

A supramolecular organometallic–metalorganic square†

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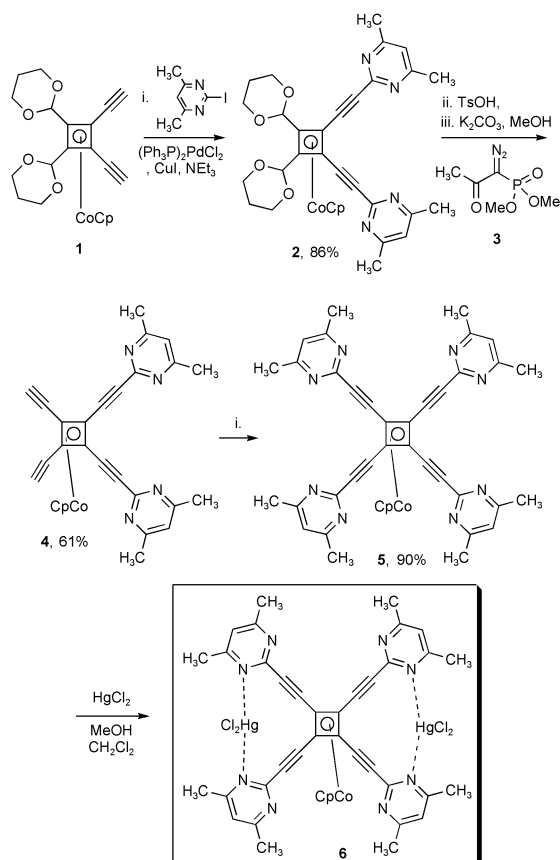
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Synthesis and structural characterization of [tetrakis(2-pyrimidinylethynyl)cyclobutadiene][(cyclopentadienyl)cobalt] and its mercury(II)chloride complex are reported; in the complex, the mercury is in an unusual square planar coordination environment.

Metallor supramolecular chemistry is a fascinating and important field that has developed from inorganic coordination chemistry.^{1–7} In metallor supramolecular chemistry a metal salt is utilized to either connect two or more ligands into a novel oligomeric or polymeric solid-state structure, or to fixate the geometry of an otherwise flexible ligand and change its properties. Metallor supramolecular chemistry can also realize coordination geometries that are normally not available.^{8–11} The strength of the metallor supramolecular interaction can vary from weak, van der Waals-like, to strong, almost covalent. We report herein a *trans*-spanning organometallic ligand, **5**, that is able to coordinate mercury chloride in a square planar fashion to give a supramolecular square structure **6**.†



Scheme 1 Synthesis of tetrakis-pyrimidine substituted tetraethynylated cyclobutadiene complex **5** and its reaction with HgCl₂ to give **6**.

† Electronic supplementary information (ESI) available: experimental, including details of preparation and spectroscopic data for **2–6**. See <http://www.rsc.org/suppdata/cc/b3/b304169g/>

The Pd-catalysed reaction of **1**^{12–14} with 2-iodo-4,6-dimethylpyrimidine¹⁵ furnishes the diyne **2** in a 86% yield after chromatography (Scheme 1). Cleavage of the ketal groups leads to a dialdehyde that is transformed into the tetrayne **4** (61%) by the diazo reagent **3**.¹⁶ In the final synthetic step, two additional pyrimidine substituents are attached to **4** to give **5** by a Sonogashira coupling.^{12,13} Tetrakis(pyrimidylethynyl)cyclobutadiene(cyclopentadienyl)cobalt (**5**) is isolated in 90%. The overall yield of this reaction sequence (**1**→**5**) is 47%, making the ligand **5** accessible on a gram scale.

Preliminary attempts to crystallise **5** from benzene or toluene failed. It was likewise not possible to obtain complexes of **5** with copper, nickel, or silver salts. Microcrystalline powders were isolated. The reaction of **5** with HgCl₂ in dichloromethane/methanol mixtures was more successful and furnished the molecular complex **6** as well-developed needle-like specimens suitable for single crystal X-ray diffraction.‡ The organometallic ligand **5** crystallizes with two molecules of mercury chloride and two molecules of DCM. In Fig. 1 the molecular structure of **6** is shown. There are several surprising features about the geometry of this complex. a) The large heterocyclic ligand composed from the four ethynylated pyrimidines and the cyclobutadiene core is almost planar and square. It forms four pockets composed of the alkyne legs and the pyrimidine rings. b) Opposite pockets are filled with DCM or mercury chloride. c) The surrounding of the mercury chloride is square-planar with

