

Depending on the donor ligand the average Fe–O distances in the double octahedron are about 1.93 Å (FpP(Mes)O<sub>2</sub>), 2.011(7) Å (MesPO<sub>3</sub>), and 2.123(7) Å ( $\mu_3$ -OH). The equatorial angles O2-Fe2-O10 and O8-Fe2-O8a were determined to be 98.9(3) and 81.7(2)°, respectively. The atoms Fe2, O8, Fe2a and O8a lie in one plane and form a rhombus with the acute angle at the iron atoms; thus, a bonding interaction between Fe2 and Fe2a is not possible (distance Fe2–Fe2a = 3.212 Å). The trigonal-bipyramidal coordination of Fe4 is slightly distorted. The longest Fe–O distance in **2** was determined for Fe4–O8(apical) to be 2.168(7) Å, the shortest for Fe4–O<sub>n</sub> (equatorial) to be about 1.895 Å. The equatorial bridges O4, O5, and O1a are bent slightly out of the ideal plane. The Fe4–C11 distance is 2.346(3) Å. The bond angles at the O bridges lie between 124.5(4) and 146.7(4)°, those at the P atoms (103.8(4)–113.1(3)°) have values close to the tetrahedron angle. The sum of angles Fe–O–Fe at the trigonal-pyramidal  $\mu_3$ -OH bridges is 345.3°; the  $\mu_3$ -OH hydrogen atom does not participate in any hydrogen bonding.

Temperature-dependent magnetic measurements for **2** revealed antiferromagnetic behavior with a Néel temperature of 40 K; the bond lengths (Fe–O) and angles (Fe–O–Fe) of the four central Fe<sup>III</sup> ions (Fe2, Fe2a, Fe4, Fe4a) allow superexchange and spin orientation. At 300 K the  $\mu_{\text{eff}}$  value was 5.48 BM.<sup>[6]</sup>

The mild aerial oxidation of the diferriophosphonium salt **1a** leads to many (sometimes drastic) changes in the functionality at both the iron and phosphorus atoms: We find both retention and elimination of the CpFe(CO)<sub>2</sub> groups as well as complete oxidation to give iron(III) centers, and oxidation of the phosphonium building blocks to give  $\mu_2$ -phosphinato and  $\mu_3$ -phosphinato ligands. This wide palette of new building blocks finally readily combines to form **2**. The new molecular framework of **2** is illustrated by the polyhedral representation in Figure 2. The structure contains a central double octahedron (FeO<sub>4</sub>(OH))<sub>2</sub>, two trigonal bipyramids (FeO<sub>3</sub>(OH)Cl), and six tetrahedrons (four Fp(Mes)PO<sub>2</sub> and two MesPO<sub>3</sub>). Compound **2** is an example for the unusual combination of classic (in the core) and organometallic complex chemistry (at the periphery). We are currently investigating similar organometalated sulfonium salts,<sup>[7]</sup> which also may be converted to similar coordination polyhedrons with sulfenato, sulfonato, and sulfonato ligands by aerial oxidation.

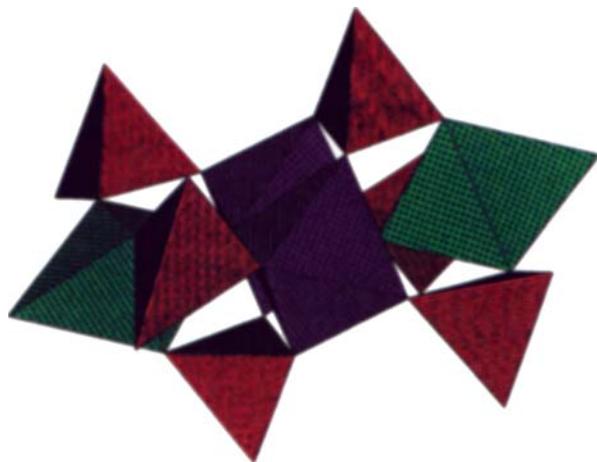


Figure 2. Polyhedral representation of **2**, consisting of two edge-shared octahedrons ((FeO<sub>4</sub>(OH))<sub>2</sub>), two trigonal bipyramids (FeO<sub>3</sub>(OH)Cl), and six tetrahedrons (four Fp(Mes)PO<sub>2</sub> and two MesPO<sub>3</sub>).

### Experimental Section

Synthesis of **1a** see reference [3].

**2**: **1a** (200 mg, 0.37 mmol) was dissolved in acetonitrile (12 mL) and this solution was exposed to air for three days. Small yellow crystals formed on the inside glass surface. They were collected and washed with acetone. Yield: 30 mg (22.4%). Additional quantities of **2** remained in the mother liquor; however, these could not be isolated in a pure form; correct elemental analysis. Compound **2** is soluble only in dimethyl sulfoxide (DMSO).

