toluene (1 mL). The clear solution was heated to 45 °C. After 0.5 h the mixture became cloudy and after 16 h a gel had formed. The product was stored at 45 °C for 30 days. During this ageing period no significant syneresis (contraction) was observed. The gel was dried at 150 °C/10^{-2} Torr. Analogous reactions with a tenfold amount of starting materials were also successful.

In a similar experiment *B*-trichloroborazene (3.9 g) and bis(trimethylsilyl)carbodiimide (9.5 mL) were dissolved in dry THF (50 mL). After 2.5 h reflux the content of the flask suddenly solidified to form a monolithic colorless gel body. The gel was dried at 140 °C/10^{-2} mbar/2.5 h and 190 °C/10^{-2} mbar/0.5 h. Owing to the short ageing period this xerogel contained significant amounts of chlorine (4.75 mass%) and silicon (6.3 mass%).

In other variants *B*-trichlorborazene (0.5 – 1.5 g) was dissolved in toluene (5 – 10 mL) or an excess of bis(trimethylsilyl)carbodiimide and stored at 45 °C. The mixtures formed a gel after 1 – 3 days depending on the concentration. After an ageing period of 2 – 40 days the gels were dried at 150 °C/10^{-2} Torr.

The xerogels were pyrolyzed in Quartz Schlenk tubes under argon at 400, 600, 800, 1000, and 1200 °C for 2 h using a heating rate of 100 °C h^{-1}. Further annealing at 1600 and 1800 °C in Ar and at 2000 °C in He was performed in a graphite furnace. Heating rates of 600 °C h^{-1} up to 1200 °C followed by 300 °C h^{-1} and holding times of 4 h were applied.

The yield of the xerogels, based on the amount of *B*-trichloroborazene and the idealized structure depicted in Scheme 1, was 110 – 125%, which is because of residual trimethylsilyl end groups. The yield of the B/C/N material obtained at 1200 °C was 58 – 61% based on the xerogel. Using this amorphous product as a reference the ceramic (boron carbide) yield at 2000 °C is 56%.

The xerogels and pyrolysis products were investigated using FT-IR (Perkin-Elmer FTIR 1750, KBr pellets), Raman (Bruker IFS 55), and ^{11}B NMR spectroscopy (Bruker MSL 400 spectrometer, external standard: $(CH_3CH_2)_2O \cdot BF_3$, 128.28 MHz) as well as nitrogen absorption measurements (Quantachrome Autosorb-3B), elemental analysis (see Table 1), X-ray diffraction (STOE STADI-P-diffractometer, Cu$_{K\alpha}$), and TGA-MS (Netzsch STA 429 coupled with a mass spectrometer Balzers QMG 420).

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Metallacoronates or One-Dimensional Polymers through Self-Assembly—Influence of Templates and Hydrogen Bonding on Product Formation[**]

Rolf W. Saalfrank,[*] Ingo Bernt, and Frank Hampel

Dedicated to Professor Dieter Sellmann
on the occasion of his 60th birthday

Design and synthesis of supramolecular inorganic structures with novel properties have provided exciting new possibilities.[1] We reported on the template-mediated self-assembly of six- and eight-membered iron coronates $[Na \subset Fe_6(L^1)_6]^+$ (**1**) and $[Cs \subset Fe_8(L^1)_8]^+$ (**2**).[2] They were prepared from triethanolamine (H_3L^1), iron(III) chloride, and sodium hydride or cesium carbonate, respectively (Scheme 1). A common feature of complexes **1** and **2** is that the ethanolato μ_1-O donors solely function as ligands for the coordinative saturation of the iron centers, whereas the ethanolato μ_2-O donors are structure-determining. Consequently, reaction of N-substituted diethanolamines **3** (H_2L^2)