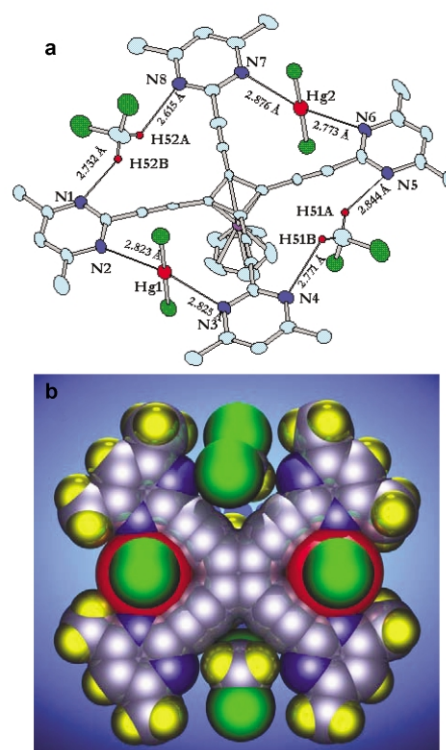


Fig. 1 a) Molecular structure and selected bond distances of **6**. b) Space filling model of **6**.

Hg–N-contacts ranging from 2.77–2.88 Å. This is unusual, because HgX₂ tends to coordinate with pyridine bases in a tetrahedral rather than in a square planar fashion. In addition, the Hg–N-bonds are shorter (2.3–2.5 Å) in the tetrahedral case.¹⁷ A search of the Cambridge crystallographic database shows that there are only three examples where an HgX₂-moiety is linear when adjacent to an N-donor. In all three examples however, the central mercury is not square planar but octahedrally or even higher coordinated,^{18–20} making the coordination environment of Hg in **6** unusual. We assume that mercury does not form a classic coordination bond with the N-donors, but that we deal here with something more akin to a van-der-Waals complex. The linear structure of the complex is dictated by the innate structure of HgCl₂.

Attempts to fill all of the four pockets with mercury chloride, mercury bromide, or mercury iodide, failed. To understand the reluctance of the system to “pick up” more than two mercury halide species we investigated its packing in the solid state (Fig. 2). Molecules of **5** are arranged in stacks along the *c*-axis (top) on top of each other. The inability of HgX₂ to fill all of the resulting pockets becomes clear from Fig. 2. The complexes **6** are arranged in *ab*-stacks, and the layers are rotated by 90° compared to the ones above and below. This packing allows the HgCl₂ and DCM to fill the pockets formed by the pyrimidine legs. The solid state arrangement is “glued together” by the strong π – π -interactions between the pyrimidine faces and the central metallocene units where the distances between the cyclobutadiene ring of one molecule to the Cp-ring of its neighbour below is only 3.55 Å.

The ligand **5** is *trans*-spanning and sterically demanding (eight methyl groups, CpCo-fragment). The coordination mode

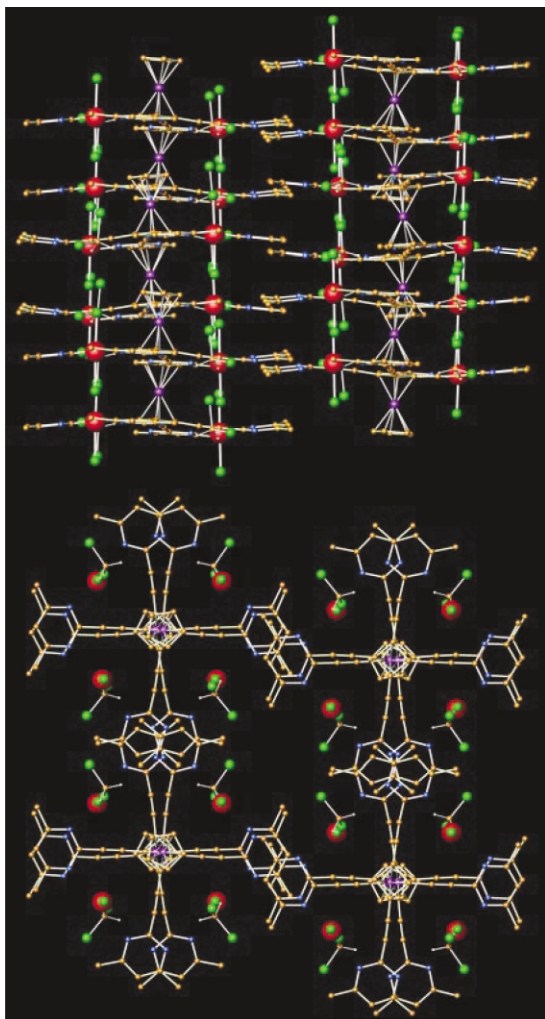


Fig. 2 Packing diagram of **6**.

of HgCl₂ in **6**, while square planar, we speculate, could be considered as “frustrated octahedral”. Due to the steric inaccessibility, the two other coordination sites of mercury stay unfilled. The rearrangement into a tetrahedrally surrounded Hg-centre would lead to shortened Hg–N distances and an unacceptably distorted ligand framework. The observed geometry is the compromise that offers both some binding of the Hg-centre to the pyrimidines yet leaves the ligand frame undistorted.

