

Corundum, Diamond, and PtS Metal–Organic Frameworks with a Difference: Self-Assembly of a Unique Pair of 3-Connecting D_{2d} -Symmetric 3,3',5,5'-Tetrakis(4-pyridyl)bimesityl**

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There is an upsurge of interest in the synthesis of coordination polymers in contemporary supramolecular chemistry, as coordination polymerization may lead to materials with controllable functions such as porosity, sensing, nonlinear optical (NLO) activity, and chirality.^[1] Crystal engineering based on predesigned organic linkers and metal centers (building blocks) with specific coordination geometries is an important approach in the preparation of coordination materials with desired functions.^[2] Based on the knowledge of the structures of the ligands and the coordination geometries of a variety of metal centers, diverse 2D and 3D nets—several of which are analogous to structures of inorganic materials—have been engineered in the field of metal–organic frameworks (MOFs). Thus, the syntheses of 3-connected nets corresponding to the topologies of SrSi_2 -(10,3)-a,^[3] ThSi_2 /(10,3)-b,^[4] (12,3),^[5] (3,4)-connected nets with the topologies of boracite,^[6] $\text{Cu}_{15}\text{Si}_4$,^[7] (5^3_4) ,^[8] and (3,6)-connected nets corresponding to the topologies of rutile^[9] and pyrite^[10] have been accomplished. Insofar as the 4-connected nets are concerned, the syntheses of MOFs with unusual topologies^[11] and with topologies corresponding to those of diamond,^[1c,d,12] NbO ,^[13] quartz,^[14] and PtS ^[15] have been reported. Similarly, the (4,8)- and 6-connected metal–organic frameworks with fluorite^[16] and cubic^[17] topologies, respectively, have been designed and synthesized. In view of the success of such building-block approaches to realize metal–organic frameworks with specific topologies, the multi-dentate ligands with novel structural features offer the possibility to construct new and unique coordination poly-

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mers.^[18] In continuation of our recent studies on the self-assembly of acids,^[19] we conceived a unique tetratopic ligand with D_{2d} -symmetry to explore the construction of 3D coordination networks by metal-directed self-assembly with O_h , T_d , and D_{4h} metal centers (Figure 1).

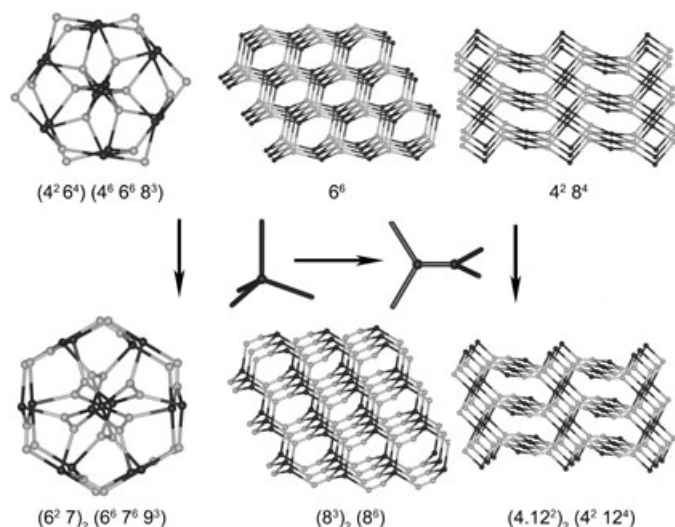
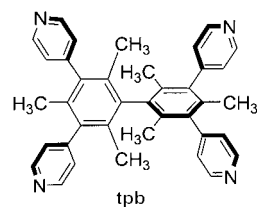


Figure 1. Top: Representation of the ideal corundum, diamond, and PtS networks. Bottom: The nets resulting from replacement of tetrahedral nodes by pairs of 3-connecting nodes. The Schläfli notations for the networks, shown below the structures, signify the changes in the network topologies.

