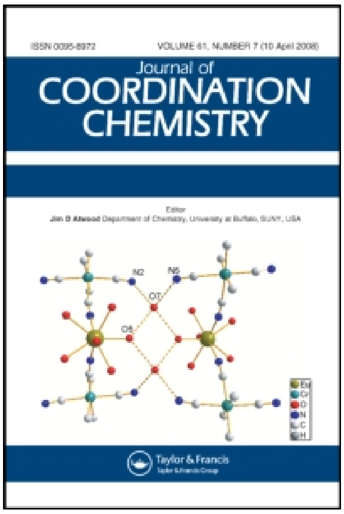

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# Solid state structures of the chiral heterobimetallic complexes $[Cu(dach)_2][Pt(CN)_4] \cdot 2H_2O$, $[Ni(dach)_3][Pt(CN)_4] \cdot 2DMF \cdot H_2O$, and $[Pd(dach)_2][Pt(CN)_4] \cdot H_2O$ (dach = 1<i>R</i>, 2<i>R</i>-diaminocyclohexane)

Fenghui Liu[a]; Wanzhi Chen[a]
[a] Department of Chemistry, Zhejiang University, Hangzhou 310023, China

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# Solid state structures of the chiral heterobimetallic complexes $[Cu(dach)_2][Pt(CN)_4] \cdot 2H_2O$, $[Ni(dach)_3][Pt(CN)_4] \cdot 2DMF \cdot H_2O$, and $[Pd(dach)_2][Pt(CN)_4] \cdot H_2O$ (dach = 1*R*, 2*R*-diaminocyclohexane)

FENGHUI LIU and WANZHI CHEN*

Department of Chemistry, Zhejiang University, Xixi campus, Hangzhou 310023, China

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The chiral dinuclear heterometallic complexes $[Cu(dach)_2][Pt(CN)_4] \cdot 2H_2O$ (**1**), $[Ni(dach)_3][Pt(CN)_4] \cdot 2DMF \cdot H_2O$ (**2**), and $[Pd(dach)_4][Pt(CN)_4] \cdot H_2O$ (**3**) (dach = 1*R*,2*R*-cyclohexanediamine) have been prepared and characterized by X-ray diffraction analysis. Crystal data: **1**, monoclinic, $P2_1$, $a = 8.108(3)$, $b = 15.552(6)$, $c = 9.914(4)$ Å, $\beta = 110.931(6)°$, $V = 1167.6(8)$ Å$^3$, $Z = 2$, $R_1 = 0.0420$, $wR_2 = 0.1122$; **2**, monoclinic, $P2_1$, $a = 13.264(11)$, $b = 9.285(7)$, $c = 16.211(13)$ Å, $\beta = 111.640(9)°$, $V = 1856(3)$ Å$^3$, $Z = 2$, $R_1 = 0.0276$, $wR_2 = 0.0698$; **3**, monoclinic, $P2_1$, $a = 6.887(2)$, $b = 12.809(4)$, $c = 12.975(4)$ Å, $\beta = 94.865(4)°$, $V = 1140.6(6)$ Å$^3$, $Z = 2$, $R_1 = 0.057$, $wR_2 = 0.156$. In complex **1**, the Pt and Cu atoms are linked by a CN bridge that presents a very bent C=N–Cu angle [136.8(8)°].

*Keywords:* Chiral complexes; Platinum; Copper; Nickel; Palladium; 1*R*,2*R*-diaminocyclohexane

## 1. Introduction

Transition metal complexes of cyanide have received a great deal of attention mainly because of their physical properties [1–3]. The ability of the cyano group to link various central metal atoms is used in organometallic and coordination chemistry for the construction of various molecular assemblies and in the field of supramolecular chemistry for building multidimensional coordination polymers. The variety of metal coordination geometries, as well as ligand size, shape, and functionality, has led to the generation of a large number of 1-, 2- and 3-dimensional materials [4–6].

It is well-known that $[Pt(CN)_4]^{2-}$ has the ability to form columnar structures with metal–metal interactions in both simple salts and one-dimensional conducting

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*Corresponding author. Email: chenwzz@zju.edu.cn

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materials [7]. Similarly, pseudo-closed-shell $d^8$ ions such as platinum(II) also show a proclivity to interact through weak Pt–Pt bonds. Such interactions are seen in dimeric complexes such as $[Pt_2(P_2O_2H_2)_4]^{4-}$ [8], in the extended chain structures present in a variety of salts of $[Pt(CN)_4]^{2-}$ [9] and in double salts such as Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$ [10]. $[Pt(CN)_4]^{2-}$ has also been used as a building block for the synthesis of multi-dimensional materials, due to the ability of the four cyano groups to connect various transition metal ions [11]. $[Pt(CN)_4]^{2-}$ may act as a *cis* bidentate bridging unit between two octahedrally coordinated nickel atoms [12] and a *trans* bidentate bridging unit between two organotin groups [13]. Recently, salts of $[Pt(CN)_4]^{2-}$ and $[Au(CN)_2]^-$ have been shown to display interesting properties used for gas sensing [14, 15].

