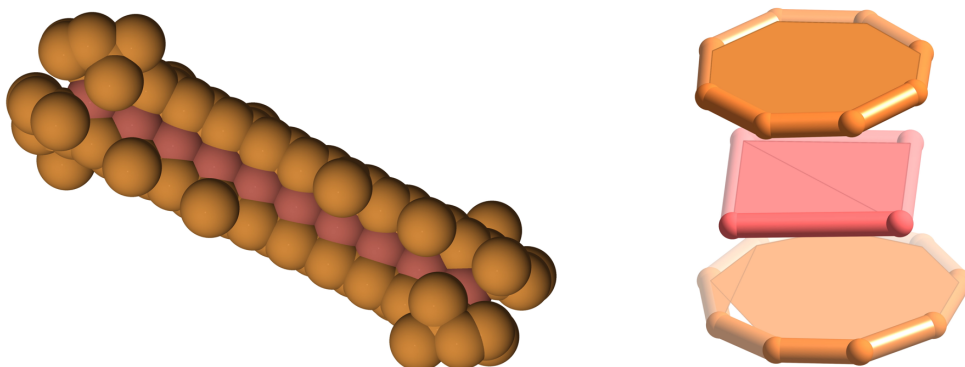


Figure 11. Two molecular sandwiches: a hot-dog sandwich (a) and a hamburger sandwich (b) in which the meat is made of palladium atoms.

Our third example is an organometallic gold(I) complex coordinated by two cyclopropenyl groups.³¹ The $\text{N}(\text{iPr})_2$ groups hanging from the cyclopropenyl rings makes the ligands look like two frogs, and they face each other to kiss at the metal atom, indeed a golden kiss (Figure 12).

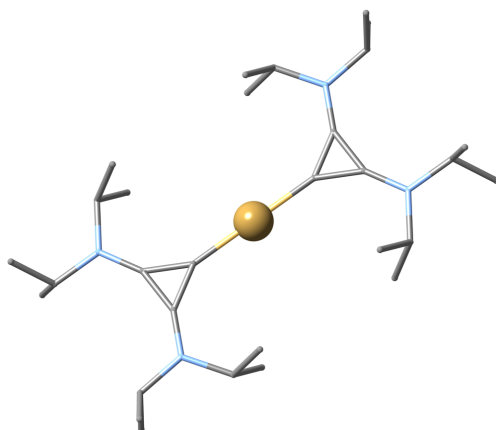


Figure 12. A bis(cyclopropenyl)gold(I) complex representing two kissing frogs.

Sticky arene rings

One of the design tools extensively developed in the last years has been the use of terphenyl groups forming a metal-carbon bond to the central ring, in such a way that the flanking arenes provide steric protection to the metal, enhanced by substituents R and R' that are commonly Me, iPr or tBu (Figure 13a). A relevant success of this strategy is showcased by the first synthesis of a quintuple bond, between two chromium atoms, obtained by Power and coworkers,³² subtended by only two such terphenyl groups (Scheme in Figure 13b and Crystal Structure in Figure 14). While initially the role of the flanking arene rings was assumed to be only to provide steric protection, it is now clear that besides preventing the approach of further ligands to the metal

centre, they are actually π -coordinated to a metal atom in both quadruple Mo-Mo and quintuple Cr-Cr bonds,^{33,34} a phenomenon often referred to as "secondary interactions".

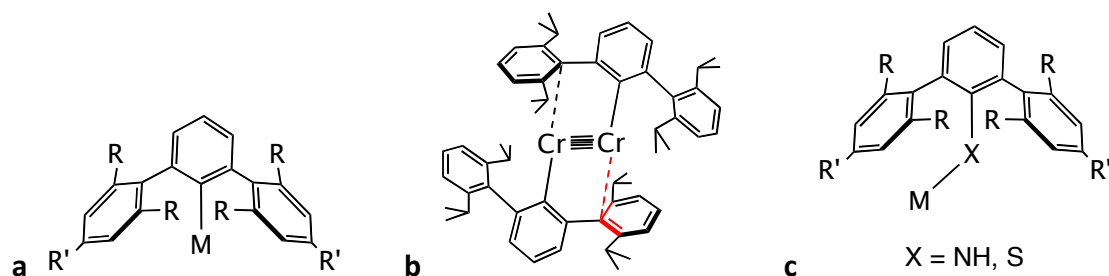


Figure 13. Ligands with a terphenyl group that form a carbon-metal bond to a single metal centre (**a**) or to a multiply bonded metal (**b**), and related amido- and thiolato-terphenyl ligands (**c**).