Construction of a network by combining T_d ligands and O_h metal centers has been regarded as being very difficult.^[20] The best compromise between a 4-connecting ligand and an octahedral metal center turns out to be that of the corundum form of Al_2O_3 , in which both Al^{3+} and O^{2-} ions are distorted from their ideal octahedral and tetrahedral geometries, respectively.^[21] Thus, by considering the D_{2d} -symmetric ligand as a distorted-tetrahedral building block, one can envisage the synthesis of metal-organic equivalents of the corundum net as shown in Figure 1. Similarly, the combination of D_{2d} -symmetric ligands and T_d metal centers should yield an analogue of the diamond net, the difference being that each ring in the resultant net is eight-membered as opposed to a six-membered ring in the ideal diamond net. Indeed, Wells pointed out that (10,3)-a and (10,3)-b nets derive from the replacement of tetrahedral nodes of a diamond net by pairs of 3-connecting nodes.^[22] He also showed that the $(8,3)_b$ net results from replacement of alternate tetrahedral nodes in a diamond net by pairs of 3-connecting nodes. Furthermore, the combination of a D_{2d} -symmetric tetratopic ligand with a square-planar D_{4h} metal center should be expected to afford a PtS network, the difference being that the resulting network would be constituted by four- and twelve-membered rings instead of four- and eight-membered rings in the ideal PtS net. The metal-organic corundum-, diamond-, and PtS-related nets arising from the replacement of a T_d ligand by a D_{2d} ligand as shown in Figure 1 are also unprecedented. Herein, we document the engineering of these three distinct 3D metal-organic net-

works shown in Figure 1 based on a rationally designed and synthesized unique D_{2d} -symmetric 3,3',5,5'-tetrakis(4-pyridyl)bimesityl (tpb) ligand.^[23]

The reaction of tpb with $Zn(ClO_4)_2 \cdot 6H_2O$, $Cd(ClO_4)_2 \cdot 6H_2O$, $AgNO_3$, and $MnCl_2 \cdot 4H_2O$ led to corresponding complexes **1–4**, whose compositions were formulated



- 1:** $\{Zn(tpb)_{1.5}(ClO_4)_2 \cdot (H_2O)_n\}_\infty$
2: $\{Cd(tpb)_{1.5}(ClO_4)_2 \cdot (H_2O)_n\}_\infty$
3: $\{Ag(tpb)(NO_3)(CH_3OH)\}_\infty$
4: $\{Mn(tpb)(Cl)_2(CH_3OH)(H_2O)_n\}_\infty$

based on microanalytical and single-crystal X-ray crystal structure determinations. Compound **1** was obtained as colorless cubic crystals by slow diffusion over two days of the ethanolic solution of $Zn(ClO_4)_2 \cdot 6H_2O$ into a solution of tpb in dichloromethane that was contained in a vial. A similar diffusion of $Cd(ClO_4)_2 \cdot 6H_2O$ in ethanol into a solution of tpb in dichloroethane yielded hexagonal colorless crystals of **2**. Both **1** and **2** were isolated in > 60% yield from preparative experiments. The crystals of compound **2** were found to be stable, while those of **1** were fragile and degraded upon removal from the mother liquor. X-ray single-crystal structure determinations^[24] revealed that both compounds are isostructural, with a cubic space group of $Ia\bar{3}d$.

The metal ions in both **1** and **2** reside on the crystallographic threefold inversion center and are perfectly octahedral. Each of the metal ions is surrounded by six pyridyl rings of independent tpb ligands. The two mesityl rings of the tpb ligand are absolutely orthogonal and each of the pyridyl rings is tilted by about 80° with respect to the mesitylene core. Figure 2b shows the crystal-packing diagram of **1**; the packing for compound **2** is virtually indistinguishable. The interatomic distances associated with the coordination bonds that involve the metal ion and the pyridyl nitrogen atom in **1** and **2** are 2.183(1) and 2.359(1) Å, respectively. The networks are not interpenetrated in both complexes and the perchlorate counterions and water molecules occupy the void space.

The seemingly complex structure of the coordination polymer can be best understood by simplification of the ligand structure to that of the D_{2d} -symmetric allene (Figure 2a) and by representing the metal as a 6-connecting octahedral node. Figure 2c shows the crystal packing based on this simplification. Decorating ligand **1** by connecting the carbon atoms of the bimesityl rings (to which the angularly disposed pyridyl rings are attached) as shown in Figure 2a leads to further simplification of the ligand structure to a distorted tetrahedron. Thus, by depicting the metal center as well as the ligand tpb as 6- and 4-connecting polyhedra, the structure of the coordination polymer is reduced to that shown in Figure 2d. This network may be readily compared to that of the corundum modification of Al_2O_3 , in which each octahedral Al^{3+} ion is surrounded by six O^{2-} ions, while each oxygen center is surrounded by four Al^{3+} ions arranged in a distorted tetrahedral configuration. Although the analogy