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- [1] A. Müller, K. Hovemeier, E. Krickemeyer, H. Böcke, *Angew. Chem.* 1995, 107, 856; *Angew. Chem. Int. Ed. Engl.* 1995, 34, 779; further examples for molecular self-assembly can be found in J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, New York, 1995.
- [2] a) W. Pohl, I.-P. Lorenz, H. Nöth, M. Schmidt, *Z. Naturforsch. B* 1995, 50, 1485; b) I.-P. Lorenz, P. Mürschel, W. Pohl, K. Polborn, *Chem. Ber.* 1995, 128, 441; c) I.-P. Lorenz, W. Pohl, K. Polborn, *ibid.* 1996, 129, 11.
- [3] I.-P. Lorenz, W. Pohl, H. Nöth, M. Schmidt, *J. Organomet. Chem.* 1994, 475, 211.
- [4] W. Pohl, PhD Thesis, University of München, 1995.
- [5] X-ray structure analysis of **2**: C<sub>82</sub>H<sub>88</sub>Cl<sub>2</sub>Fe<sub>8</sub>O<sub>24</sub>P<sub>6</sub>, brown plates, 0.30 × 0.26 × 0.1 mm<sup>3</sup>, triclinic, space group *P*, *a* = 12.991(7), *b* = 14.660(7), *c* = 14.776(7) Å,  $\alpha$  = 119.25(1),  $\beta$  = 106.41(2),  $\gamma$  = 94.88(1)°, *Z* = 2, *V* = 2270(2) Å<sup>3</sup>,  $\rho_{\text{calc}}$  = 1.581 g cm<sup>-3</sup>,  $\mu$  = 1.476 mm<sup>-1</sup>, *F*(000) = 1104, diffractometer: Siemens P4, MoK $\alpha$  ( $\lambda$  = 0.71073 Å), *T* = 213 K,  $2\theta$  = 3.24–47.00,  $\omega$  scan, scan range ( $\omega$ ) 1.2°, reflections: 5241 measured, 4967 of which were independent (*R*(int) = 0.1251), 3022 observed [*F* > 4 $\sigma$ (*F*)]. The structure was solved with the programs XS (Siemens) and SHELXL (G. M. Sheldrick, Göttingen, 1993) by direct methods and refined by full-matrix least squares refinement. The hydrogen atoms were refined as riding atoms with fixed isotropic temperature parameters. 553 refined parameters, *R* = 0.0693, *wR*<sub>2</sub> = 0.1308, GOOF = 1.049. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405885.
- [6] The measurements of magnetic susceptibility were made between 10–300 K with 20 mg of microcrystalline **2** on a Quantum Design MPMS Squid magnetometer at a field strength of 2 T. Calculations (without diamagnetic correction) were made with one molecule of CH<sub>3</sub>CN per molecule of **2**.
- [7] I.-P. Lorenz, K. Thurow, *J. Organomet. Chem.* 1995, 496, 191.

### Linear Pentanuclear Complexes Containing a Chain of Metal Atoms: [Co<sub>5</sub><sup>II</sup>( $\mu_5$ -tpda)<sub>4</sub>(NCS)<sub>2</sub>] und [Ni<sub>5</sub><sup>II</sup>( $\mu_5$ -tpda)<sub>4</sub>Cl<sub>2</sub>]\*\*

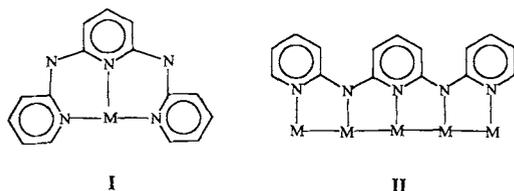
Shen-Jye Shieh, Chin-Cheng Chou,  
Gene-Hsiang Lee, Chih-Chieh Wang, and  
Shie-Ming Peng\*

Metal–metal bonding in dinuclear metal complexes is well understood.<sup>[1–3]</sup> Our efforts to extend dinuclear metal complexes to form trinuclear metal complexes with a *syn–syn* bis-

[\*] Prof. S.-M. Peng, Dr. S.-J. Shieh, C.-C. Chou, G.-H. Lee, Dr. C.-C. Wang  
Department of Chemistry  
National Taiwan University  
Taipei, Taiwan, 107 (Republic of China)  
Fax: Int. code + (2)3636359

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(H<sub>2</sub>tpda = *N,N'*-bis( $\alpha$ -pyridyl)-2,6-diaminopyridine).

( $\alpha$ -pyridyl)amido ligand have been reported.<sup>[4, 5]</sup> In order to achieve a further extension to pentanuclear metal complexes a new ligand, *N,N'*-bis( $\alpha$ -pyridyl)-2,6-diaminopyridine (the common name in our system is tripyridyldiamine abbreviated as  $H_2tpda$ ), was synthesized. It was found that the ligand can bind metal ions in two conformations, the *anti-anti-anti-anti* form **I** and the *syn-syn-syn-syn* form **II**.



In **I** the ligand is tridentate and coordinates to metal ion through the nitrogen atoms of pyridine moieties. The ligand can be either neutral or dianionic.  $[Co^{II}(H_2tpda)Cl_2]$  illustrates this coordination mode. In **II** the ligands have been deprotonated and act as bridging pentadentate ligands. The unprecedented linear pentanuclear nickel(II) and cobalt(II) complexes ( $[M_5(\mu_5-tpda)_4X_2]$ ,  $M = Ni$ ,  $X = Cl$ , and  $M = Co$ ,  $X = NCS$ ) are reported here.