Table. Geometry of the MX_2 core of bis(terphenylthiolato) and bis(terphenylamido) ($\text{X} = \text{S}$ and NH , respectively) complexes and hapticity of the flanking arene rings, together with the ranges of close interatomic $\text{M}\cdots\text{C}$ distances.

	M	R	R'	X-M-X (°)	hapticity	$\text{M}\cdots\text{C}$ (Å)	Σcov^\dagger	refcode	ref.
X = S									
a	Cr	iPr	iPr	180	2 x 1	2.50	2.15	jarjoc	35
a	Mn	iPr	iPr	180	2 x 3	2.95 - 3.33	2.37	jarjui	35
a	Co	iPr	iPr	180	2 x 1	2.66	2.26	jarket	35
a	Ni	iPr	iPr	174	2 x 1	2.64 - 2.66	2.00	jarkix	35
a	Zn	iPr	iPr	180	2 x 1	2.80	1.98	jarkod	35
a	Zn	iPr	H	180	2 x 3	2.96 - 3.28	1.98	lextoa	36
b	Fe	Me	H	117	2 x 2	2.46 - 2.92	2.28	vilhuu	37
b	Fe	Me	Me	122	2 x 3	2.47 - 2.87	2.28	piyzec	38
b	Zn	Me	Me	152	2 x 3	2.65 - 3.06	1.98	ligbae	39
c	Fe	iPr	H	120	1 x 6	2.48 - 2.61	2.28	lexsuf	36
c	Co	iPr	H	92	1 x 6	2.08 - 2.19	2.26	lextam	36
c	Ni	Me	Me	95	1 x 6	2.07 - 2.30	2.00	foqxix	40
X = NH									
a	Cr	iPr	H	180	2 x 1	2.63	2.15	sebjib	41
a	Cr	iPr	iPr	180	2 x 1	2.48	2.15	sebjex	41
a	Fe	iPr	iPr	180	2 x 2	2.79 - 2.94	2.28	wulweg	42
b	Co	Me	Me	144	2 x 1	2.56 - 2.57	2.26	sebwih	41
b	Ni	Me	Me	155	2 x 1	2.56 - 2.57	2.00	sebwon	41
b	Mn	Me	Me	138	2, 3	2.60 - 2.87	2.37	wugcad	43
b	Fe	Me	Me	141	2, 3	2.59 - 2.90	2.28	wulwac	42

[†] Sum of covalent radii of the high spin metal atom and a carbon atom.

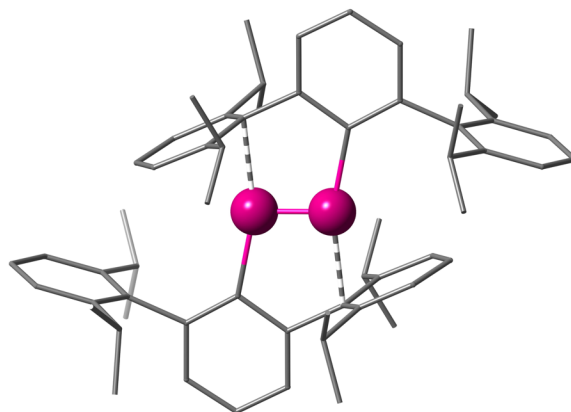


Figure 14. Crystal structure of the first reported compound with a quintuple Cr-Cr bond.³²

A further step on this direction has been the addition of a coordinating group such as amido^{41,43,44} or thiolato³⁵ to the central phenyl ring, in such a way that the terphenyl group is somewhat separated from the metal atom while at the same time moving it laterally (Figure 13c).