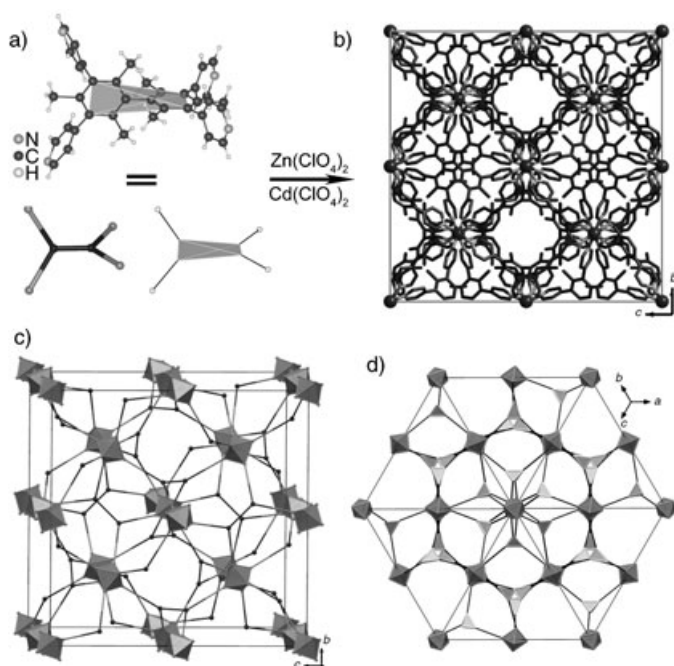


Figure 2. a) Illustration of the formal equivalence of the ligand tpb to that of the D_{2d} -symmetric allene; b) the crystal packing of compounds **1** and **2**; c) the crystal packing by depicting the ligand tpb as a pair of 3-connecting topological equivalents of allene and the metal as a 6-connecting octahedron; d) the crystal packing shown again by depicting the ligand as a distorted 4-connecting tetrahedron and the metal as a 6-connecting octahedron, which is similar to that of the corundum. Hydrogen atoms, solvent molecules, and counterions have been removed for clarity.

between Zn/Cd-coordination polymers of the ligand tpb and the corundum form of Al_2O_3 is established by simplification of the structure of the ligand to a distorted tetrahedral 4-connecting node (Figure 2d), the tetradentate tpb is in reality a pair of 3-connected nodes that are linked together. Accordingly, the Schläfli notation for the topology of the coordination polymer based on a 4-connecting tetrahedral ligand is similar to that of the corundum and is given by $(4^26^4)(4^66^88^3)$. However, tpb is best described as a pair of 3-connecting nodes and thus the Schläfli topological description for the Zn/Cd-coordination polymers of tpb takes the form $(6^27)_2(6^67^69^3)$.

The colorless crystals of compound **3** were obtained by slow diffusion of a methanolic solution of $AgNO_3$ into a solution of tpb in methanol followed by keeping the resultant solution at room temperature in the dark for 2–3 days. The crystals were found to decay as soon as they were removed from the mother liquor. Single-crystal X-ray diffraction analysis^[24] revealed that the complex crystallizes in the monoclinic space group $C2/c$. The geometry of the metal ion is found to be tetrahedral as it is coordinated by the pyridyl groups of four distinct molecules. The bond lengths associated with the metal ion and pyridyl nitrogen atoms are 2.326(5) and 2.330(1) Å. The metal ion and the tpb ligand assemble into a diamond network with the incorporation of solvent molecules. A typical adamantanoid unit formed by the unique assembly of six molecules of tpb (only two pyridyl

rings contribute to the construction of adamantanoid unit, the other two are used for 3D propagation) and four Ag^+ ions that act as nodes is shown in Figure 3; the assembly involves two of the tpb ligands coordinating to the metal through two of their