The ligand was synthesized by treating 2.5 equivalents of 2-bromopyridine with 1 equivalent of 2,6-diaminopyridine under basic conditions. Remaining 2,6-diaminopyridine and *N*-( $\alpha$ -pyridyl)-2,6-diaminopyridine were washed away with water. The crude product of *N,N'*-bis(2-pyridyl)-2,6-diaminopyridine was recrystallized from dichloromethane and methanol. The cobalt complex of type **I** was synthesized by treating equimolar amounts of  $CoCl_2 \cdot 6H_2O$  with  $H_2tpda$  in dichloromethane. The crystal structure of the neutral complex  $[Co(H_2tpda)Cl_2]$  reveals that the coordination geometry around the cobalt(II) ion is trigonal bipyramidal with two chloride ions and the nitrogen atom of the central pyridine as the basal plane and two nitrogen atoms of the terminal pyridine group as the apex. The ligand  $H_2tpda$  is planar and coordinates to cobalt ion in *anti-anti-anti-anti* conformation.

The pentanuclear cobalt(II) complex was synthesized similarly to the trinuclear metal complex.<sup>[4-7]</sup> It was characterized by various spectroscopic methods, in particular mass spectrometry (FAB) and X-ray diffraction. The parent peak of  $[Co_5(\mu_5-tpda)_4(NCS)_2]$  is clearly assigned and peaks of the fragments of  $[Co_5(\mu-tpda)_4(NCS)]$ ,  $[Co_5(\mu-tpda)_4]$ ,  $[Co_4(\mu-tpda)_3(NCS)]$ ,  $[Co_4(\mu-tpda)_3]$ , and  $[Co_3(\mu-tpda)_3]$  are observed. The structure of the complex, obtained by X-ray single crystal diffraction study, has several uncommon features (Figure 1). First, the pentacobalt metal chain is helically wrapped by four *syn-syn-syn-syn* type ligands. The complex exhibits approximate  $D_4$  symmetry. Secondly, the five cobalt(II) ions are collinear, linked by multicentered Co-Co  $\sigma$  bonding. The Co-Co distances are 2.277(2), 2.232(2), 2.229(2), and 2.274(2) Å, which are comparable with those of dinuclear cobalt complexes.<sup>[8]</sup> The preliminary MO analyses indicate there are two  $\sigma$  bonds among five cobalt(II) ions, and the HOMO is of nonbonding character and singly occupied. The average Co1-N(py) (1.97(1)), Co2-N(amido) (1.90(1)), Co3-N(py) (1.93(1)), Co4-N(amido) (1.90(1)), and Co5-N(py) distances (1.97(1) Å) are consistent with a low spin state for the cobalt(II) ion ( $\mu = 1.9 \mu_B$  and temperature-independent). Thirdly, the negative charges of the an-