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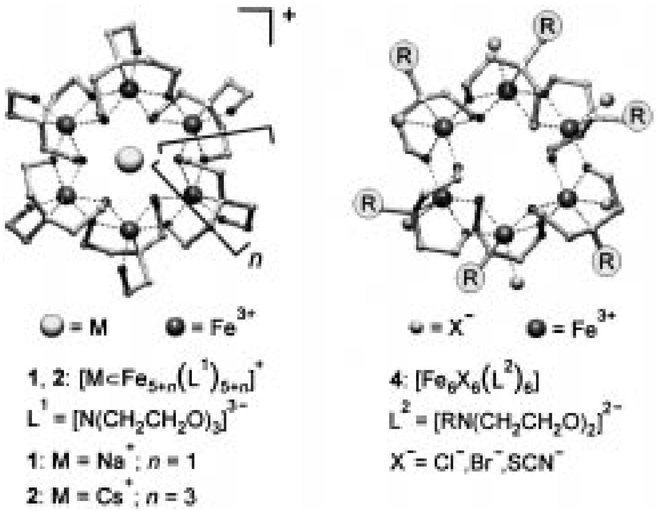


Scheme 1. Schematic representation of the metallacoronates **1** and **2** and the metallacoronands **4**.

($L^2 = [RN(CH_2CH_2O)_2]^{2-}$) with calcium hydride, iron(III) chloride, and sodium bromide or sodium rhodanide yielded the unoccupied neutral iron cryptands $[Fe_6X_6(L^2)_6]$ **4** ($X = Cl^-$, Br^-, NCS^-; Scheme 1).[2c]

Like in **1** and **2**, in **4**, the μ_2-O donors of the *N*-alkyldiethanolamine ligands are structure-determining. Completion of the octahedral coordination sphere at iron and charge compensation is achieved by the halogenato or pseudo-halogenato co-ligands. By changing from hexacoordinating iron(III) to pentacoordinating divalent metal ions it should be possible to synthesize neutral unoccupied metallacrowns of the type $[M^{II}(L^2)_6]$ with *N*-alkyldiethanolamine ligands alone.

To prove this hypothesis, we allowed *N*-(2,5-dimethylbenzyl)iminodiethanol (**3a**; H_2L^{2a}) to react with sodium hydride and copper(II) bromide and obtained the blue material **5a** (Scheme 2). For an unambiguous characterization, we carried out an X-ray crystallographic structure analysis of **5a** (Figure 1).[3] As expected, **5a** is present in the crystal as a cyclic hexanuclear copper(II) complex of composition $[(NaBr)_2\cap Cu_6(L^{2a})_6]$. The six copper centers of the centrosymmetric $[Cu_6(L^{2a})_6]$ framework are located in the corners of a regular hexagon. The mean Cu–Cu distance is 3.05 Å. The square-pyramidal coordination sphere of the copper ions is composed of one nitrogen donor, two μ_2-oxygen donors, and two μ_3-oxygen donors. $(L^{2a})^{2-}$ acts as a tridentate tritopic ligand and links three copper(II) ions with each other. The twelve oxygen donors of **5a** are located in the corners of two pairs of equilateral triangles, which are rotated 60° relative to each other. One set of triangles comprises the μ_3-oxygen donors and one set comprises the μ_2-oxygen donors. The trigonal planes are located parallel and equidistant in pairs above and below the plane generated by the copper ions and share a common C_3 axis (Figure 1, left).

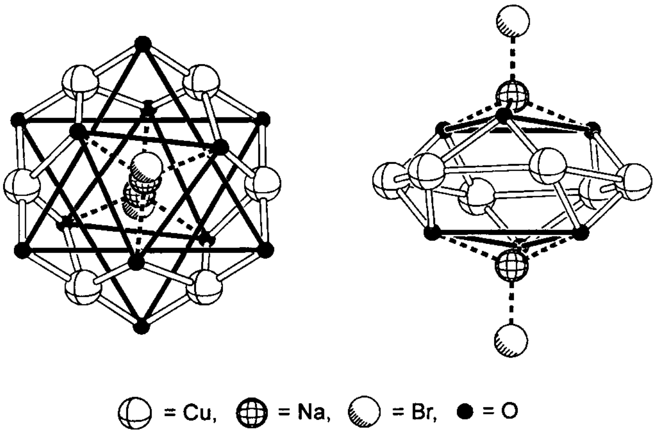
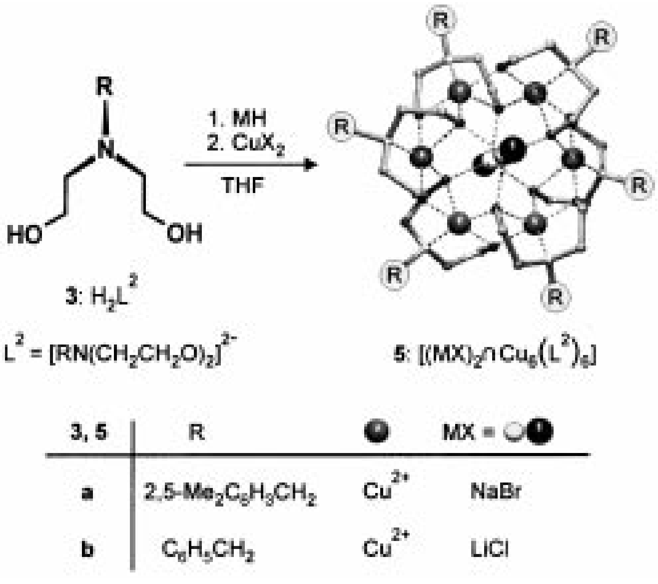