In addition, the use of chiral transition metal complexes as catalysts for enantioselective organic transformations continues to be an area of intense research. Materials based on chiral transition metal complexes may also be applicable to the development of new optoelectronic devices. Here, we report the preparation and solid-state characterization of the chiral dinuclear complexes $[Cu(dach)_2][Pt(CN)_4]\cdot 2H_2O$, $[Ni(dach)_3][Pt(CN)_4]\cdot 2DMF\cdot H_2O$, and $[Pd(dach)_2][Pt(CN)_4]\cdot H_2O$ (dach = 1*R*,2*R*-diaminocyclohexane).

## 2. Experimental

All reagents and solvents were commercially available and used without further purification. C, H, and N microanalyses were performed with a Perkin Elmer 2400II CHNO/S instrument. FT-IR spectra were recorded in the range 4000–400 $cm^{-1}$ on a Shimadzu FTIR-8900 spectrometer using the KBr pellet technique.

### 2.1. $[Cu(dach)_2][Pt(CN)_4]\cdot H_2O$ (1)

To a mixture of $CuSO_4\cdot 5H_2O$ (0.25 g, 1.0 mmol) and 1*R*,2*R*-diaminocyclohexane (0.23 g, 2.0 mmol) in 6 $cm^3$ of $H_2O$ was added $K_2[Pt(CN)_4]\cdot 3H_3O$ (0.43 g, 1.0 mmol). A blue solid was immediately precipitated. Addition of acetone dissolved the precipitate and slow evaporation of the solution yielded blue crystals in 72% yield. Anal. Calcd for $C_{16}H_{32}CuN_8O_2Pt$ (%): C, 30.64; H, 5.14; N, 17.87. Found: C, 30.82; H, 5.02; N, 18.25.

### 2.2. Preparation of $[Ni(dach)_3][Pt(CN)_4]\cdot 2DMF\cdot H_2O$ (2)

To a mixture of $Ni(NO_3)_2\cdot 6H_2O$ (0.29 g, 1.0 mmol) and 1*R*,2*R*-diaminocyclohexane (0.23 g, 2.0 mmol) in 6 $cm^3$ of $H_2O$ was added $K_2[Pt(CN)_4]\cdot 3H_3O$ (0.43 g, 1.0 mmol). The resulting violet solid was collected by filtration, and washed by water and EtOH. The crude product was then dissolved in hot DMF. Violet crystals were obtained during one week in 24% yield. Anal. Calcd for $C_{28}H_{58}N_{12}NiO_3Pt$ (%): C, 38.90; H, 6.76; N, 19.44. Found: C, 38.66; H, 6.92; N, 19.17.

### 2.3. $[Pd(dach)_2][Pt(CN)_4]\cdot 2H_2O$ (3)

To a mixture of $K_2PdCl_4$ (0.33 g, 1.0 mmol) and 1*R*,2*R*-diaminocyclohexane (0.23 g, 2.0 mmol) in $cm^3$ of $H_2O$ was added $K_2[Pt(CN)_4]\cdot 3H_3O$ (0.43 g, 1.0 mmol).

An off-white solid was immediately formed. Addition of acetone dissolved the precipitate and slow evaporation of the solution yielded colourless crystals in 84% yield. Anal. Calcd for $C_{16}H_{30}N_8OPdPt$ (%): C, 29.48; H, 4.64; N, 17.19. Found: C, 29.10; H, 4.52; N, 17.63.

### 2.4. *Crystallographic data collection and structure determination*

Suitable crystals were mounted on glass fibres on a Bruker SMART 1000 CCD diffractometer using Mo-K$\alpha$ radiation (0.71073 Å). Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction was performed using SMART and SAINT software [16]. The structures were solved by direct methods, and non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares methods on $F^2$ using SHELXTXL [17]. Hydrogen atoms were generated geometrically and included in the structure factor calculations. Crystal data and refinement details are given table 1. Atomic coordinates of complexes **1–3** are given in tables 2–4, respectively.

## 3. Results and discussion

### 3.1. *Preparation of complexes*

Reactions of $K_2[Pt(CN)_4]$ with the $[M(dach)_x]^{2+}$ (M = Cu, Ni, Pd), which were formed *in situ* from $M^{2+}$ and two equivalent of 1*R*,2*R*-diaminocyclohexane in water, afforded $[Cu(dach)_2][Pt(CN)_4] \cdot 2H_2O$ (**1**), $[Ni(dach)_3][Pt(CN)_4] \cdot 2DMF{\cdot}H_2O$ (**2**), and $[Pd(dach)_2][Pt(CN)_4] \cdot H_2O$ (**3**). In the case of nickel, $[Ni(dach)_3]^{2+}$ was obtained although only two equivalent of dach were used. The reactions were carried out in aqueous solution, but

Table 1. Crystal data and structure refinement for complexes **1–3**.