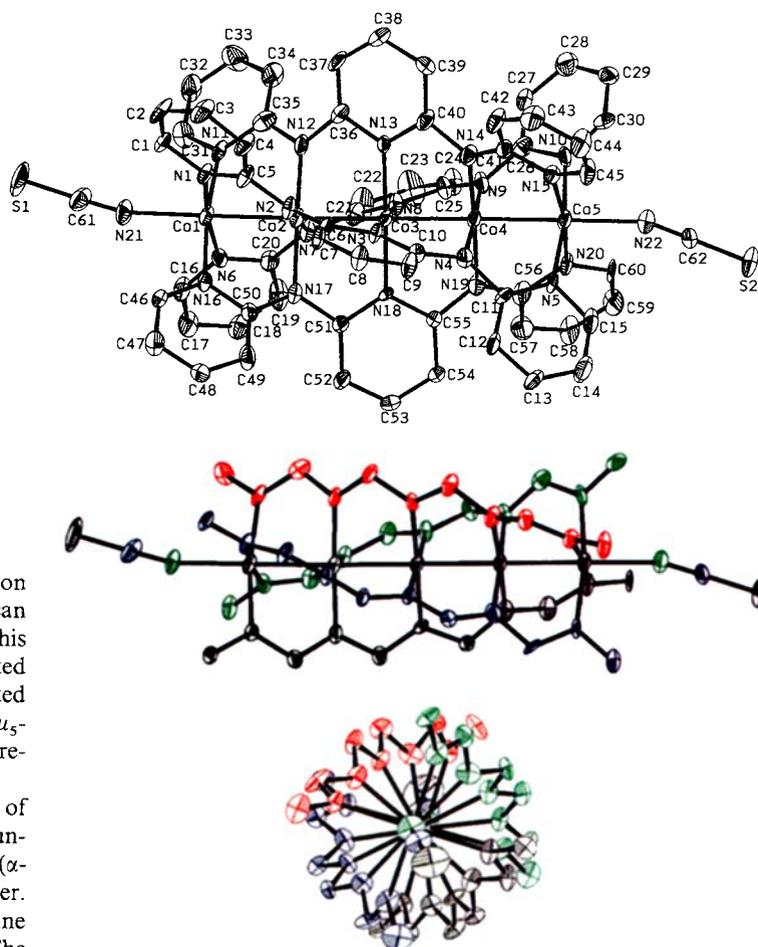


Figure 1. Top: Crystal structure of  $[Co_5(\mu_5-tpda)_4(NCS)_2]$  (ORTEP view). Pertinent bond lengths (Å) and angles ( $^\circ$ ): Co1-Co2 2.277(2), Co2-Co3 2.232(2), Co3-Co4 2.229(2), Co4-Co5 2.274(2), Co1-N21 2.07(1), Co1-N(py) (averaged) 1.97(1), Co2-N (averaged) 1.90(1), Co3-N (averaged) 1.93(1), Co4-N (averaged) 1.90(1), Co5-N(py) (averaged) 1.97(1), Co5-N22 2.06(1), N21-Co1-Co2 178.8(3), Co1-Co2-Co3 178.7(1), Co2-Co3-Co4 179.9(1), Co3-Co4-Co5 178.8(1), Co4-Co5-N22 179.3(3), N(py)-Co1-Co2 (averaged) 86(1), N-Co2-Co3 (averaged) 89(1), N-Co3-Co4 (averaged) 90(1), N-Co4-Co3 (averaged) 89(1), N(py)-Co5-Co4 (averaged) 86(1). Center: Illustration of the helical ligands wrapped around the linear metal chain (along the metal chain axis). The three carbon atoms of pyridine rings are omitted for clarity. Bottom: Another illustration down the metal chain axis.

ionic ligand are delocalized on the five nitrogen atoms of the ligand. The observed bond pattern is qualitatively consistent with the delocalization model.

The pentanuclear nickel(II) complex has also been synthesized similarly to the trinuclear metal complexes.<sup>[4-7]</sup> The parent peak of  $[Ni_5(\mu_5-tpda)_4Cl_2]$  is clearly assigned, and peaks of the  $[Ni_4(\mu-tpda)_3]$  and  $[Ni_5(\mu-tpda)_4Cl]$  fragments are also observed. The single-crystal X-ray diffraction study of  $[Ni_5^II(\mu_5-tpda)_4Cl_2]$  reveals that the asymmetric unit contains half of the complex and two dichloromethane molecules. The complex is located at the crystallographic center of inversion. The atomic positions are averaged, because right-turn and left-turn helical complexes are disordered in the crystal. Eight nitrogen atoms from amido groups that are coordinated to nickel ions ( $Ni_2$ , occupancy factor 0.5) and the  $\alpha$ -carbon atoms of the pyridyl groups have high anisotropic thermal parameters. One of the helical forms is shown in Figure 2. The pentanuclear

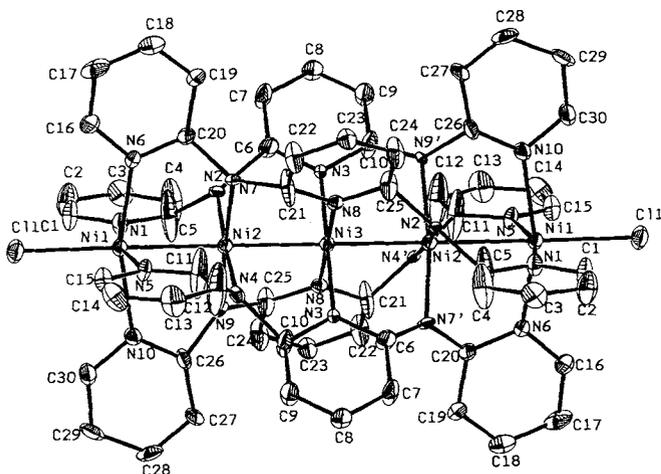


Figure 2. Crystal structure of  $[\text{Ni}_3(\mu_5\text{-tpda})_4\text{Cl}_2]$  (ORTEP view). Pertinent bond lengths (Å) and angles ( $^\circ$ ): Ni1–Cl 2.346(3), Ni1–Ni2 2.385(2), Ni2–Ni3 2.305(1), Ni1–N (averaged) 2.111(9), Ni2–N (averaged) 1.897(15), Ni3–N 1.904(8), Cl–Ni1–Ni2 179.1(1), Ni1–Ni2–Ni3 179.5(1), Ni2–Ni3–Ni2 180, N–Ni3–N2 (averaged) 90, N–Ni2–Ni3 (averaged) 88(1), N–Ni1–Ni2 (averaged) 82(1).

linear metal chain is helically wrapped by four *syn–syn–syn–syn* type ligands. The five nickel ions and two chloride ions are collinear (Cl–Ni1–Ni2 179.1(1) $^\circ$ , Ni1–Ni2–Ni3 179.5(1) $^\circ$ , and Ni2–Ni3–Ni2' 180 $^\circ$ ). The Ni–Ni distances are very short (Ni1–Ni2 2.385(2); Ni2–Ni3 2.306(2) Å). The latter is the shortest known Ni–Ni distance.<sup>19–11</sup> According to MO analyses, no bonding interactions exist between the nickel ions, which is consistent with the magnetic data (see below).