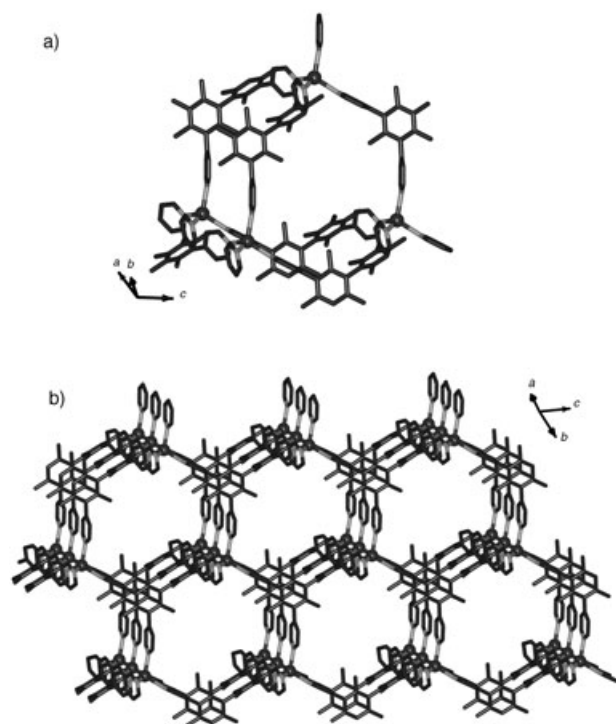


Figure 3. a) The core adamantanoid unit of compound **3**. Notice that the shortest circuit of the unit is an eight-membered ring. b) The diamond-related net of **3**, which undergoes interpenetration. Hydrogen atoms, solvent molecules, and counteranions have been removed for clarity. The solid spheres represent metal cations.

pyridyl rings linked to two mesitylene rings of the bimesityl core, while the remaining four use two pyridyl rings linked to the same mesitylene ring for coordinative covalent bonding. The 3D propagation of these adamantanoid units leads to a porous network as shown in Figure 3. Unfortunately, the porosity is destroyed by interpenetration of an independent second diamondoid network. The overall network is topologically equivalent to that resulting from the replacement of alternative tetrahedral nodes of an adamantanoid unit by D_{2d} -symmetric pairs of 3-connecting nodes as shown in Figure 1. When alternative tetrahedral nodes of an adamantanoid unit are replaced by pairs of 3-connecting nodes as those represented by the tpb ligands, the shortest circuit of the resultant (3,4)-connected net is an eight-membered ring leading to the topology of $(8^3_4)_b$. Indeed, this net was predicted by Wells 25 years ago and has surprisingly not been realized so far in metal-coordination chemistry.^[22] The Schläfli symbol for the network of **3** is $(8^3)_2(8^6)$, which illustrates that the shortest circuits meeting at both 3- and 4-connected points are eight-membered. This network is thus different from that of the ideal diamond net for which the Schläfli notation is 6^6 .

Compound **4** was obtained by slow diffusion of the methanolic solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ into a solution of *tpb* in CH_2Cl_2 . Single-crystal X-ray analysis^[24] of **4** revealed a coordination polymer in which the geometry of the metal ion is octahedral. Whereas the two Cl^- ions coordinate axially to the metal ion, the pyridyl rings of four distinct *tpb* ligands are found to occupy the equatorial positions about the metal center (Figure 4); the four metal-ion–pyridine–nitrogen bond