| | 1 | 2 | 3 |
|---|---|---|---|
| Empirical formula | $C_{16}H_{32}CuN_8O_2Pt$ | $C_{28}H_{58}N_{12}NiO_3Pt$ | $C_{16}H_{30}N_8OPdPt$ |
| Formula weight | 627.13 | 864.66 | 651.97 |
| Temperature (K) | 293(29) | 123(2) | 173(2) |
| Crystal size (mm$^3$) | 0.37 × 0.46 × 0.63 | 0.10 × 0.18 × 0.27 | 0.10 × 0.28 × 0.41 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1$ | $P2_1$ | $P2_1$ |
| $a$ (Å) | 8.108(3) | 13.264(11) | 6.887(2) |
| $b$ (Å) | 15.552(6) | 9.285(7) | 12.809(4) |
| $c$ (Å) | 9.914(4) | 16.211(13) | 12.975(4) |
| $\beta$ (°) | 110.931(6) | 111.640(9) | 94.865(4) |
| $V$ (Å$^3$) | 1167.6(8) | 1856(3) | 1140.6(6) |
| $Z$ | 2 | 2 | 2 |
| $D_c$ (Mg m$^{-3}$) | 1.784 | 1.547 | 1.898 |
| Reflections collected | 6941 | 5214 | 3545 |
| Independent reflections ($R_{int}$) | 4224(0.0674) | 3752(0.0224) | 2602(0.0502) |
| Goodness-of-fit on $F^2$ | 1.031 | 1.036 | 1.094 |
| $R$ indices [$I > 2\sigma(I)$] | 0.0368, 0.0942 | 0.0276, 0.0698 | 0.057, 0.1560 |
| $R$ indices (all data) | 0.0427, 0.1127 | 0.0287, 0.0731 | 0.0574, 0.1564 |
| Abs. struc. parameter | 0.003(10) | 0.00 | 0.00 |
| Largest diff. peak and hole (e Å$^{-3}$) | 1.524, −1.525 | 1.050, −1.176 | 1.344, −1.683 |

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathrm{\AA}^2 \times 10^3$) for **1**. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ |
|---|---|---|---|---|
| C(1) | 8577(10) | 3146(4) | 10527(8) | 34(1) |
| C(2) | 9499(10) | 1706(5) | 12444(8) | 38(2) |
| C(3) | 12962(9) | 1869(5) | 12710(8) | 36(1) |
| C(4) | 12043(9) | 3271(5) | 10700(9) | 39(2) |
| C(5) | 6925(12) | 6184(5) | 10768(8) | 40(2) |
| C(6) | 5447(11) | 5568(5) | 10717(9) | 41(2) |
| C(7) | 4038(14) | 6009(8) | 11139(12) | 58(2) |
| C(8) | 4870(20) | 6433(11) | 12628(14) | 81(4) |
| C(9) | 6342(18) | 7080(8) | 12648(13) | 76(3) |
| C(10) | 7732(15) | 6598(8) | 12243(11) | 62(3) |
| C(11) | 8396(11) | 4001(5) | 6888(8) | 38(2) |
| C(12) | 6550(12) | 4217(6) | 5891(9) | 43(2) |
| C(13) | 5845(14) | 3553(8) | 4661(10) | 63(3) |
| C(14) | 7171(18) | 3481(9) | 3844(12) | 73(3) |
| C(15) | 8998(19) | 3272(8) | 4845(12) | 70(3) |
| C(16) | 9685(14) | 3929(7) | 6065(11) | 56(2) |
| Cu(2) | 6846(1) | 4885(1) | 8678(1) | 33(1) |
| N(1) | 7385(9) | 3571(5) | 9938(9) | 48(2) |
| N(2) | 8776(13) | 1191(6) | 12880(12) | 61(2) |
| N(3) | 14157(9) | 1459(8) | 13358(8) | 58(3) |
| N(4) | 12677(13) | 3744(7) | 10114(12) | 72(3) |
| N(5) | 8201(8) | 5701(4) | 10281(7) | 37(1) |
| N(6) | 4753(8) | 5165(4) | 9247(7) | 37(1) |
| N(7) | 8916(9) | 4669(5) | 8031(8) | 39(1) |
| N(8) | 5435(9) | 4276(5) | 6809(8) | 42(1) |
| O(1) | 7307(9) | 564(6) | 4859(9) | 66(2) |
| O(2) | 859(13) | 4817(7) | 2589(10) | 100(4) |
| Pt(1) | 10783(1) | 2505(1) | 11604(1) | 31(1) |

addition of acetone is necessary to increase the solubility of certain complexes formed. Complexes **1** and **3** are moderately soluble in acetone and methanol, but **2** is only soluble in hot DMF. They are stable in the solid states. The structures of **1–3** were characterized by X-ray diffraction analysis since NMR spectroscopy is not definitive for these complexes.