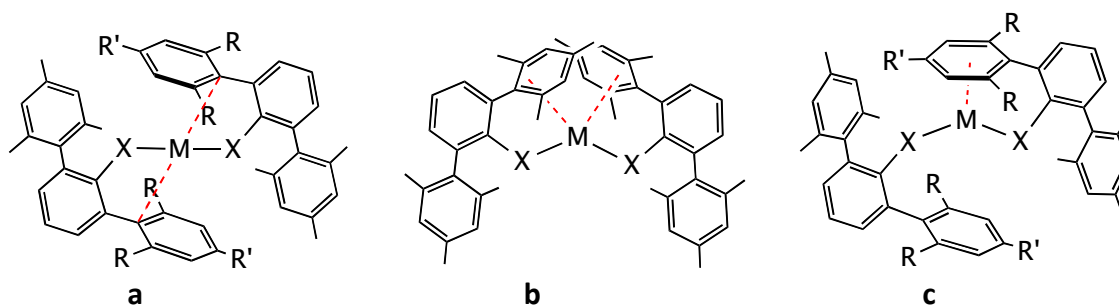


Figure 15. Different stereochemistries of formally dicoordinated transition metal atoms with two amido- or thiolato-terphenyl ligands.

In all the complexes with those ligands, the flanking arene rings act as sticky flaps that try to compensate the electronic unsaturation of nearby metal centres through π -coordination with varying hapticities, which are apparently affected by the nature of the R and R' substituents. All the structures can be classified in one of the following three cases (Table 1): (i) When both R and R' are iPr groups, the MX_2 core is linear and one flanking arene from each terphenyl makes a low hapticity contact (η^1 to η^3) with the metal (Figure 15a), although for Zn(II) and high spin Mn(II) these contacts are at relatively long distances; (ii) when R is Me and R' is Me or H, the MX_2 core is bent and one flanking arene from each terphenyl group interacts with the metal in an η^2 or η^3 mode, resulting in a pseudo tetrahedral coordination (Figure 15b), and (iii) when R is iPr and R' is H, the MX_2 core may be either linear or bent, in which case one of the flanking arene groups coordinates in an η^6 mode (Figure 15c). Although it seems clear that the substituents have some influence on the choice of one of the three alternative structures, one should not rule out the possible existence of stereoisomers.

Concluding remarks

We chemists probably feel more comfortable with two-dimensional representations of the atomic connectivities in molecules than with their spatial arrangement. In part because the more than one million crystal structures determined so far, including small molecules, proteins and

extended solids, represent only a small fraction of the total number of chemical compounds known. For that reason, many interesting molecular shapes go unnoticed except for the small group of specialists in a particular area of Chemistry. Of course, there are exceptions, and from time to time some innovative or beautiful molecules become widely known, as was the case for buckminsterfullerene, and for the widely developed families of supramolecular knots, rings and cages.⁴⁵ Many of the less famous molecules commented in this paper have been detected only after hours of careful observation of the molecular structures contained in structural databases such as the CSD and the ICSD. In some cases, though, the creators of new molecules themselves have called our attention in their communications to a particular way in which we can see them, which helps our visual memory to remind them for the rest of our lives.

Acknowledgments

Financial support from MINECO CTQ2015-64579-C3-1-P, the Spanish Structures of Excellence María de Maeztu program through grant MDM-2017-0767, and AGAUR (Generalitat de Catalunya) through grant 2017-SGR-1289 is gratefully acknowledged.

