

Challenging the limitation: Synthesis and application of complexes with the highest carbon coordination number in plane

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With the support by the National Natural Science Foundation of China and the National Basic Research Program of China, the research team led by Prof. Xia Haiping (夏海平) of Xiamen University described the first example of CCCCC pentadentate chelate with all binding atoms being carbon atoms. This result represents a new record of planar carbon coordination number for a transition metal, which was published in *Science Advances* (2016, DOI: 10.1126/sciadv.1601031).

Carbon is one of the most fundamental elements in chemistry. Carbon is also the protagonist in organic chemistry. However, the coordinating atoms in polydentate chelates are mainly occupied by a variety of donor heteroatoms, such as N, P, O, and S. Examples of polydentate chelates with carbon as binding atoms have proven to be much more difficult to realize.

Recently, Xia's group described the first example of pentadentate chelates with all binding atoms being carbon atoms, which have been named carbolong complexes. Having up to five metal-carbon bonds in the equatorial plane has not been previously observed in transition metal chemistry. The carbolong complex can be viewed as a 12-atom carbon chain (named carbolong ligand) coordinating to a transition metal center. DFT calculations show that these carbolong complexes possess extended Craig-Möbius aromaticity arising from twelve-centre-twelve-electron $d-p$ π -conjugation within their equatorial fused-ring, thus leading to the high stability and broad absorption in the ultraviolet-visible-near-infrared region. This molecule is also the largest planar Möbius aromatic system synthesized so far.

The broad absorbance spectra in the NIR region make these pentadentate carbolong chelates promising candidates for photothermal therapy (PTT). The mice bearing SCC7 tumors that received both intravenous injection and irradiation showed tumor ablation 2 days after treatment and exhibited thorough regression of the tumor in 2 weeks. This work represents the first example of organometallics used for PTT, although the long-term toxicity should be investigated before clinical translation

In addition, the framework of carbolong complexes is also a kind of CCCCC pincer complex. Thus, the concept of the pincer complex can be extended from tridentate to planar polydentate chelates. Furthermore, this result extends our perception of the chelating ability of carbon chain. Overall, because of their facile syntheses, high thermodynamic stability, broad absorption spectra, and significant photothermal properties, these novel pentadentate carbon chain chelates not only provide a promising material for biomedicine and solar energy utilization, but also make carbolong liganda novel building block in chemistry.

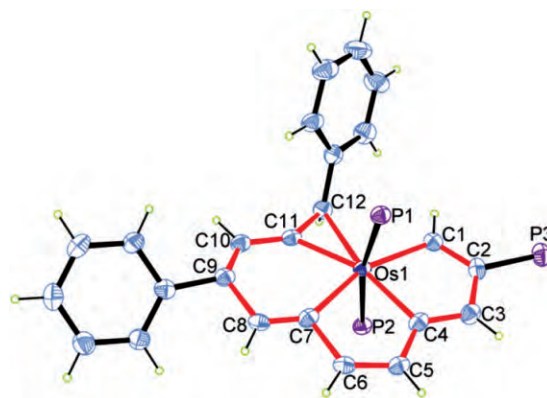


Figure X-ray crystal structure of the first example of pentadentate chelate with all binding atoms being carbons.