### 3.2. *Structure of [Cu(dach)$_2$][Pt(CN)$_4$]•2H$_2$O (1)*

The structure is shown in figure 1, and selected bond distances and angles are summarized in table 5. The compound is composed of $[\mathrm{Pt(CN)_4}]^{2-}$ and $[\mathrm{Cu(dach)_2}]^{2+}$ ions held together by a bridging cyanide group. The copper ion is thus coordinated by four $NH_2$ groups and the cyanide bridge, forming a square pyramid. Pt–C(bridge) and Pt–C(terminal) bond distances do not display any significant difference, being in the range of 1.968(10) to 2.000(10) Å. The C≡N distance of the bridging cyanide [1.170(15) Å] is the longest of the four CN distances, suggesting some electron delocalization.

Although $[\mathrm{M(CN)_4}]^{2-}$ units (M = Ni, Pd, and Pt) often act as multidentate linkers to form extended bimetallic networks [11], in **1** only one of the four terminal cyanide of $[\mathrm{Pt(CN)_4}]^{2-}$ acts as a bridge to yield a discrete dinuclear complex. Another feature of the compound is that it contains a severely bent C≡N–Cu bridge. This

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ |
|---|---|---|---|---|
| C(1) | 3906(5) | 4120(20) | 1390(4) | 25(2) |
| C(2) | 5674(8) | 3548(9) | 2995(5) | 29(2) |
| C(3) | 4266(6) | 3926(11) | 3945(5) | 22(2) |
| C(4) | 2645(7) | 4832(9) | 2372(5) | 25(2) |
| C(5) | 7032(6) | 9390(12) | 3589(5) | 22(2) |
| C(6) | 6889(5) | 7750(9) | 3423(5) | 23(2) |
| C(7) | 7913(6) | 7050(10) | 3390(6) | 36(2) |
| C(8) | 8916(6) | 7419(12) | 4212(7) | 47(3) |
| C(9) | 9050(5) | 8983(17) | 4351(5) | 36(3) |
| C(10) | 8034(6) | 9684(10) | 4419(5) | 34(2) |
| C(11) | 3997(9) | 10045(13) | 733(7) | 21(2) |
| C(12) | 3814(8) | 8419(12) | 682(7) | 21(2) |
| C(13) | 2981(6) | 7946(10) | −195(5) | 27(2) |
| C(14) | 3261(9) | 8473(14) | −972(7) | 32(3) |
| C(15) | 3403(10) | 10083(14) | −944(8) | 32(3) |
| C(16) | 4211(7) | 10624(9) | −61(5) | 29(2) |
| C(17) | 3244(9) | 9916(13) | 3504(8) | 25(3) |
| C(18) | 3159(9) | 8291(12) | 3475(7) | 21(2) |
| C(19) | 2875(7) | 7710(11) | 4245(6) | 34(2) |
| C(20) | 1802(12) | 8364(18) | 4213(11) | 44(4) |
| C(21) | 1837(12) | 9984(19) | 4228(10) | 44(4) |
| C(22) | 2147(7) | 10586(10) | 3485(6) | 35(2) |
| C(23) | −776(7) | 3525(11) | 8874(6) | 40(2) |
| C(24) | 811(9) | 4530(20) | 9996(8) | 83(7) |
| C(25) | 953(9) | 2295(14) | 9230(9) | 64(3) |
| C(26) | 8936(8) | 1525(16) | 2509(8) | 60(3) |
| C(27) | 9678(12) | 3903(16) | 2924(9) | 81(4) |
| C(28) | 9989(8) | 2586(15) | 1737(8) | 65(3) |
| N(1) | 3711(4) | 4123(18) | 636(4) | 34(1) |
| N(2) | 6590(6) | 3206(9) | 3172(5) | 42(2) |
| N(3) | 4290(6) | 3820(9) | 4639(5) | 39(3) |
| N(4) | 1794(6) | 5346(9) | 2236(5) | 40(2) |
| N(5) | 6014(5) | 9966(7) | 3624(4) | 23(1) |
| N(6) | 5934(5) | 7557(7) | 2606(4) | 22(1) |
| N(7) | 4870(4) | 10358(7) | 1593(4) | 20(1) |
| N(8) | 3562(5) | 7971(7) | 1459(4) | 21(1) |
| N(9) | 3489(5) | 10423(7) | 2722(4) | 25(2) |
| N(10) | 4231(4) | 7774(7) | 3498(4) | 19(1) |
| N(11) | 290(6) | 3435(9) | 9360(5) | 40(2) |
| N(12) | 9537(6) | 2610(11) | 2441(6) | 52(2) |
| Ni(1) | 4687(1) | 9028(2) | 2592(1) | 18(1) |
| O(1) | −1406(5) | 4449(10) | 8901(4) | 46(2) |
| O(2) | 8802(5) | 381(9) | 2099(5) | 55(2) |
| O(3) | 6803(4) | 9037(14) | 1278(3) | 30(1) |
| Pt(1) | 4140(1) | 4159(1) | 2675(1) | 23(1) |

structure is one of the rare examples of heterobimetallic complexes having a bent cyanide bridge. Recently, a similar complex, $[Cu(NH_3)_4][Pt(CN)_4]$, has been reported; it also has a bent C=N–Cu link and stacks in extended linear $Pt\cdots Pt\cdots Pt$ chains [18]. Unlike the analogous complex $[Cu(NH_3)_4][Pt(CN)_4]$, the crystal structure of the present platinum-copper complex has a two-dimensional character, which can be viewed along the *a* axis, as shown in figure 2. There are two lattice water molecules in the unit cell and the cyano groups participate in hydrogen bonding with them. Important hydrogen bond parameters are given in table 6. These hydrogen bonds