The average Ni2–N (1.897(15) Å) and Ni3–N distances (1.904(8) Å) are short, consistent with a square-planar, diamagnetic arrangement of nickel(II) ions. The terminal Ni<sup>II</sup> ions (Ni1) are in a square-pyramidal environment and exhibit a long Ni1–Cl bond (2.346(3) Å) and long Ni1–N bonds (av. 2.111(9) Å), consistent with high-spin nickel(II) ions ( $S = 1$ ,  $\mu = 2.8 \mu_B$ ). A temperature-dependent magnetic study of the complex (Figure 3) indicates the antiferromagnetic interaction of terminal high-spin nickel ions with  $J = -14.6 \text{ cm}^{-1}$ . This interaction is one order of magnitude smaller than those of similar trinuclear nickel(II) complexes.<sup>7, 12</sup>

Attempts to isolate other linear pentanuclear metal complexes and demonstration of their potential application as molecular wires are under way.

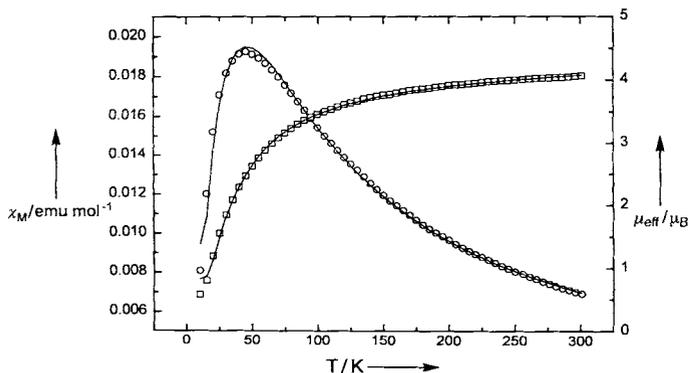


Figure 3. Magnetic data for  $[\text{Ni}_3(\mu_5\text{-tpda})_4\text{Cl}_2]$ . Solid curves represent calculation based on the equation  $\chi_M = C(2e^{2x} + 10e^{0x}) / (1 + 3e^{2x} + 5e^{0x})$ ,  $C = Ng^2\beta^2 / kT$ ,  $x = J/kT$ ,  $\mathcal{H} = -2JS_1 \cdot S_5$  ( $S_2 = S_3 = S_4 = 0$ ,  $S_1 = S_5 = 1$ ) and  $\mu_{\text{eff}} = 2.84(\chi_M T)^{1/2}$ .  $\circ$  is the observed  $\chi_M$  and  $\square$  the observed  $\mu_{\text{eff}}$ .

## Experimental Section

**H<sub>2</sub>tpda:** Under a nitrogen atmosphere 2-bromopyridine (36 mL) was added to a solution of 2,6-diaminopyridine (10 g, 0.09 mol) and *t*BuOK (30.24 g, 0.27 mol) in THF (150 mL). The reaction mixture was heated under reflux for 24 h. After cooling to room temperature, the solvent was removed by rotary evaporator. Then the mixture was extracted with dichloromethane, and the solvent removed under reduced pressure. Unchanged 2,6-diaminopyridine and *N*-( $\alpha$ -pyridyl)-2,6-diaminopyridine were rinsed away with water. The crude product of *N,N'*-bis(2-pyridyl)-2,6-diaminopyridine was recrystallized from dichloromethane and hexane (Yield 26%). IR (KBr)  $\tilde{\nu} = 3442, 3180 \text{ cm}^{-1}$  (NH). UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}(\epsilon) = 268 (3.76 \times 10^3)$ , 321 nm ( $4.13 \times 10^3$ ). MS (FAB):  $m/z$  (%) 264 (60)  $[M + 1]^+$ , 186 (100)  $[\text{C}_{10}\text{N}_4\text{H}_9]^+$ , 77 (20)  $[\text{C}_5\text{H}_5\text{N}]^+$ .

**$[\text{Co}(\text{H}_2\text{tpda})\text{Cl}_2]$ :**  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (23 mg, 0.09 mmol) was added to a solution of H<sub>2</sub>tpda (25 mg, 0.09 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL). The yellow solution was stirred for 6 h. A green precipitate was formed, filtered off, washed with ether, and air-dried. Green prismatic crystals were formed by slow diffusion of diethyl ether into a  $\text{CH}_3\text{CN}/\text{DMF}$  solution of the compound (yield 70%). IR (KBr):  $\tilde{\nu} = 3397, 3316, 3203 \text{ cm}^{-1}$  (NH). UV/Vis (DMF)  $\lambda_{\text{max}}(\epsilon) = 330 (3.34 \times 10^4)$ . MS (FAB):  $m/z$  (%) 321 (40)  $[M - \text{Cl}]^+$ .

