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ARTICLE TYPE

Stepwise formation of heteronuclear coordination networks based on quadruple-bonded dimolybdenum units containing formamidinate ligands

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Reactions of [Mo_2(4-pyf)$_4$] (4-Hpyf = 4-pyridylformamidine) with HgX_2 (X = Cl, Br and I) afforded the first 2D and 3D heteronuclear coordination networks based on quadruple-bonded dimolybdenum units.

Coordination polymers have attracted much attention not only due to their numerous potential applications in catalysis, separation, storage and optics, but also their intriguing structure and diverse topologies.[1] The coordination ability, geometry, and relative orientation of the donor group of the organic ligand, as well as the natures of the metal ions and counterions, play important roles in constructing the framework topologies.[2] Most of the coordination polymers reported so far are of homometallic type, whereas the heterometallic networks involving two or more different metal ions are rare, and the control of their structural dimensionality remains a challenge.[3]

The paddle-wheel motif comprising two metal centers bridged by four carboxylate or symmetry-related ligands have been investigated extensively, which can be used as a secondary building unit in the formation of 1D, 2D and 3D-coordination polymers.[4] In nearly all cases, the paddle-wheel secondary building units were formed *in situ*.[4a] Most of the coordination polymers based on the multiple-bonded paddle-wheel motif reported so far show the spacer ligands in the axial positions of the paddlewheel motif, Fig. 1(a). For examples, the 1D structures of the type [$Mo_2(O_2CR)_4$(linker)]$_n$ (R = CH_3 and CF_3) comprise an infinite array of $Mo_2(O_2CR)_4$ units bridged by various linkers.[5,6] 1D heteronuclear chain has been reported for [{$Rh_2(O_2CMe)_4$}{Mo_2(TiPB)$_2$(nic)$_2$}]$_\infty$, in which axial ligation of the nic$^-$ to the Rh_2^{4-} unit was shown.[7] In the other type of bonding mode, Fig. 1(b), the paddlewheel unit acts as both a donor and a acceptor, which can be seen in the 3D structure of [Mo_2(TiPB)$_2$(nic)$_2$]$_n$, (TiPB = 2,4,6-triisopropylbenzoate, nic = 4-isonicotinate),[7] and the 2D layer of {Mo_2[μ-$O_2CC_6H_4$-4-P(O)Ph_2]$_4$·4EtOH}$_n$.[8] The 3D quadruple-bonded metal-organic framework TUDMOF-1[9a] formed via equatorial linkage of *in situ* formed paddlewheel units has been shown to be isostructural to [$Cu_3(BTC)_2$] (H_3BTC = 1,3,5-benzenetricarboxylic acid)[9b] and [$Cr_3(BTC)_2$].[9c]

The coordination chemistry of metal complexes containing formamidinate ligands has been investigated extensively during

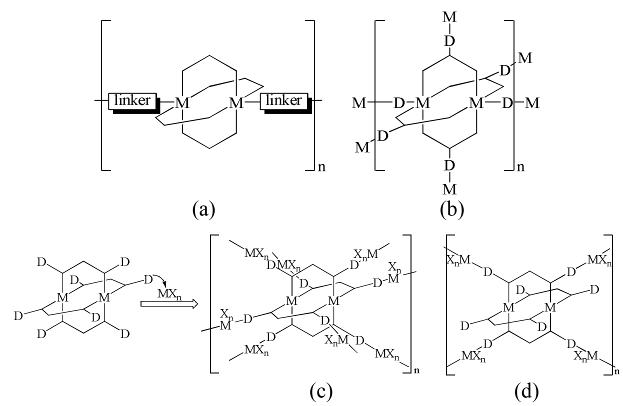
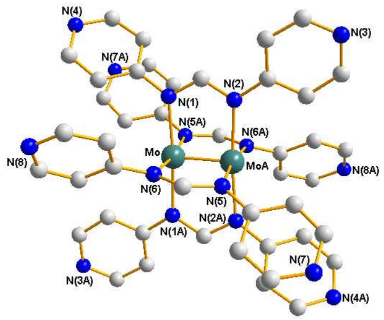