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3**. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ |
|---|---|---|---|---|
| C(1) | 4610(30) | 220(20) | 4169(16) | 32(6) |
| C(2) | 4710(40) | 1920(30) | 2737(16) | 30(6) |
| C(3) | 4060(30) | 480(20) | 1118(14) | 29(5) |
| C(4) | 3870(40) | −1170(30) | 2448(19) | 41(7) |
| C(5) | 10720(30) | −1576(17) | 8753(16) | 23(5) |
| C(6) | 9000(30) | −1006(16) | 9122(17) | 21(5) |
| C(7) | 7650(30) | −1740(20) | 9712(19) | 37(7) |
| C(8) | 8880(40) | −2250(20) | 10630(20) | 43(7) |
| C(9) | 10530(40) | −2850(20) | 10220(20) | 48(7) |
| C(10) | 11920(40) | −2140(20) | 9650(20) | 35(6) |
| C(11) | 9170(30) | 1586(18) | 5660(16) | 26(5) |
| C(12) | 11110(30) | 1906(19) | 6154(16) | 25(5) |
| C(13) | 12370(40) | 2490(20) | 5410(20) | 38(6) |
| C(14) | 11240(40) | 3380(20) | 4880(20) | 38(7) |
| C(15) | 9260(40) | 3010(20) | 4380(20) | 36(6) |
| C(16) | 8040(40) | 2480(20) | 5120(20) | 32(6) |
| N(1) | 4770(30) | 102(14) | 5053(14) | 31(5) |
| N(2) | 4990(30) | 2794(19) | 2762(15) | 38(5) |
| N(3) | 3850(30) | 520(20) | 220(13) | 42(5) |
| N(4) | 3610(40) | −2040(20) | 2370(16) | 51(6) |
| N(5) | 11880(20) | −783(14) | 8248(13) | 25(4) |
| N(6) | 7970(20) | −537(16) | 8172(13) | 25(4) |
| N(7) | 8100(20) | 1052(15) | 6473(12) | 26(4) |
| N(8) | 12040(20) | 957(15) | 6633(12) | 24(4) |
| O(1) | 4890(20) | 6108(13) | 1657(11) | 29(3) |
| Pd(1) | 10005(2) | 146(1) | 7357(1) | 20(1) |
| Pt(1) | 4329(1) | 367(1) | 2635(1) | 30(1) |

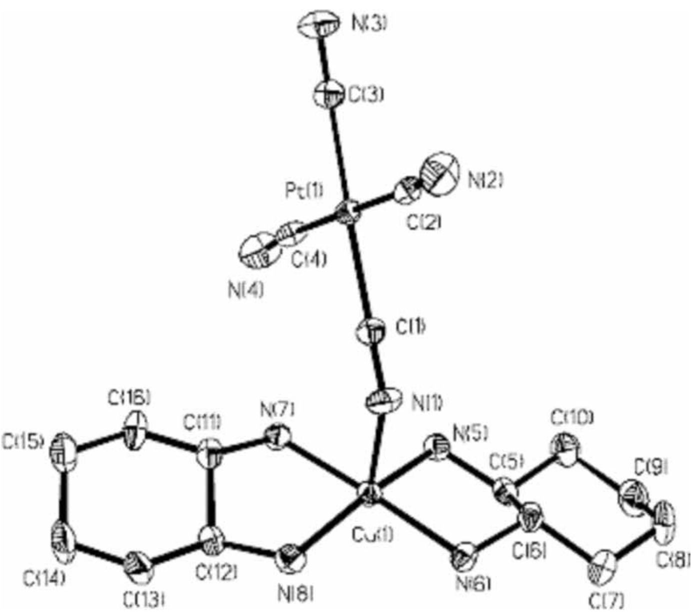

Figure 1. X-ray crystal structure of **1**, drawn at the 30% probability level for ellipsoids, showing the atom numbering scheme.

Table 5. Selected bond lengths [Å] and angles [°] for **1**.