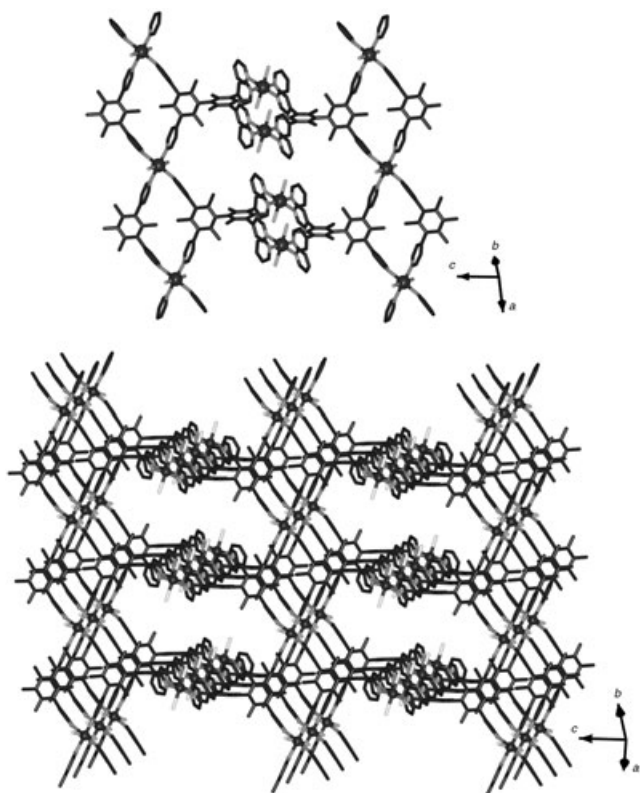


Figure 4. The PtS-related net of compound **4**, which undergoes interpenetration. The top picture is a basic unit of the network. Hydrogen atoms and the solvent molecules have been removed for clarity. The solid spheres represent metal cations.

lengths ($d_{\text{Mn-N}}$) are 2.318(1), 2.285(1), 2.257(1), and 2.332(1) Å. From the point of view of structural description of the coordination polymer, the metal ion may be considered equivalent to a 4-connecting square-planar node, as the Cl^- ions merely serve to fill the coordination sphere. Thus, the coordination polymer built up of 4-connecting D_{4h} -symmetric metal ions (by considering only pyridyl ligands) and a pair of 3-connecting *tpb* ligands shown in Figure 4 is precisely equivalent to the PtS network in which the tetrahedral ligand is replaced by a pair of 3-connecting ligand as exemplified in Figure 1. While the Schläfli notation for the ideal PtS network is 4^28^4 , that of the network of compound **4** is $(4.12^2)_2(4^2.12^4)$, which illustrates that the eight-membered ring in PtS net is replaced by a twelve-membered ring. Thus, the PtS-related net observed with **4** is unique and unknown. The network is twofold interpenetrated with solvent water molecules incorporated in the pores of the crystal lattice.

According to thermogravimetric analyses, the compounds **1**, **2**, and **4** lose their included solvent molecules upon heating. The complexes are stable after the initial loss of the solvent molecules up to about 340, 395, and 388 °C for **1**, **2**, and **4**, respectively (see Supporting Information). The porosity coupled with stability promises potential for their usage as storage devices.^[1a] The variation in the network topologies in going from Ag^I to Mn^{II} to $\text{Zn}^{II}/\text{Cd}^{II}$ centers must be due to the coordination preferences of the metal ions and the choice of the counteranions. While the preferred coordination geometry for an Ag^I center is tetrahedral, as is observed, the square-planar connectivity with the pyridyl ligands in the case of Mn^{II} complex is dictated by the two Cl^- ions that occupy the axial positions about the metal. The observed octahedral geometry about the $\text{Zn}^{II}/\text{Cd}^{II}$ ions must be connected with the ability of the perchlorate anions to reside away from the metal centers. We wish to point out that well-characterized hexapyridinate metal complexes are rare. We are aware of only one instance of a coordination polymer in which six pyridine ligands are octahedrally coordinated to the metal center.^[10a]

In summary, we have designed and synthesized a unique D_{2d} -symmetric tetratopic tetrapyridylbimesityl ligand, *tpb*, which can be readily used as a pair of 3-connecting nodes in coordination polymerization. Thus, it is shown that the combination of a D_{2d} -symmetric ligand with O_h , T_d , and D_{4h} metal centers leads to MOFs with the topologies related to those of corundum, diamond, and PtS, which have not previously been realized.

Experimental Section

1: A solution of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0341 g, 0.0915 mmol) in 10 mL of MeOH was layered over a solution of *tpb* (0.05 g, 0.0915 mmol) in 10 mL of CH_2Cl_2 , and the resultant solution was kept at room temperature. Colorless cubic crystals formed in 2 days (yield 60%). Elemental analysis (%) calcd for $\text{Zn}(\text{tpb})_{1.5}(\text{ClO}_4)_2 \cdot (\text{H}_2\text{O})_{12}$: C 52.72, H 5.82, N 6.47; found: C 52.65, H 5.16, N 6.20.

2: A similar procedure to that described above was applied with dichloroethane in place of CH_2Cl_2 to obtain colorless hexagonal crystals in 2 days. Elemental analysis (%) calcd for $\text{Cd}(\text{tpb})_{1.5}(\text{ClO}_4)_2 \cdot (\text{H}_2\text{O})_{13}$: C 50.13, H 5.68, N 6.15; found: C 49.85, H 5.71, N 6.12.