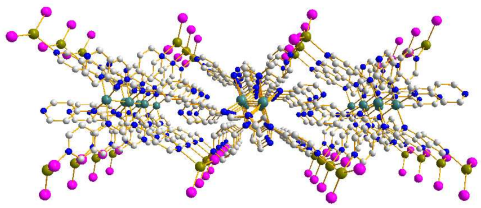
Fig. 1 (a) and (b) Representative structures for coordination polymers containing multiple-bonded paddlewheel motif. (c) and (d) Schematic drawings for the complexes **2** – **4**.

recent years.[10] We have reported several trinuclear and tetranuclear Cu(I) and Cu(II) complexes containing anions of *N,N'*-bis(pyrimidine-2-yl)formamidine (Hpmf).[11] Obviously, this type of formamidinate ligands could be improved by having different directions of donor sites to construct coordination polymers with higher dimensionality. By taking account of the above-mentioned factors, we designed and synthesized the dimolybdenum paddlewheel complex [Mo_2(4-pyf)$_4$] (4-Hpyf = 4-pyridylformamidine),[12] which can form a maximum of 8-connection node by the coordination of the dangling pyridyl nitrogen atoms to the other metal complexes, thus forming heteronuclear coordination polymers with higher dimensionalities, as shown in Fig. 1(c) and 1(d).

The reaction of [$Mo_2(O_2CCH_3)_4$] with *in situ* prepared lithium salt Li(4-pyf) in THF gave [Mo_2(4-pyf)$_4$], **1**. Reactions of **1** with $HgBr_2$ and HgI_2 afforded {[Mo_2(4-pyf)$_4$($HgBr_2$)$_2$]·(CH_3OH)}$_n$, **2**, and {[Mo_2(4-pyf)$_4$(HgI_2)$_2$]·(CH_3OH)}$_n$, **3**, respectively, whereas the reaction of **1** with $HgCl_2$ gave [Mo_2(4-pyf)$_4$($HgCl_2$)$_{3.6}$]$_n$, **4**. Complexes **2** – **4** are insoluble in most of the common solvents. Their structures have been characterized by X-ray crystallography and the purities of **2** – **4** checked by the powder XRD patterns, Fig. S1 – Fig. S3. Several molar ratios of HgX_2 to **1** have been used to prepare complexes **2** – **4**. The crystals from each experiment have been rechecked by X-ray crystallography,



(a)



(b)

Fig. 2 (a) The structure of complex **1**. (b) A representative structure for complexes **2** and **3**.

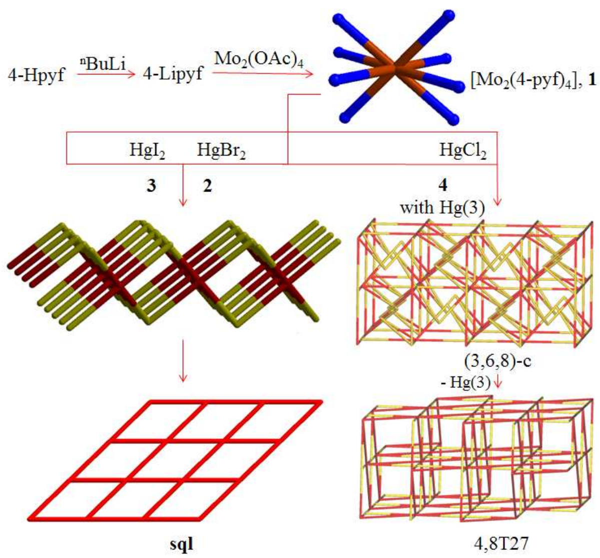
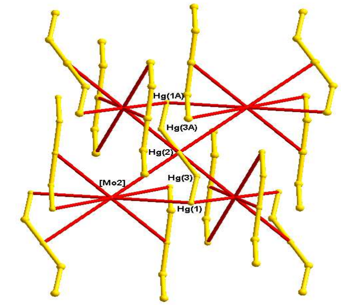
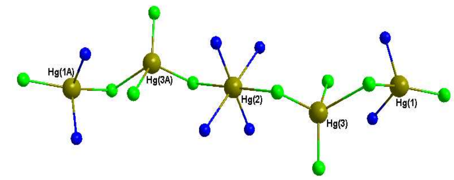