| | | | |
|---|---|---|---|
| C(1)–Pt(1) | 1.995(9) | C(2)–Pt(1) | 1.972(10) |
| C(3)–Pt(1) | 1.968(10) | C(4)–Pt(1) | 2.000(10) |
| C(1)–N(1) | 1.170(13) | C(2)–N(2) | 1.151(15) |
| C(3)–N(3) | 1.147(15) | C(4)–N(4) | 1.149(15) |
| Cu(1)–N(1) | 2.328(10) | Cu(1)–N(5) | 2.040(8) |
| Cu(1)–N(6) | 2.018(7) | Cu(1)–N(7) | 2.030(8) |
| Cu(1)–N(8) | 2.023(8) | | |
| N(1)–C(1)–Pt(1) | 176.3(9) | N(2)–C(2)–Pt(1) | 174.9(9) |
| N(3)–C(3)–Pt(1) | 174.6(10) | N(4)–C(4)–Pt(1) | 175.2(11) |
| N(6)–Cu(1)–N(8) | 95.9(4) | N(6)–Cu(1)–N(7) | 176.0(4) |
| N(8)–Cu(1)–N(7) | 84.2(4) | N(6)–Cu(1)–N(5) | 84.9(3) |
| N(8)–Cu(1)–N(5) | 167.7(4) | N(7)–Cu(1)–N(5) | 94.2(3) |
| N(6)–Cu(1)–N(1) | 93.2(3) | N(8)–Cu(1)–N(1) | 91.4(4) |
| N(7)–Cu(1)–N(1) | 90.8(4) | N(5)–Cu(1)–N(1) | 100.8(4) |
| C(1)–N(1)–Cu(1) | 136.8(8) | C(5)–N(5)–Cu(1) | 108.9(6) |
| C(6)–N(6)–Cu(1) | 108.3(6) | C(11)–N(7)–Cu(1) | 108.5(6) |
| C(12)–N(8)–Cu(1) | 108.5(6) | C(3)–Pt(1)–C(2) | 88.0(4) |
| C(3)–Pt(1)–C(1) | 178.0(4) | C(2)–Pt(1)–C(1) | 92.3(4) |
| C(3)–Pt(1)–C(4) | 92.6(4) | C(2)–Pt(1)–C(4) | 178.0(4) |
| C(1)–Pt(1)–C(4) | 87.2(4) | | |

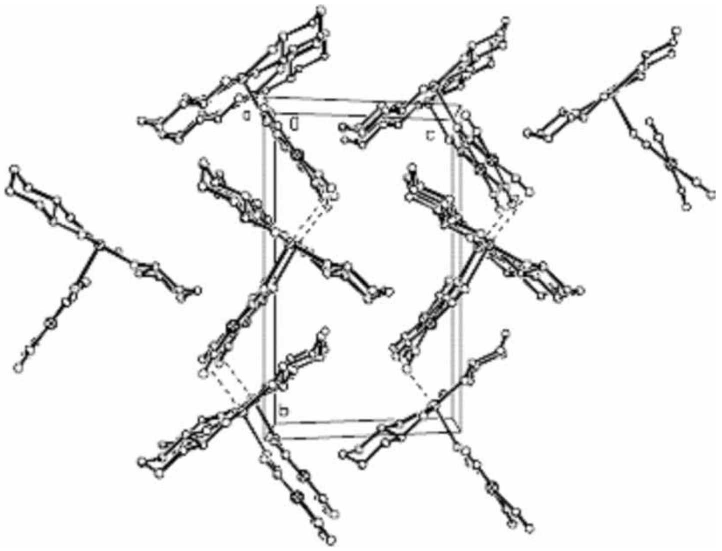

Figure 2. Packing diagram of **1** in the unit cell showing the weak intermolecular interactions.

link the water molecules and the bimetallic units into a two-dimensional network structure.

### 3.3. *Structure of* $[Ni(dach)_3][Pt(CN)_4]\cdot 2DMF\cdot H_2O$ *(2)*

Complex **2**, consists of discrete $[Ni(dach)_3]^{2+}$ and $[Pt(CN)_4]^{2-}$ ions, and one water and two DMF molecules of crystallisation. The structure is shown in figure 3 and

Table 6. Hydrogen bonds with H···A ∠ r(A) + 2.00 Å and ∠DHA >110° for complex **1**.

| D–H···A | D(D–H) | d(H···A) | ∠DHA | d(D···A) |
|---|---|---|---|---|
| N5–H5A···O2#1 | 0.90 | 1.977 | 172.53 | 2.872 |
| N6–H6A···N2#2 | 0.90 | 2.447 | 157.65 | 3.297 |
| N6–H6B···N4#3 | 0.90 | 2.232 | 157.30 | 3.082 |
| N7–H7C···N2#4 | 0.90 | 2.494 | 155.96 | 3.336 |
| N7–H7D···N4 | 0.90 | 2.481 | 158.90 | 3.337 |
| N8–H8D···O1#5 | 0.90 | 2.144 | 161.25 | 3.010 |
| O1–H2W···N2#6 | 1.01 | 1.998 | 135.60 | 2.809 |
| O2–H4W···O1#5 | 1.02 | 1.983 | 124.78 | 2.696 |

Symmetry transformations used to generate equivalent atoms are #1: $x+1, y, z+1$; #2: $-x+1, y+1/2, -z+2$; #3: $x-1, y, z$; #4: $-x+2, y+1/2, -z+2$; #5: $-x+1, y+1/2, -z+1$; #6: $x, y, z-1$.