3: A methanolic solution of AgNO_3 (0.031 g, 0.183 mmol) in 10 mL) was added slowly to a solution of *tpb* (0.05 g, 0.0915 mmol) in 10 mL of MeOH. The container was closed tightly and kept in the dark. Colorless crystals were observed after 2–3 days and were isolated in about 55% yield in three independent experiments. These crystals turned brown when exposed to light and air.

4: A solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.0217 g, 0.0109 mmol) in 15 mL of MeOH was layered over a solution of *tpb* (0.03 g, 0.0549 mmol) in 10 mL of CH_2Cl_2 and the resultant solution was allowed to evaporate slowly over 10 days. Colorless crystals were obtained in 55% yield. Elemental analysis (%) calcd for $\text{Mn}(\text{tpb})(\text{Cl})_2(\text{CH}_3\text{OH})(\text{H}_2\text{O})_8$: C 55.72, H 5.52, N 6.66; found C 55.01, H 5.42, N 6.45.

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- [23] The synthesis of tetrapyridylbimesityl ligand, tpb, was accomplished starting from the readily synthesized bimesityl (P. Kovacic, C. Wu, *J. Org. Chem.* **1961**, *26*, 759–762). Tetraiodination of bimesityl by using iodine/H₂SO₄/HNO₃ yielded 3,3',5,5'-tetraiodobimesityl in 86% yield. Suzuki coupling of this compound with the 4-pyridineboronate ester 2-(4-pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane (6 equiv) in the presence of [Pd(PPh₃)₄] (5 mol %) and K₃PO₄ afforded **1** in 57% yield.
- [24] Crystal data for **1**: Moiety formula C₅₇H₅₁N₆Cl₂O_{9.5}Zn, cubic, space group *Ia3d* (no. 230); *a* = 32.198(4) Å, *V* = 33380.03(7) Å³, *Z* = 16; *T* = 100 K, μ = 0.358 mm⁻¹; *R*₁ = 0.0709, *wR*₂ = 0.1802 (*I* > 2σ(*I*)), *S* = 0.831, data/restraints/parameter = 1467/54/101. Crystal data for **2**: Moiety formula C₅₇H₅₁N₆Cl₂O_{9.5}Cd, cubic, space group *Ia3d* (no. 230); *a* = 32.727(4) Å, *V* = 35052.82(7) Å³, *Z* = 16; *T* = 100 K, μ = 0.310 mm⁻¹; *R*₁ = 0.0728, *wR*₂ = 0.1741 (*I* > 2σ(*I*)), *S* = 0.670, data/restraints/parameter = 1525/54/89. Out of the expected 32 perchlorate ions in the unit cell of each of the Zn and Cd compounds (**1** and **2**), only 16 could be located. The solvent molecules and the remaining counteranions that reside in the regions of diffuse electron density were treated by the Platon/Squeeze procedure (A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13), which suggested, after accounting for the missing counteranions, a solvent accessible volume of about 44% and 46% in the case of **1** and **2**, respectively. Crystal data for **3**: Moiety formula C₃₉H₃₈N₅O₄Ag, monoclinic, space group *C2/c* (no. 15); *a* = 21.169(4), *b* = 17.027(3), *c* = 16.501 Å(3), *V* = 4580.79(1) Å³, *Z* = 4; *T* = 100 K, μ = 0.463 mm⁻¹; *R*₁ = 0.1296, *wR*₂ = 0.2126 (*I* > 2σ(*I*)), *S* = 1.160, data/restraints/parameter = 2216/0/223. Crystal data for **4**: Moiety formula C₃₉H₃₄N₄Cl₂O₆Mn, monoclinic, space group *C2/c* (no. 15); *a* = 20.9751(1), *b* = 15.3662(1), *c* = 25.8748(1) Å, *V* = 8196.9(1) Å³, *Z* = 8; *T* = 100 K; *R*₁ = 0.0919, *wR*₂ = 0.2668 (*I* > 2σ(*I*)), *S* = 1.062, data/restraints/parameter = 10056/0/420. Structure solutions were done by direct methods and refinements on *F*² with Shelxtl. Non-hydrogen atoms were refined anisotropically and H-atoms were generated at idealized geometries and refined isotropically. The hydrogen atoms for the solvent molecules were not fixed. CCDC-216293 and CCDC-247028–247030 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.