Fig. 3 Stepwise formation for complexes **1** – **4**.

showing the formation of the same compound but with different yields. The molar ratios that gave higher yields are 3 for complexes **2** and **3** and 6 for **4**, respectively; see experimental details in ESI and Table S1. In the structure of **4**, the site for one of the $HgCl_2$ units, the one involving Hg(3), is occupied only at 30%, which is verified both by X-ray crystallography and elemental analysis. To further confirm the mercury content in the compound, we used SEM-EDS (Scanning Electron Microscopy, Energy Dispersive X-ray Spectrometry) to measure the molar ratio of Hg to Mo (Hg/Mo ratio) for the crystalline samples of **2** - **4**. The result shows that the Hg/Mo ratios of **4** from three samples are 1.75, 1.76 and 1.82, respectively, which are similar to the ratio of 1.8 found crystallographically, indicating the existence of one $HgCl_2$ position partially occupied, Fig. S4, Fig. S5 and Table S2. The absorption spectrum of **1** in CH_2Cl_2 show the lowest



(a)



(b)

Fig. 4 (a) A schematic drawing of **4** containing Hg(3), where $[Mo_2]$ represents the center of $Mo_2(4\text{-pyf})_4$. (b) The pentanuclear chain. The pyf⁻ ligands are represented by their nitrogen atoms

energy band at 467 nm (ε = 4733 $M^{-1}cm^{-1}$), Fig. S6, whereas those of **1** – **4** show the lowest energy bands in the solid state at 518, 554, 594 and 572 nm, respectively, Fig. S10, which can be assigned to the $\delta \rightarrow \delta^*$ transitions.[10]

The structures of **1** – **3** are shown in Fig. 2 and the coordination environments about the Mo(II) ions for **1** – **4** are shown in Fig. S11 – Fig. S14. The dimolybdenum moieties of **1** – **4** are all spanned by four 4-pyf⁻ ligands, forming the paddle-wheel type structures with the Mo-N bond distances in the range of 2.1434(17) – 2.1943(17) Å. The Mo-Mo bond distances of **1** – **4** are 2.0914(3), 2.0948(11), 2.0965(11) and 2.0990(18) Å, and the torsional angles looking down the Mo-Mo bonds are 4.0, 3.6, 3.5 and 1.6°, respectively. The small torsional angles indicate that the dimolybdenum units are supported by the quadruple bonds,[10] and the coordination of mercury(II) halide to **1** hardly changes the bond strength of the quadruple bond. The Hg-N distances in **2** – **4** are in the range 2.268(10) – 2.550(10) Å that are shorter than the upper limit of 2.75 Å for the Hg-N bond,[13] and can be regarded as bonds.

In the isomorphous complexes **2** and **3**, four mercury(II) halide molecules are coordinated to the pyridyl nitrogen atoms of two *trans* 4-pyf⁻ ligands [Hg-N = 2.372(6) and 2.425(7) Å for **2**; 2.397(6) and 2.455(7) Å for **3**], leaving the other two *trans* 4-pyf⁻ ligands non-coordinated, Fig. 1(d), and resulting in a 2D double layer with 1D channels, Fig. 2(b). Guest methanol molecules reside in the voids of **2** and **3** and the solvent-accessible volumes calculated by PLATON[15] program are 380.5 and 406 $Å^3$, which occupy 14.0 and 14.4 % of the unit cell volumes, respectively. Using TOPOS[14] we can simplify both complexes **2** and **3** to their underlying topology considering the dimolybdenun unit as 4-connected node and mercury(II) halides as spacer, as result we get square layers (**sql**) packing as ABAB (left side of Fig. 3). In marked contrast to the 2D structures of **2** and **3**, complex **4** forms a 3D coordination network, in which eight $HgCl_2$ molecules involving four Hg(1) [Hg-N = 2.40(2) and 2.361(12) Å] and four Hg(2) [Hg-N = 2.268(10) and 2.550(10) Å] are coordinated to the pyridyl nitrogen atoms of the four 4-pyf⁻ ligands of the [Mo₂(4-