References

1. R. Hoffmann, "Molecular Beauty", *J. Aesthetics Art Crit.* **1991**, *48*, 191-204.
2. X. Shen, D. M. Ho, R. A. Pascal Junior, "Synthesis and Structure of a Polyphenylene Macrocycle Related to "Cubic Graphite"", *Org. Lett.* **2003**, *5*, 369-371.
3. S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell, D. Avnir, "Shape Maps and Polyhedral Interconversion Paths in Transition Metal Chemistry", *Coord. Chem. Rev.* **2005**, *249*, 1693-1708.
4. A. Nickon, E. Silversmith; *Organic Chemistry: The Name Game*; Pergamon Press: New York, 1988.
5. S. N. Spisak, A. S. Filatov, M. A. Petrukhina, "Palladium π -adduct of corannulene", *J. Organomet. Chem.* **2011**, *696*, 1228-1231.
6. K. Yamamoto, T. Harada, M. Nakazaki, T. Naka, Y. Kai, S. Harada, N. Kasai, "Synthesis and characterization of [7]circulene", *J. Am. Chem. Soc.* **1983**, *105*, 7171-7172.
7. A.-C. Bedard, A. Vlassova, A. C. Hernandez-Perez, A. Bessette, G. S. Hanan, M. A. Heuft, S. K. Collins, "Synthesis, Crystal Structure and Photophysical Properties of Pyrene-Helicene Hybrids", *Chem. Eur. J.* **2013**, *19*, 16295-16302.
8. G. Le Bas, A. Navaza, M. Knossow, C. de Rango, *Cryst. Struct. Commun.* **1976**, *5*, 713-.
9. K. Mori, T. Murase, M. Fujita, "One-Step Synthesis of [16]Helicene", *Angew. Chem., Int. Ed.* **2015**, *54*, 6847-6851.
10. S. Alvarez, "Polyhedra in (Inorganic) Chemistry", *Dalton Trans.* **2005**, 2209-2233.
11. S. Alvarez, "Nesting of Fullerenes and Frank-Kasper Polyhedra", *Dalton Trans.* **2006**, 2045-2051.
12. J. Echeverría, D. Casanova, M. Llunell, P. Alemany, S. Alvarez, "Molecules and Crystals with Both Icosahedral and Cubic Symmetry", *Chem. Commun.* **2008**, 2717-2725.
13. J. Echeverría, A. Carreras, D. Casanova, P. Alemany, S. Alvarez, "Concurrent Symmetries. The Interplay Between Local and Global Molecular Symmetries", *Chem. Eur. J.* **2011**, *17*, 359-367.
14. S. Alvarez, E. Ruiz, en *Supramolecular Chemistry, From Molecules to Nanomaterials*, J. W. Steed, Gale P. A., Eds.; John Wiley & Sons, Chichester, UK, **2012**, Vol. 5, pp 1993-2044.
15. S. Alvarez, "Zero- and Mono-Coordinated Transition Metals in Crystal Structures", *Inorg. Chim. Acta* **2018**, *470*, 74-81.
16. T. S. Cameron, A. Decken, I. Krossing, J. Passmore, J. M. Rautiainen, X. Wang, X. Zeng, "Reactions of a Cyclodimethylsiloxane (Me₂SiO)₆ with Silver Salts of Weakly Coordinating Anions; Crystal Structures of [Ag(Me₂SiO)₆][Al] ([Al] = [FAl{OC(CF₃)₃}₃], [Al{OC(CF₃)₃}₄]) and Their Comparison with [Ag(18-Crown-6)]₂[SbF₆]₂", *Inorg. Chem.* **2013**, *52*, 3113-3126.