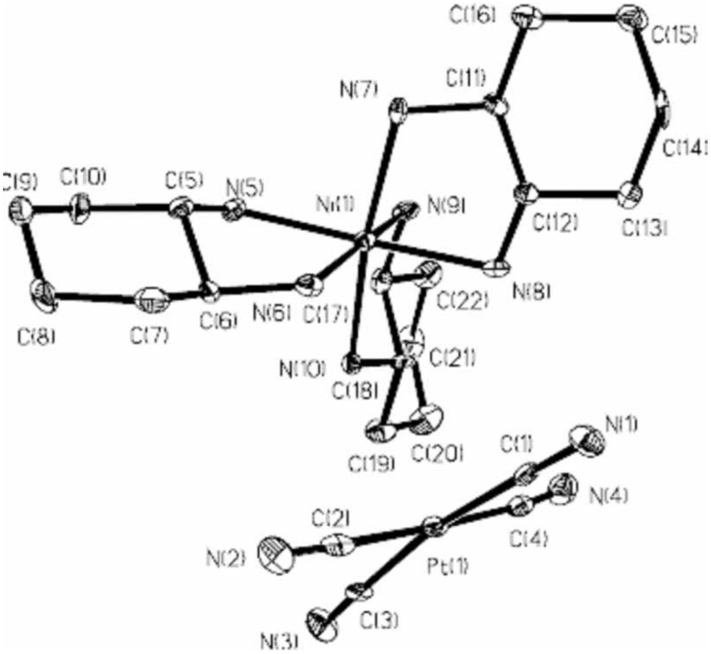

Figure 3. X-ray structure of **2**, drawn at the 30% probability level for ellipsoids, showing the atom numbering scheme.

selected bond distances and angles are listed in table 7. The nickel atom in $[Ni(dach)_3]^{2+}$ is coordinated by six $NH_2$ groups, forming a distorted octahedron. Ni–N bond distances fall in the narrow range of 2.118(6)–2.139(6) Å and are not unusual.

### 3.4. *Structure of [Pd(dach)$_2$][Pt(CN)$_4$]•H$_2$O*

The structure of complex **3** is shown in figure 4, and the selected bond distances and angles are listed in table 8. The asymmetric unit contains discrete $[Pt(CN)_4]^{2-}$ and

Table 7. Selected bond lengths [Å] and angles [°] for **2**.

| | | | |
|---|---|---|---|
| C(1)–Pt(1) | 1.990(6) | C(2)–Pt(1) | 1.988(10) |
| C(3)–Pt(1) | 2.015(8) | C(4)–Pt(1) | 1.961(9) |
| C(1)–N(1) | 1.152(8) | C(2)–N(2) | 1.185(11) |
| C(3)–N(3) | 1.118(10) | C(4)–N(4) | 1.170(11) |
| N(5)–Ni(1) | 2.118(6) | N(6)–Ni(1) | 2.139(6) |
| N(7)–Ni(1) | 2.120(7) | N(8)–Ni(1) | 2.131(6) |
| N(9)–Ni(1) | 2.120(6) | N(10)–Ni(1) | 2.130(6) |
| N(1)–C(1)–Pt(1) | 176.1(8) | N(2)–C(2)–Pt(1) | 178.5(7) |
| N(3)–C(3)–Pt(1) | 176.9(7) | N(4)–C(4)–Pt(1) | 173.8(7) |
| N(7)–Ni(1)–N(5) | 93.9(2) | N(7)–Ni(1)–N(9) | 91.2(3) |
| N(5)–Ni(1)–N(9) | 96.0(3) | N(7)–Ni(1)–N(8) | 81.4(2) |
| N(5)–Ni(1)–N(8) | 169.8(2) | N(9)–Ni(1)–N(8) | 93.2(3) |
| N(7)–Ni(1)–N(10) | 170.7(2) | N(5)–Ni(1)–N(10) | 92.6(2) |
| N(9)–Ni(1)–N(10) | 81.4(2) | N(8)–Ni(1)–N(10) | 93.2(2) |
| N(7)–Ni(1)–N(6) | 94.3(2) | N(5)–Ni(1)–N(6) | 80.8(3) |
| N(9)–Ni(1)–N(6) | 173.8(2) | N(8)–Ni(1)–N(6) | 90.4(2) |
| N(10)–Ni(1)–N(6) | 93.4(2) | C(4)–Pt(1)–C(2) | 178.0(3) |
| C(4)–Pt(1)–C(1) | 89.4(3) | C(2)–Pt(1)–C(1) | 91.0(3) |
| C(4)–Pt(1)–C(3) | 89.2(3) | C(2)–Pt(1)–C(3) | 90.7(3) |
| C(1)–Pt(1)–C(3) | | 171.9(6) | |