Figure 1. Left: View along the C_3 axis of the $[Cu_6O_{12}]$ core of **5a** with two exohedrally coordinated sodium bromide guests. The small triangles highlight the μ_3-oxygen atoms and the larger triangles the μ_2-oxygen atoms. Right: View perpendicular to the C_3 axis; μ_2-oxygen atoms are omitted for clarity.



3, 5	R	●	MX = ○●
a	$2,5\text{-}Me_2C_6H_3CH_2$	Cu^{2+}	NaBr
b	$C_6H_5CH_2$	Cu^{2+}	LiCl

Scheme 2. Synthesis of copper coronate **5**.

In contrast to the aforementioned ferric wheels **1** and **2**, no endohedral cation inclusion is observed for **5a**. Instead, two sodium ions are found exohedrally bound to the outer faces of the copper wheel through three of the six μ_3-oxygen atoms, each. The tetragonal coordination spheres of the sodium ions are completed by bromide ions, giving cluster **5a** the shape of a molecular gyroscope (Figure 1, right; Figure 2). The sodium and bromide ions are located on the molecular C_3 axis. The distance between Na^+ and Br^- is remarkably short (2.81 Å; sum of ionic radii: 2.95 Å).[4]

Provided that the core of **5** is flexible, it might be possible, that further templates besides sodium bromide are suitable for the formation of the $[Cu_6(L^2)_6]$ acceptor. Consequently, we allowed *N*-benzyliminodiethanol **3b** (H_2L^{2b}) to react with lithium hydride and copper(II) chloride and isolated **5b** as a blue powder. The X-ray structure analysis of a single crystal of **5b** revealed[3] that $[(LiCl)_2\cap Cu_6(L^{2b})_6]$ (**5b**) is basically isostructural to **5a**. Two lithium chloride guests are bound on opposite μ_3-O faces of the copper wheel. In contrast to **5a** the μ_3-oxygen atoms in **5b** are tilted more towards the center of the $[Cu_6(L^2)_6]$ torus, leading to tighter cavities to

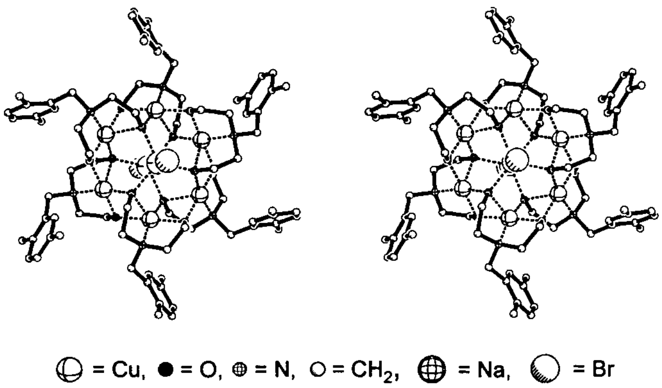


Figure 2. Stereoview of **5a** in the crystal along the molecular C_3 axis (PLUTON representation; hydrogen atoms are omitted for clarity).

accommodate the smaller guests. Like **5a**, cluster **5b** resembles a molecular gyroscope. In **5b**, two polar chloride ions form the tips of the gyro and the unpolar benzyl substituents the disk-shaped torso. The remarkable polar anisotropy results in a noteworthy crystal packing of **5b**. In the crystal, the copper wheels are arranged coplanar in layers, which are separated by 11.09 Å. The interstitial void is terminated by the chloride tips of the exohedral adducts **5b** and is occupied by solvent molecules (Figure 3).