17. J. W. Steed, K. Johnson, C. Legido, P. C. Junk, "Influence of hydrogen bonding on "soft" coordination geometries: further examples", *Polyhedron* **2003**, *22*, 769-774.
18. I. A. Popov, T. Jian, G. V. Lopez, A. I. Boldyrev, L.-S. Wang, "Cobalt-centred boron molecular drum with the highest coordination number in the CoB₁₆⁻ cluster", *Nature Commun.* **2015**, *6*, 8654.
19. M. Elghali, M. Abdellaoui, V. Paul-Boncour, M. Latroche, "Synthesis and structural characterization of mechanically alloyed A B3-type based material: La Zr₂ Mn₄ Ni₅", *Intermetallics* **2013**, *41*, 76-81.
20. D. Chabach, A. De Cian, J. Fischer, R. Weiss, M. E. M. Bibout, "Mixed-Metal Triple-Decker Sandwich Complexes with the Porphyrin/Phthalocyanine/Porphyrin Ligand System", *Angew. Chem., Int. Ed.* **1996**, *35*, 898.
21. T. Iwamoto, Y. Watanabe, H. Takaya, T. Haino, N. Yasuda, S. Yamago, "Size- and Orientation-Selective Encapsulation of C70 by Cycloparaphenylenes", *Chem. Eur. J.* **2013**, *19*, 14061-.
22. K. O. Christe, E. C. Curtis, D. A. Dixon, H. P. Mercier, J. C. P. Sanders, G. J. Schrobilgen, "The pentafluoroxenate(IV) anion, XeF₅⁻: the first example of a pentagonal planar AX₅ species", *J. Am. Chem. Soc.* **1991**, *113*, 3351-3361.
23. R. Gajda, A. Katrusiak, "The Interplay of Molecular Conformation and Crystal Packing in Pressure-Frozen Tetramethylsilane", *Cryst. Growth Des.* **2008**, *8*, 211-214.
24. S. Alvarez; *Dones, homes i molècules. Notes d'història, art i literatura de la química*; Universitat de Barcelona Edicions: Barcelona, 2017.
25. V. Marvaud, C. Decrois, A. Sculler, C. Guyard-Duhayon, J. Vaissermann, F. Gonnet, M. Verdagner, "Hexacyanometalate Molecular Chemistry: Heptanuclear Heterobimetallic Complexes; Control of the Ground Spin State", *Chem. Eur. J.* **2003**, *9*, 1677-1691.
26. M. Teramoto, K. Iwata, H. Yamaura, K. Kurashima, K. Miyazawa, Y. Kurashige, K. Yamamoto, T. Murahashi, "Three-Dimensional Sandwich Nanocubes Composed of 13-Atom Palladium Core and Hexakis-Carbo-cyclo Shell", *J. Am. Chem. Soc.* **2018**, *140*, 12682-12686.
27. C. Couldwell, K. Prout, "The crystal and molecular structure of $\{[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\mu\text{-OH})]_4\}[\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\mu\text{-Cl})_2(\mu\text{-OH})\text{Mo}(\eta^7\text{-C}_7\text{H}_7)]^+\cdot\text{Cl}^-\cdot\text{C}_6\text{H}_5\text{Cl}$, a hydrolysis product of $[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\mu\text{-Cl})_3\text{Mo}(\eta^7\text{-C}_7\text{H}_7)]$, at 173 K", *Acta Cryst. B* **1978**, *34*, 2439-2444.
28. H. R. van der Wal, F. Overzet, H. O. van Oven, J. L. de Boer, H. J. d. L. Meijer, F. Jellinek, "Cyclooctatetraenetitanium chloride and its adducts with THF and some amines", *J. Organomet. Chem.* **1975**, *92*, 329-340.
29. S. Horiuchi, Y. Tachibana, M. Yamashita, K. Yamamoto, K. Masai, K. Takase, T. Matsutani, S. Kawamata, Y. Kurashige, T. Yanai, T. Murahashi, "Multinuclear metal-binding ability of a carotene", *Nature Commun.* **2015**, *6*, 6742.
30. T. Murahashi, R. Inoue, K. Usui, S. Ogoshi, "Square Tetrapalladium Sheet Sandwich Complexes: Cyclononatetraenyl as a Versatile Face-Capping Ligand", *J. Am. Chem. Soc.* **2009**, *131*, 9888-9889.
31. Y. D. Bidal, M. Lesieur, M. Melaimi, D. B. Cordes, A. M. Z. Slawin, G. Bertrand, C. S. J. Cazin, "A simple access to transition metal cyclopropenyliidene complexes", *Chem. Commun.* **2015**, *51*, 4778-4781.