pyf)$_4$] unit, Fig. 1(c) and Fig. S9. Due to the existence of the partially occupied positions for the $HgCl_2$ units that involve Hg(3), two structural types can be evaluated. The inclusion of partially occupied molecules to the 3D framework generates pentanuclear Hg_5Cl_{10} chain, with the Hg-Cl distances in the range 2.279(16) – 2.785(5) Å that can be considered as bonds,[16] Fig. 4(a) and 4(b), resulting in a novel 3,6,8-connected trinodal net with point symbol $(3^2{\cdot}4)_2(3^4{\cdot}4^2{\cdot}6^3{\cdot}7^4{\cdot}8^2)(3^4{\cdot}6^9{\cdot}7^9{\cdot}8^5{\cdot}9)$, Fig. 3. In a more conservative view, if Hg(3) is not considered, the underlying net becomes the binodal (4,8)-c 4,8T27 with point symbol $(3^2{\cdot}5^3{\cdot}6)(3^4{\cdot}4^4{\cdot}5^{12}{\cdot}6^7{\cdot}7)$, which is reported in the TTO database[17] of TOPOS for a copper coordination network.[18]

In summary, the first 2D and 3D heteronuclear coordination networks based on the quadruple-bonded dimolybdenum units containing the formamidinate ligands have been successfully accomplished by the stepwise reactions of the paddlewheel unit **1** and mercury(II) halide. The molar ratio of Mo and Hg in **4** derived from SEM-EDS matches quite well with that from single crystal X-ray crystallography. The structural types of **2** – **4** are subject to the change of the halide anions. The bromide and iodide anions play the same role in the crystal structures, while the chloride anion is distinct, suggesting that the size of the halide anion is one of the structure-determining factors.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental datils. Powder XRD patterns (Fig. S1– Fig. S3). SEM images and EDS spectra (Fig. S4 – Fig. S5). Solution and solid state UV-vis spectra of starting materials and **1** - **4** (Fig. S6 – S10). ORTEP drawings (Fig. S11– Fig. S14). Conditions of experiments (Table S1). SEM-EDS molar ratios (Table S2). CCDC 965985-965988. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