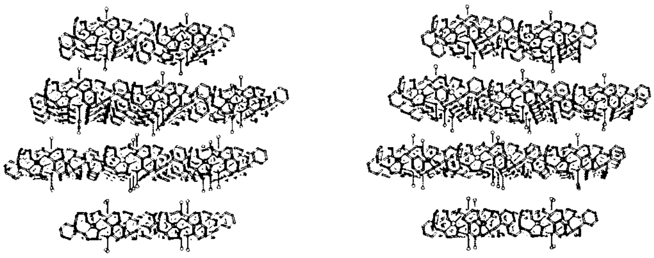
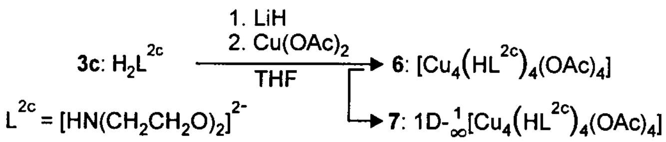


Figure 3. Stereoview of the crystal packing of **5b** along the *a* axis, showing the layers of the interdigitated planar cupric wheels and the chloride ions pointing towards the interstitial voids (PLUTON representation; solvent molecules and hydrogen atoms are omitted for clarity).

Investigation of the hexa- and octanuclear ferric wheels $[Na \subset Fe_6(L^1)_6]^+$ (**1**) and $[Cs \subset Fe_8(L^1)_8]^+$ (**2**) has revealed that the formation of distinct host molecules from a virtual pool of acceptor systems is determined by the presence of appropriate guests.[5] Nevertheless, it is not necessarily the templating effect of the cation alone that determines the product. This was evident when copper(II) acetate was treated with diethanolamine **3c** and lithium hydride. After work-up, a blue powder was isolated, which according to a single-crystal X-ray structure analysis was the one-dimensional coordination polymer 1D-$^1_\infty[Cu_4(HL^{2c})_4(OAc)_4]$ (**7**) rather than a hexanuclear copper wheel.[6] The structure of **7** becomes clear if one assumes the formation of the self-complementary tetranuclear building blocks $[Cu_4(HL^{2c})_4(OAc)_4]$ (**6**) and their linkage through hydrogen bonds (Scheme 3).

In module **6** four copper centers are linked in an alternating way by two μ_2- and two μ_3-oxygen atoms in an *anti*-tricyclo[4.2.0.0^{2,5}]octane-like fashion. Two $(HL^{2c})^-$ ligands (outer ligands) coordinate to the two outer copper centers by one nitrogen, a μ_1-oxygen, and a μ_2-oxygen donor. Whereas, the second pair of $(HL^{2c})^-$ ligands (inner ligands) coordinate to the two inner copper centers through the nitrogen and the μ_3-oxygen donors alone; the ethanol arm does not participate in the coordination. The square-pyramidal coordination geometry at the inner and outer copper centers is completed by four acetate ligands. The ideal conformation necessary for the polymerization of the self-complementary building block **6** is stabilized by additional intramolecular hydrogen bonds. The modules **6** polymerize to give **7** through formation of NH-μ_2-O-HO hydrogen bonds (Figure 4).[7] In the crystal, two sets of parallel strands of **7** are packed in equidistant alternating layers, which are rotated approximately 40° relative to each other (Figure 5).



Scheme 3. Synthesis of polymeric strands **7**.

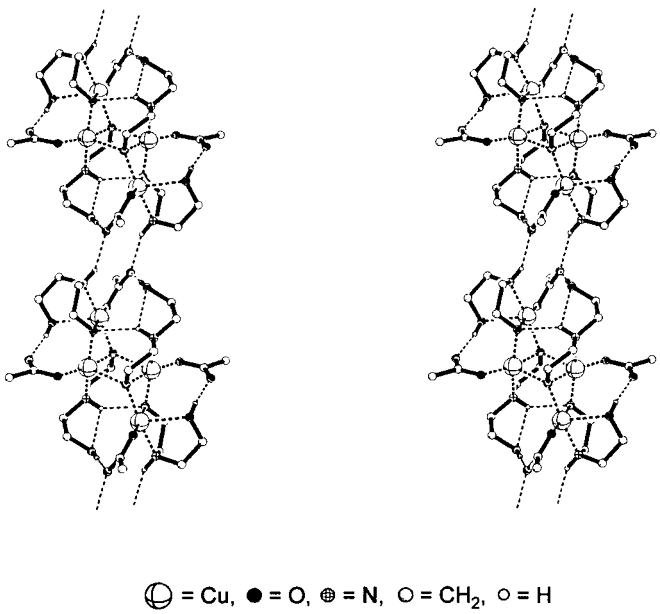


Figure 4. Stereoview of a single strand of the 1D polymer **7**, which shows the linkage of the self-complimentary building block **6** through hydrogen bonds (PLUTON representation; hydrogen atoms are omitted, except those involved in hydrogen bonds).