This study demonstrates that the *trans*-spanning ligand **5** forms an unusual columnar coordination geometry with HgCl₂ that is held together by strong π – π -interactions. It is surprising that the co-crystallization of **5** with HgCl₂ does not lead to intermolecular solid-state polymers in which the pyrimidine rings would be twisted out of the plane (defined by the tetraethynylated cyclobutadiene ring) leading to a more stable tetrahedrally coordinated HgCl₂-moiety.¹⁷ In the future we will report upon the structural characterization of the corresponding tetrakis(pyrimidinylethynyl) analogues that feature benzene as the central unit.

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Notes and references

‡ Details of structure solutions are available from CCDC 207565 and deposited as supplementary material. Crystal data for **6**: Crystal system: Monoclinic; *P*2₁/*c*; *a* = 14.1779(8), *b* = 28.5958(2), *c* = 13.7478(8) Å, α = 90°, β = 106.904(1)°, γ = 90°. *V* = 5332.9(5) Å³, *Z* = 4, ρ_{calcd} = 1.808 Mg m^{−3}. Absorption coefficient = 6.540 mm^{−1}, *F*(000) = 2780, crystal size = 0.22 × 0.16 × 0.04 mm³. Θ = 1.42 to 25.02° with $-15 \leq h \leq 16$, $-34 \leq k \leq 34$, $-16 \leq l \leq 16$. Reflections collected 37390. Independent reflections 9407 [*R*(int) = 0.0684]. Absorption correction: Semi-empirical from equivalents. Refinement: Full-matrix least-squares on *F*². Data/restraints/parameters: 9407/18/636. Final *R* indices [*I* > 2 σ (*I*)] *R*₁ = 0.0593, *wR*₂ = 0.1484. *R* indices (all data) *R*₁ = 0.0820, *wR*₂ = 0.1567. See <http://www.rsc.org/suppdata/cc/b3/b304169g/> for crystallographic data in .cif or other electronic format.

- B. Olenyuk, J. A. Whiteford, A. Fechenkötter and P. J. Stang, *Nature*, 1999, **398**, 796; B. Olenyuk, A. Fechenkötter and P. J. Stang, *J. Chem. Soc., Dalton Trans.*, 1988, 1707.
- G. W. Orr, L. J. Barbour and J. L. Atwood, *Science*, 1999, **285**, 1049; L. R. MacGillivray and J. L. Atwood, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 1018.
- S. J. Lee, A. G. Hu and W. B. Lin, *J. Am. Chem. Soc.*, 2002, **124**, 12948.
- C. Piguet, *J. Inclusion Phenom. Macro. Chem.*, 1999, **34**, 361.
- Y.-B. Dong, M. D. Smith and H.-C. zur Loye, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 4271.
- M. Albrecht, *J. Inclusion Phenom. Macro. Chem.*, 2000, **36**, 127.
- J. M. Lehn, *Chem. Eur. J.*, 2000, **6**, 2097.
- J. E. Fiscus, S. Shotwell, R. C. Layland, M. D. Smith, H.-C. zur Loye and U. H. F. Bunz, *Chem. Commun.*, 2001, 2674; S. Shotwell, H. L. Ricks, J. G. M. Morton, M. Laskoski, J. Fiscus, M. D. Smith, K. D. Shimizu, H.-C. zur Loye and U. H. F. Bunz, *J. Organomet. Chem.*, 2003, **671**, 43.
- E. Bosch and C. L. Barnes, *Inorg. Chem.*, 2001, **40**, 3097.
- Y.-Z. Hu, C. Chamchoumis, J. S. Grebowicz and R. P. Thummel, *Inorg. Chem.*, 2002, **41**, 2296.
- T. Kawano, J. Kuwana, T. Shinomaru, C.-X. Du and I. Ueda, *Chem. Lett.*, 2001, 1230.
- K. Sonogashira, *J. Organomet. Chem.*, 2002, **653**, 46.
- U. H. F. Bunz, *Chem. Rev.*, 2000, **100**, 1605.
- M. Laskoski, J. G. M. Morton, M. D. Smith and U. H. F. Bunz, *J. Organomet. Chem.*, 2002, **652**, 21.
- G. Vlad and I. T. Horvath, *J. Org. Chem.*, 2002, **67**, 6550.
- S. Ohira, *Synth. Commun.*, 1989, **19**, 561.
- D. M. Ciurtin, N. G. Pschirer, M. D. Smith, H.-C. zur Loye and U. H. F. Bunz, *Chem. Mater.*, 2001, **13**, 2743.
- J. Pickardt, G. T. Gong and D. Roleke, *Z. Naturforsch. B*, 1994, **49**, 321.
- B. J. Graves and D. J. Hodgson, *Inorg. Chem.*, 1981, **20**, 2223.
- L.-A. Malmsten, *Acta Cryst. B*, 1979, **35**, 1702.