‡ Synthesis of **1**: **1** was prepared by mixing Li(4-pyf) (0.40 g, 2.02 mmol of 4-Hpyf and 0.8 mL of 2.5 M ^{n}BuLi in 20 mL THF) and $Mo_2(OAc)_4$ (0.22 g, 0.51 mmol in 10 mL THF) at -78 °C. Yield: 0.36 g (73%). ^1H NMR (400 MHz, *δ*, ppm in $CDCl_3$): 8.7273 (s, 1 H, C-*H*), 8.2358 (d, 4 H, py), 6.1346 (d, 4 H, py). Anal. Calcd. for $C_{44}H_{36}N_{16}Mo_2$: C, 53.88; H, 3.70; N, 22.85. Found: C, 53.96; H, 3.53; N, 22.79%. **2** and **3**: A methanol solution of $HgBr_2$ (0.34 g, 0.94 mmol) or HgI_2 (0.41 g, 0.90 mmol) was layered on top of a dichloromethane solution of **1** (0.30 g, 0.31mmol). After a week, plate yellow crystals were found at the interface. Yield: 0.44 g (80%) for **2**. Anal. Calcd. for $C_{22.5}H_{20}N_8MoHgBr_2O_{0.5}$: C, 31.18; H, 2.33; N, 12.93. Found: C, 30.38; H, 2.06; N, 12.15%. Yield: 0.37 g (61%) for **3**. Anal. Calcd. for $C_{22.5}H_{20}N_8O_{0.5}MoHgI_2$: C, 28.13; H, 2.10; N, 11.66. Found: C, 28.55; H, 1.98; N, 11.97%. **4**: An acetonitrile solution of $HgCl_2$ (0.50 g, 1.84 mmol) was layered on top of a dichloromethane solution of **1** (0.30 g, 0.31 mmol). After two weeks, arborization like of sorrel crystals were found. Yield: 0.31 g (51%). Anal. Calcd. for $C_{22}H_{18}N_8MoHg_{1.8}Cl_{3.6}$: C, 26.99; H, 1.85; N, 11.44. Found: C, 26.54; H, 1.85; N, 11.93%. Crystal data for **1**: $C_{44}H_{36}Mo_2N_{16}$, M = 980.77, orthorhombic, space group *Pccn*, a = 17.9447(4), b = 19.1082(4), c = 11.5533(2) Å, $\alpha = \beta = \gamma$ = 90°, V = 3961.52(14) Å^3, T = 296(2) K, Z = 4, D_c = 1.644 g cm^{-3}, μ = 0.691 mm^{-1}, 34032 collected reflections, 4935 independent (R_{int} = 0.0437), GOF = 1.018, R_1 = 0.0289, wR_2 = 0.0591 for $I > 2\sigma(I)$ and R_1 = 0.0525, wR_2 = 0.0673 for all data. Crystal data for **2**: $C_{22.5}H_{20}Br_2HgMoN_8O_{0.5}$, M = 866.82, monoclinic, space group $P2_1/n$, a = 14.9903(8), b = 9.2196(5), c = 20.0369(11) Å, $\alpha = \gamma$ = 90°, β = 101.615(3) °, V = 2712.5(3) Å^3, T = 296(2) K, Z = 4, D_c = 2.123 g cm^{-3}, μ = 9.090 mm^{-1}, 39876 collected reflections, 5344 independent (R_{int} = 0.0826), GOF = 1.025, R_1 = 0.0458, wR_2 = 0.1127 for $I > 2\sigma(I)$ and R_1 = 0.0770, wR_2 = 0.1275 for all data. Crystal data for **3**: $C_{22.5}H_{20}HgI_2MoN_8O_{0.5}$, M = 960.8, monoclinic, space group $P2_1/n$, a = 15.3948(3), b = 9.2721(2), c = 20.2932(3) Å, $\alpha = \gamma$ = 90°, β = 103.0880(1) °, V = 2821.45(9) Å^3, T = 298(2) K, Z = 4, D_c = 2.262 g cm^{-3}, μ = 8.096 mm^{-1}, 21153 collected reflections, 5544 independent (R_{int} = 0.0476), GOF = 1.060, R_1 = 0.0497, wR_2 = 0.1496 for $I > 2\sigma(I)$ and R_1 = 0.0605, wR_2 = 0.1618 for all data. Crystal data for **4**: $C_{44}H_{36}Cl_{7.2}Hg_{3.6}Mo_2N_{16}$, M = 1958.13, monoclinic, space group $P2_1/n$, a = 12.8206(7), b = 12.7766(7), c = 17.2962(9) Å, $\alpha = \gamma$ = 90°, β = 95.517(2) °, V = 2820.1(3) Å^3, T = 99(2) K, Z = 2, D_c = 2.306 g cm^{-3}, μ = 10.584 mm^{-1}, 22370 collected reflections, 5535 independent (R_{int} = 0.0430), GOF = 1.043, R_1 = 0.0598, wR_2 = 0.1541 for $I > 2\sigma(I)$ and R_1 = 0.0742, wR_2 = 0.1631 for all data.

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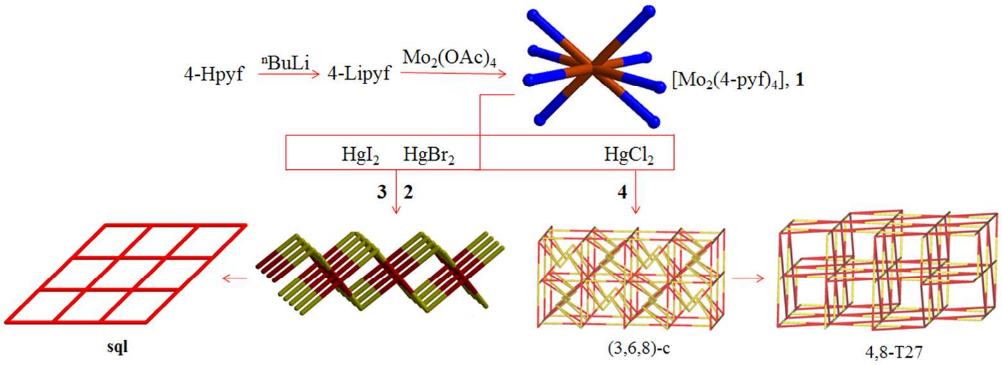

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