**$[\text{Co}_2(\mu_5\text{-tpda})_4(\text{SCN})_2]$ :**  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.936 g, 4 mmol) and H<sub>2</sub>tpda (1.02 g, 4 mmol) were placed in an Erlenmeyer flask, and naphthalene (7.2 g) was added. The mixture was heated (about 160–180 $^\circ\text{C}$ ) for 10 min to remove water. Then *n*-butanol (3 mL) was added to the heated mixture, and heating was continued until the *n*-butanol had almost completely evaporated. A solution of potassium *n*-butoxide (0.88 g, 8 mmol) *n*-butanol (20 mL) was added dropwise. Heating was continued until the remaining *n*-butanol had evaporated completely, after which an excess of sodium thiocyanate (1.0 g) was added. After the mixture had cooled, *n*-hexane was added to wash out naphthalene. The remaining solid was extracted with  $\text{CH}_2\text{Cl}_2$  and recrystallized from  $\text{CH}_2\text{Cl}_2/n$ -hexane solution. Deep brown crystals were obtained (yield 5%). IR (KBr)  $\tilde{\nu} = 2058$  (CN), 1594, 1565, 1536 (C=C). UV/Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}(\epsilon) = 279 (1.13 \times 10^5)$ , 338 ( $6.21 \times 10^4$ ), 393 ( $5.84 \times 10^4$ ), 513 ( $9.75 \times 10^3$ ), 725  $\text{cm}^{-1}$  ( $1.01 \times 10^3$ ). MS (FAB):  $m/z$  (%) 1455 (2)  $[M]^+$ , 1397 (4)  $[M - \text{SCN}]^+$ , 1339 (1)  $[\text{Co}_2(\mu\text{-tpda})_4]^+$ , 1077 (6)  $[\text{Co}_2(\mu\text{-tpda})_3\text{SCN}]^+$ , 1019 (4)  $[\text{Co}_2(\mu\text{-tpda})_3]^+$ .

**$[\text{Ni}_3(\mu_5\text{-tpda})_4\text{Cl}_2]$ :**  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.948 g, 4 mmol) and H<sub>2</sub>tpda (1.02 g, 4 mmol) were placed in an Erlenmeyer flask, and naphthalene (7.2 g) was added. The mixture was heated (about 160–180 $^\circ\text{C}$ ) for 10 min to remove water. Then *n*-butanol (3 mL) was added to the heated mixture, and heating was continued until the *n*-butanol had almost completely evaporated. A solution of potassium *n*-butoxide (0.88 g, 8 mmol, in 20 mL *n*-butanol) was added dropwise. Heating was continued until the remaining *n*-butanol had evaporated completely. After the mixture had cooled, *n*-hexane was added to wash out naphthalene. The remaining solid was extracted with  $\text{CH}_2\text{Cl}_2$  and recrystallized from  $\text{CH}_2\text{Cl}_2/n$ -hexane solution. Deep purple crystals were obtained (yield 50%). IR (KBr)  $\tilde{\nu} = 1591, 1562, 1541 \text{ cm}^{-1}$  (C=C). UV/Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}(\epsilon) = 253(1.02 \times 10^5)$ , 293( $1.28 \times 10^5$ ), 373( $1.55 \times 10^5$ ), 592 nm ( $1.28 \times 10^4$ ). MS (FAB):  $m/z$  (%) 1408 (4)  $[M]^+$ , 1373 (3),  $[M - \text{Cl}]^+$ , 1017 (10)  $[\text{Ni}_4(\mu\text{-tpda})_4]^+$ , 698 (10)  $[\text{Ni}_3(\mu\text{-tpda})_4]^+$ .

Crystal data for  $[\text{Co}^{\text{II}}(\text{H}_2\text{tpda})\text{Cl}_2]$ : Monoclinic, space group  $C2/c$ ,  $a = 7.482(1)$ ,  $b = 17.172(3)$ ,  $c = 12.833(1)$  Å,  $\beta = 104.1(1)^\circ$ ,  $V = 1598.8(4)$  Å<sup>3</sup>,  $\rho = 1.633 \text{ g cm}^{-3}$ ,  $Z = 4$ ; CAD4 diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation,  $\Psi$ -scan absorption correction (0.91–1.00); of 1406 unique reflections ( $2\theta < 50^\circ$ ) measured, 1125 with  $I > 2\sigma(I)$  were used in the refinement.  $R = 0.027$ ,  $R_w = 0.026$  (133 variables).

Crystal data for  $[\text{Ni}_3^{\text{II}}(\mu_5\text{-tpda})_4\text{Cl}_2](\text{CH}_2\text{Cl}_2)_4$ : Monoclinic, space group  $P2_1/n$ ,  $a = 13.416(3)$ ,  $b = 16.894(3)$ ,  $c = 15.8807(4)$  Å,  $\beta = 92.54(2)^\circ$ ,  $V = 3578(1)$  Å<sup>3</sup>,  $\rho = 1.623 \text{ g cm}^{-3}$ ,  $Z = 4$ ;  $\Psi$ -scan absorption correction (0.92–1.00); of 6280 unique reflections ( $2\theta < 50^\circ$ ) measured, 3188 with  $I > 2\sigma(I)$  were used in the refinement.  $R = 0.072$ ,  $R_w = 0.071$  (485 variables).