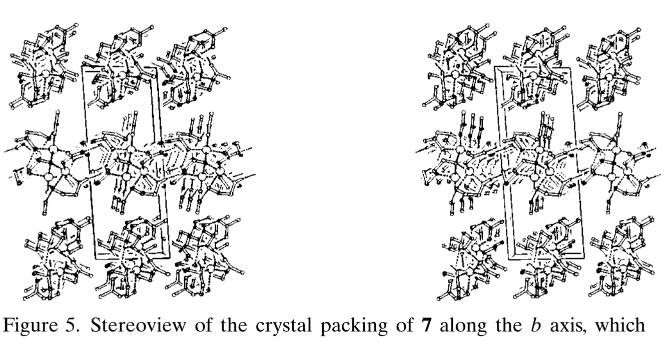


Figure 5. Stereoview of the crystal packing of **7** along the *b* axis, which shows two sets of alternating layers of parallel 1D strands. (PLUTON representation; solvent molecules and hydrogen atoms omitted for clarity).

We have shown that for the rational design of supramolecular systems a multitude of effects such as the denticity of the ligands, the coordination geometry of the metal centers, the influence of the templates as well as the possibility of hydrogen bonding have to be considered. Nevertheless, accurate predictions of self-assembly processes are possible, if one approaches the unknown territory in a stepwise manner from a safe camp.

Experimental Section

General method: *N*-(2,5-dimethylbenzyl)iminodiethanol (**3a**) (4 mmol, 0.89 g) (for **5a**), *N*-benzyliminodiethanol **3b** (4 mmol, 0.78 g) (for **5b**), or diethanolamine **3c** (4 mmol, 0.42 g) (for **6**) were added to a suspension of sodium hydride (9 mmol, 0.22 g) (for **5a**) or lithium hydride (9 mmol, 0.07 g) (for **5b** and **6**) in anhydrous tetrahydrofuran (60 mL). After the mixture had been stirred for 1 h at 20°C, copper(II) bromide (4 mmol, 0.89 g) (for **5a**), copper(II) chloride (4 mmol, 0.54 g) (for **5b**), or $Cu(OAc)_2 \cdot H_2O$ (4 mmol, 0.80 g) (for **5a**) were added. The reaction mixture was stirred for four days at 20°C and the blue precipitate was subsequently collected on a glass frit. In the case of **5a** and **6** the solid was extracted with dichloromethane (100 mL). After partial evaporation of the solvent, diethyl ether was added and blue crystals were obtained after two days. In the case of **5b** the solid was extracted with dimethyl sulfoxide (20 mL); chloroform (20 mL) and pentane (20 mL) were added, and upon standing for three days at 20°C deep blue crystals were obtained. The microanalytical data for **5a** and **5b** deviate from theory due to crystal solvents and are not recorded here.

5a$\cdot 9\,CH_2Cl_2$: yield: 0.55 g (31%), blue, rhombic crystals from dichloromethane/diethyl ether (1/1), m.p. >240°C (decomp); IR (KBr): $\tilde{\nu} = 2963$, 2868,1630 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol-matrix): *m*/*z*: 1139 $[Cu_4(L^{2a})_4{}^+]$.

5b$\cdot 6\,CHCl_3 \cdot LiH$: yield: 0.45 g (29%), blue, rhombic crystals from chloroform/dimethyl sulfoxide (1/1) by diffusion of pentane, m.p. >240°C (decomp); IR (KBr): $\tilde{\nu} = 2848$, 1639 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol matrix): *m*/*z*: 1027 $[Cu_4(L^{2b})_4{}^+]$.