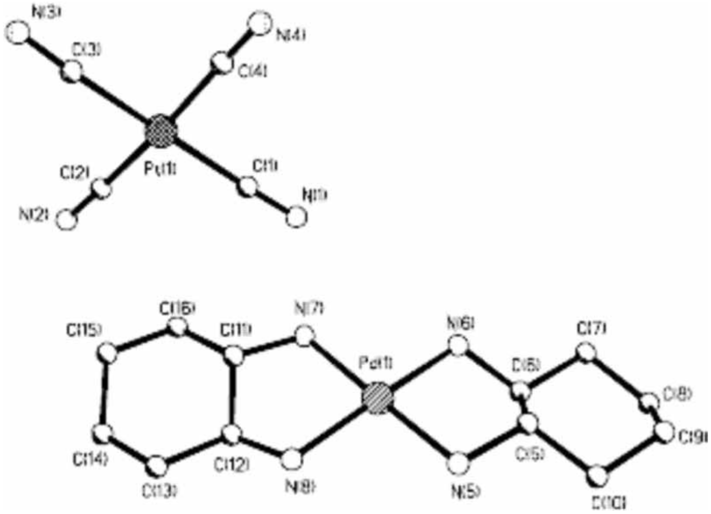

Figure 4. X-ray structure of compound **3**, drawn at the 30% probability level for ellipsoids, showing the atom numbering scheme.

$[Pd(dach)_2]^{2+}$ ions, and one molecule of water. Both platinum and palladium atoms are tetra-coordinate with square planar geometry. Pt–C and Pd–N bond distances are 1.994 and 2.033 Å, respectively, and are usual. Although $[Pt(CN)_4]^{2-}$ ions stack into one-dimensional columns, as shown in figure 5, the Pt–Pt interaction can be neglected because of the long Pt–Pt separation ( >5 Å). The $[Pd(dach)_2]^{2+}$ cation fills in between the tetragonal channels formed by $[Pt(CN)_4]^{2-}$ stacks.

Table 8. Selected bond lengths [Å] and angles [°] for **3**.

| | | | |
|---|---|---|---|
| C(1)–Pt(1) | 1.99(2) | C(2)–Pt(1) | 2.01(3) |
| C(3)–Pt(1) | 1.966(19) | C(4)–Pt(1) | 2.01(3) |
| C(1)–N(1) | 1.15(3) | C(2)–N(2) | 1.13(3) |
| C(3)–N(3) | 1.16(2) | C(4)–N(4) | 1.13(4) |
| N(5)–Pd(1) | 2.039(18) | N(6)–Pd(1) | 2.024(17) |
| N(7)–Pd(1) | 2.031(17) | N(8)–Pd(1) | 2.037(16) |
| N(1)–C(1)–Pt(1) | 178(2) | N(2)–C(2)–Pt(1) | 177(2) |
| N(3)–C(3)–Pt(1) | 177(2) | N(4)–C(4)–Pt(1) | 178(2) |
| C(5)–N(5)–Pd(1) | 108.3(12) | C(6)–N(6)–Pd(1) | 107.8(12) |
| C(11)–N(7)–Pd(1) | 109.2(12) | C(12)–N(8)–Pd(1) | 108.7(12) |
| N(6)–Pd(1)–N(7) | 95.8(7) | N(6)–Pd(1)–N(8) | 174.3(8) |
| N(7)–Pd(1)–N(8) | 83.3(7) | N(6)–Pd(1)–N(5) | 83.3(7) |
| N(7)–Pd(1)–N(5) | 178.9(7) | N(8)–Pd(1)–N(5) | 97.6(7) |
| C(3)–Pt(1)–C(1) | 179.0(13) | C(3)–Pt(1)–C(4) | 87.3(10) |
| C(1)–Pt(1)–C(4) | 91.7(10) | C(3)–Pt(1)–C(2) | 89.6(10) |
| C(1)–Pt(1)–C(2) | 91.4(10) | C(4)–Pt(1)–C(2) | 176.6(12) |

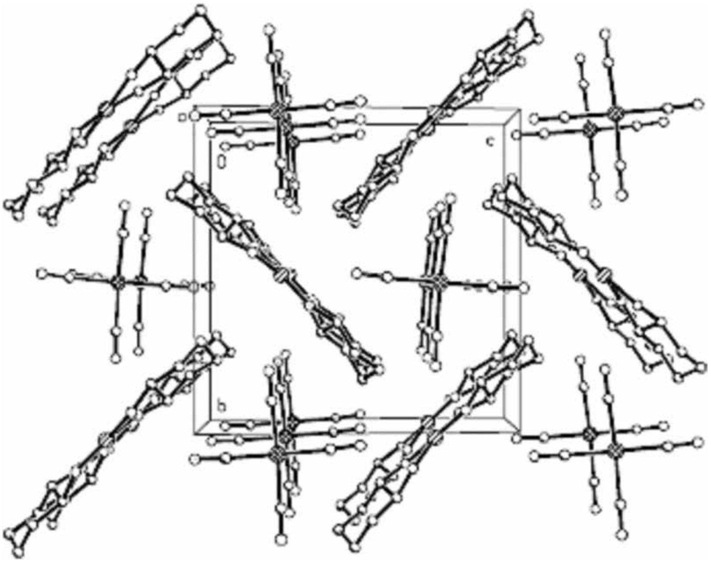

Figure 5. Perspective view of the stacking of $[Pt(CN)_4]^{2-}$ ions in **3** along the *a* axis.

## Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 203810-203812 for compound **1–3**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. Fax: +44(1223)336-033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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