Crystal data for  $[\text{Co}_2^{\text{II}}(\mu_5\text{-tpda})_4(\text{SCN})_2] \cdot \text{CH}_2\text{Cl}_2 \cdot (\text{C}_2\text{H}_5\text{O})_{0.5} \cdot (\text{H}_2\text{O})_{0.5}$ : Triclinic, space group  $P\bar{1}$ ,  $a = 11.802(1)$ ,  $b = 14.631(7)$ ,  $c = 20.184(4)$  Å,  $\alpha = 73.42(3)$ ,  $\beta = 77.77(1)$ ,  $\gamma = 87.56(3)^\circ$ ,  $V = 3264(2)$  Å<sup>3</sup>,  $\rho = 1.615 \text{ g cm}^{-3}$ ,  $Z = 2$ ;  $\Psi$ -scan absorption correction (0.83–1.00); of 8645 unique reflections ( $2\theta < 45^\circ$ ) measured, 3400 with  $I > 2\sigma(I)$  were used in the refinement.  $R = 0.049$ ,  $R_w = 0.046$  (847 variables).

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-145. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code + (1223) 336-033; e-mail: [teched@chemcryst.cam.ac.uk](mailto:teched@chemcryst.cam.ac.uk)).

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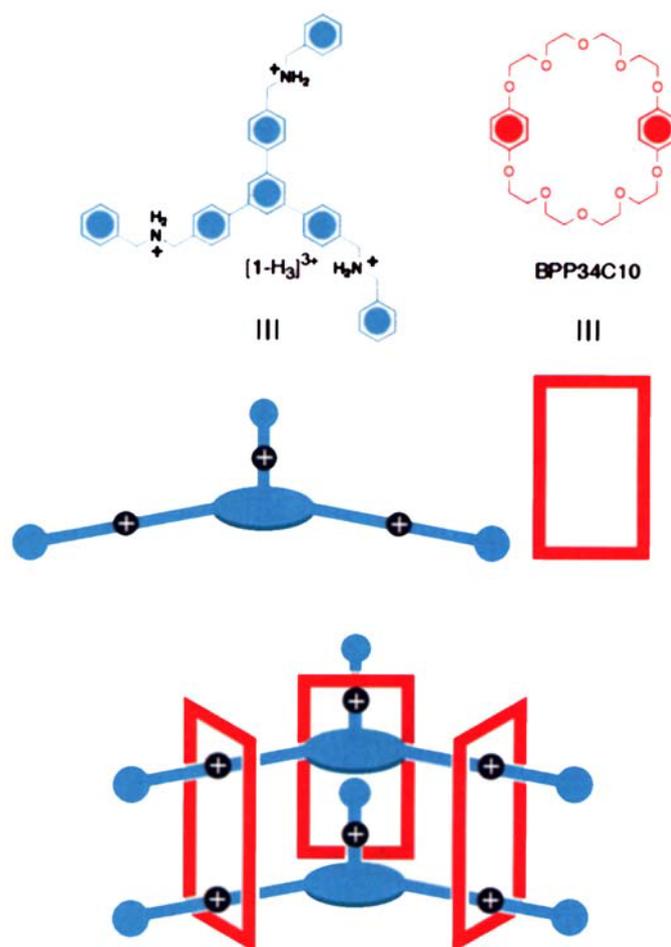
- [1] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, 1988, Chap. 23.
- [2] F. A. Cotton, R. A. Walton, *Multiple Bonds Between Metal Atoms*, 2nd ed., Clarendon Press, Oxford, 1993.
- [3] *Metal-Metal Bonds Clusters in Chemistry and Catalysis*, Plenum, New York, 1989.
- [4] E. C. Yang, M. C. Cheng, M. S. Tsai, S. M. Peng, *J. Chem. Soc. Chem. Commun.* 1994, 2377.
- [5] J. T. Sheu, C. C. Lin, I. Chao, C. C. Wang, S. M. Peng, *Chem. Commun.* 1996, 315.
- [6] L. P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathway, *J. Chem. Soc. Dalton Trans.* 1990, 3835.
- [7] S. Aduldech, B. Hathway, *J. Chem. Soc. Dalton Trans.* 1991, 993.
- [8] F. A. Cotton, R. Poli, *Inorg. Chem.* 1987, 26, 3653. Co-Co = 2.265(2) Å in  $[\text{Co}_2^{\text{II}}(\text{triaz})_4]$  (triaz = di-*p*-tolyltriazinato).
- [9] O. Jarchow, H. Schultz, R. Nast, *Angew. Chem.* 1970, 84, 43; *Angew. Chem. Int. Ed. Engl.* 1970, 9, 71. Ni-Ni = 2.32 Å in  $[\text{Ni}_2^{\text{II}}(\text{CN})_6]^{4-}$ .
- [10] L. Sacconi, C. Mealli, D. Gatteschi, *Inorg. Chem.* 1974, 13, 1985. Ni-Ni = 2.42 Å in  $[\text{Ni}_2^{\text{II}}(\text{napy})_2\text{Br}_2]^+$  (napy = 1,8-naphthyridine).
- [11] M. Corbett, B. Hoskins, *Chem. Commun.* 1969, 1602. Ni-Ni = 2.38 Å in  $[\text{Ni}_2^{\text{II}}(\text{PhN}_3\text{Ph})_2]$  (PhN<sub>3</sub>Ph = diphenyltriazinato).
- [12] C. Lin, C. Chou, S. Peng, unpublished. The *J* for  $[\text{Ni}_3(\mu_3\text{-dpa})_2\text{X}_2]^{n+}$  (dpa = dipyridylamido ion) is -96, -122 and -550  $\text{cm}^{-1}$  for X = Cl<sup>-</sup> (*n* = 0), X = NCS<sup>-</sup> (*n* = 0) and X = NCMe (*n* = 2), respectively.