6$\cdot 2\,CH_2Cl_2$: yield: 0.84 g (78%), deep blue, rhombic crystals from dichloromethane/diethyl ether (1/1). Elemental analysis (%): calcd for $Cu_4C_{24}H_{52}N_4O_{16}$: C 31.79, H 5.78, N 6.18; found: C 31.69, H 6.07, N 5.93; m.p. >220°C (decomp); IR (KBr): $\tilde{\nu} = 2924$, 2875, 1584, 1403 cm^{-1}; FAB-MS (3-nitrobenzyl alcohol matrix): *m*/*z*: 788 $[Cu_4(HL^{2c})_4(OAc)_2]^+$.

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[3] X-ray crystal structure analyses: X-ray data were collected on a Nonius Kappa CCD area detector using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Semiempirical absorption corrections were employed. The structures were solved by direct methods with SHELXS-97[8] and refined with full-matrix least-squares against F^2 with SHELXL-97.[9] Hydrogen atoms were attached in idealized positions and refined by using the riding model. **5a**: $C_{78}H_{114}Br_2Cu_6N_6Na_2O_{12} \cdot 9\,CH_2Cl_2$; $M_r = 2679.11$; triclinic, $P\bar{1}$; crystal size $0.30 \times 0.10 \times 0.10$ mm^3; $a = 14.349(3)$, $b = 15.534(3)$, $c = 15.604(3)$ Å; $\alpha = 64.34(3)$, $\beta = 87.60(3)$, $\gamma = 65.68(3)°$; $V = 2817.2(10)$ Å^3; $T = 173(2)$ K; $Z = 1$; $\rho_{calcd} = 1.578$ Mg m^{-3}; section of the reciprocal lattice $-17 < h < 17$, $-16 < k < 18$, $-18 < l < 18$; $\Theta = 2.54-25.03°$; 17129 reflections observed, 9905 unique; 8206 reflections with $I > 2\sigma(I)$; $R1 = 0.0544$, $wR2$: 0.1420 $[I > 2\sigma(I)]$; $R1 = 0.0674$, $wR2 = 0.1525$ (all data); largest difference peak and hole: 1.564/−0.859 e Å^{-3}. **5b**: $C_{66}H_{90}Cl_2Cu_6Li_2N_6O_{12} \cdot 6\,CHCl_3 \cdot 1\,LiH$; $M_r = 2349.61$; rhombohedral, $R\bar{3}$; crystal size $0.20 \times 0.20 \times 0.20$ mm^3; $a = b = 16.2876(5)$, $c = 33.2846(9)$ Å; $V = 7646.9(4)$ Å^3; $T = 173(2)$ K; $Z = 3$; $\rho_{calcd} = 1.527$ Mg m^{-3}; section of the reciprocal lattice $-17 < h < 19$, $-19 < k < 19$, $-39 < l < 38$; $\Theta = 2.50-25.02°$; 10793 reflections observed, 2994 unique; 2191 reflections with $I > 2\sigma(I)$; $R1 = 0.0484$, $wR2 = 0.1364$ $[I > 2\sigma(I)]$; $R1 = 0.0754$, $wR2 = 0.1467$ (all data); largest difference peak and hole: 0.884/−0.472 e Å^{-3}. **6**: $C_{24}H_{52}Cu_4N_4O_{16} \cdot 2\,CH_2Cl_2$; $M_r = 1076.71$; triclinic, $P\bar{1}$; crystal size $0.30 \times 0.30 \times 0.25$ mm^3; $a = 8.7582(2)$, $b = 12.1347(2)$, $c = 21.6381(4)$ Å; $\alpha = 88.9647(11)$, $\beta = 85.6537(10)$, $\gamma = 69.9782(10)°$; $V = 2154.38(7)$ Å^3; $T = 173(2)$ K; $Z = 2$; $\rho_{calcd} = 1.658$ Mg m^{-3}; section of the reciprocal lattice $-11 < h < 11$, $-13 < k < 15$, $-28 < l < 28$; $\Theta = 2.01-27.51°$; 16651 reflections observed, 9790 unique; 7759 reflections with $I > 2\sigma(I)$; $R1 = 0.0365$, $wR2 = 0.0870$ $[I > 2\sigma(I)]$; $R1 = 0.0556$, $wR2 = 0.0958$ (all data); largest residue: 1.034/−0.578 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153792 (**5a**), CCDC-153793 (**5b**), and CCDC-153791 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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