32. T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long, P. P. Power, "Synthesis of a stable compound with fivefold bonding between two chromium(I) centers", *Science* **2005**, *310*, 844-847.
33. M. Carrasco, I. Mendoza, E. Alvarez, A. Girrane, C. Maya, R. Peloso, A. Rodríguez, A. Falceto, S. Alvarez, E. Carmona, "Experimental and Computational Studies of the Molybdenum-Flanking Arene Interaction in Quadruply Bonded Dimolybdenum Complexes with Terphenyl Ligands", *Chem. Eur. J.* **2015**, *21*, 410-421.
34. A. Falceto, E. Alvarez, "Comparison of the Cr-Cr Quadruple and Quintuple Bonding Mechanisms", *Struct. Bond.* **2016**, *170*, 149-264.
35. T. Nguyen, A. Panda, M. M. Olmstead, A. F. Richards, M. Stender, M. Brynda, P. P. Power, "Synthesis and Characterization of Quasi-Two-Coordinate Transition Metal Dithiolates M(SAr*)₂ (M = Cr, Mn, Fe, Co, Ni, Zn; Ar* = C₆H₃-2,6(C₆H₂-2,4,6-Prⁱ)₂)", *J. Am. Chem. Soc.* **2005**, *127*, 8545-8552.
36. J. Pratt, A. M. Bryan, M. Faust, J. N. Boynton, P. Vasko, B. D. Reken, A. Mansikkamaki, J. C. Fettinger, H. M. Tuononen, P. P. Power, "Effects of Remote Ligand Substituents on the Structures, Spectroscopic and Magnetic Properties of Two-Coordinate Transition-Metal Thiolate Complexes", *Inorg. Chem.* **2018**, *57*, 6491-6502.
37. S. Ohta, Y. Ohki, Y. Ikagawa, R. Suizu, K. Tatsumi, "Synthesis and characterization of heteroleptic iron(II) thiolate complexes with weak iron-arene interactions", *J. Organomet. Chem.* **2007**, *692*, 4792-4799.
38. J. J. Ellison, K. Ruhlandt-Senge, P. P. Power, "Synthesis and Characterization of Thiolato Complexes with Two-Coordinate Iron(II)", *Angew. Chem., Int. Ed.* **1994**, *33*, 1178-1180.
39. J. J. Ellison, P. P. Power, "Synthesis and Characterization of New Thiolato Derivatives of Lithium, Magnesium, and Zinc: Examples of Two-Coordinate Lithium and Zinc Species Ligated by Sulfur", *Inorg. Chem.* **1994**, *33*, 4231-4234.
40. M. Ito, T. Matsumoto, K. Tatsumi, "Synthesis and Reactions of Mono- and Dinuclear Ni(I) Thiolate Complexes", *Inorg. Chem.* **2009**, *48*, 2215-2223.
41. J. N. Boynton, W. A. Merrill, W. M. Reiff, J. C. Fettinger, P. P. Power, "Two-Coordinate, Quasi-Two-Coordinate, and Distorted Three Coordinate, T-Shaped Chromium(II) Amido Complexes: Unusual Effects of Coordination Geometry on the Lowering of Ground State Magnetic Moments", *Inorg. Chem.* **2012**, *51*, 3212-3219.
42. W. A. Merrill, T. A. Stich, M. Brynda, G. J. Yeagle, J. C. Fettinger, R. De Hont, W. M. Reiff, C. E. Schulz, R. D. Britt, P. P. Power, "Direct Spectroscopic Observation of Large Quenching of First-Order Orbital Angular Momentum with Bending in Monomeric, Two-Coordinate Fe(II) Primary Amido Complexes and the Profound Magnetic Effects of the Absence of Jahn- and Renner-Teller Distortions in Rigorously Linear Coordination", *J. Am. Chem. Soc.* **2009**, *131*, 12693-12702.
43. C. Ni, B. Reken, J. C. Fettinger, G. J. Long, P. P. Power, "Two-coordinate, homoleptic manganese(II) primary terphenyl amido complexes: the effects of secondary coordination on geometry and Lewis base complexation", *Dalton Trans.* **2009**, 8349-8355.
44. A. M. Bryan, W. A. Merrill, W. M. Reiff, J. C. Fettinger, P. P. Power, "Synthesis, Structural, and Magnetic Characterization of Linear and Bent Geometry Cobalt(II) and Nickel(II) Amido

Complexes: Evidence of Very Large Spin-Orbit Coupling Effects in Rigorously Linear Coordinated Co^{2+} , *Inorg. Chem.* **2012**, *51*, 3366-3373.

45. J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh, R. T. McBurney, "Strategies and Tactics for the Metal-Directed Synthesis of Rotaxanes, Knots, Catenanes, and Higher Order Links.", *Angew. Chem., Int. Ed.* **2011**, *50*, 9260-9327.