## An Interwoven Supramolecular Cage\*\*

Peter R. Ashton, Andrew N. Collins,  
Matthew C. T. Fyfe, Peter T. Glink, Stephan Menzer,  
J. Fraser Stoddart,\* and David J. Williams

Dedicated to Professor Vincenzo Balzani  
on the occasion of his 60th birthday

In recent times, supramolecular, noncovalent synthesis<sup>[1]</sup> has provided the chemist convenient access to some remarkable superstructures, many of which are produced with a high degree of architectural control and have the potential to perform specific functions. One of the most challenging domains within this field of endeavor involves self-assembling<sup>[2]</sup> discrete supramolecular cages that are held together by intermolecular interactions<sup>[3]</sup> and can act as synthetic receptors. However, none of the systems reported to date involve interlocked or interwoven structures.<sup>[4]</sup> We have designed such a system (Scheme 1), which relies upon the simultaneous threading of two secondary dialkylammonium ions through the cavity of a ditopic crown ether, namely bis-*p*-phenylene[34]crown-10 (BPP34C10).<sup>[5]</sup> The trifurcated trisammonium ion  $[\text{I-H}_3]^{3+}$  has three secondary ammonium centers in branches radiating from a central polyaromatic core. Each branch can insert itself through the cavity of a BPP34C10 molecule, but then utilizes only half of the potential receptor



Scheme 1. Schematic representation of the anticipated [3 + 2] self-assembly between two  $[\text{I-H}_3]^{3+}$  ions and three BPP34C10 macrocycles to form an interwoven supramolecular cage.

sites. The vacant receptor sites remaining in each of the cavities of the three macrocyclic polyethers are then free to accept another branch from a second trication, which leads to a cagelike supermolecule. Here we report the synthesis of the trifurcated trisammonium salt  $\text{I-H}_3 \cdot 3\text{PF}_6$  and the self-assembly of a five-component interwoven supramolecular cage in the solid state from the  $[\text{I-H}_3]^{3+}$  ion and BPP34C10.

The trisammonium ion  $[\text{I-H}_3]^{3+}$  was prepared as its hexafluorophosphate salt in good overall yield: condensation of 1,3,5-tris(4-formylphenyl)benzene<sup>[6]</sup> with benzylamine, followed by reduction of the resultant trisaldimine, gave the trifurcated trisamine 1,3,5-tris[(4-benzylaminomethyl)phenyl]benzene, which afforded  $\text{I-H}_3 \cdot 3\text{PF}_6$  after treatment with hydrochloric acid and counterion exchange from chloride to hexafluorophosphate.

Single crystals suitable for X-ray analysis were obtained when a  $\text{MeNO}_2$  solution containing BPP34C10 (3 equiv) and  $\text{I-H}_3 \cdot 3\text{PF}_6$  (2 equiv) was layered with  $\text{Et}_2\text{O}$ . Gratifyingly, the crystallographic analysis of one of these crystals (Figure 1) reveals<sup>[7]</sup> the formation of a highly symmetrical cagelike superstructure in which two  $[\text{I-H}_3]^{3+}$  ions are threaded through three BPP34C10 macrocycles.<sup>[8]</sup> The supermolecule has  $D_3$  symmetry, and the principal axis passes through the centers of the two 1,3,5-triarylbenzene rings,<sup>[7]</sup> which have a mean interplanar separation of about 4.0 Å (Figure 2). The three *para*-phenylene rings of each trication are rotated by about 37° out of the plane

[\*] Prof. J. F. Stoddart, P. R. Ashton, M. C. T. Fyfe, Dr. P. T. Glink  
School of Chemistry, University of Birmingham  
Edgbaston, GB-Birmingham B15 2TT (UK)  
Fax: Int. code + (121) 414-3531  
e-mail: j.f.stoddart@bham.ac.uk  
Dr. S. Menzer, Prof. D. J. Williams  
Chemical Crystallography Laboratory, Imperial College, London (UK)  
Dr. A. N. Collins  
ZENECA Specialities, Manchester (UK)

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