

Directed Synthesis of $\{\text{Mn}_{18}\text{Cu}_6\}$ Heterometallic Complexes**

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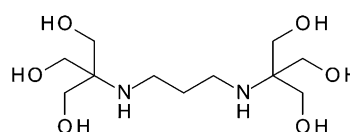
Dedicated to Professor David Collison on the occasion of his 60th birthday

The development of new synthetic strategies to assemble high-nuclearity transition metal complexes is a key target in modern coordination chemistry.^[1] One of the driving forces for this is their fascinating magnetic properties for example, single-molecule magnets^[2] or magnetic refrigerants^[3] and molecules with large spin ground states^[4] or large anisotropy barriers.^[5] The use of two, or more, different metal ions to assemble these clusters is an attractive synthetic target and controlling the bottom-up assembly of large heterometallic molecules is a considerable challenge.^[6,7] However, the potential rewards are significant, as there is a real possibility of control/design over the individual magnetic parameters that contribute to the overall molecular properties.^[8] Furthermore, new functionality can be added, such as the combination of magnetic and optical properties,^[9] or the production of catalysts or catalyst precursors with high activity and/or selectivity.^[10]

Previously, polydentate ligands with specific binding sites/donor atoms,^[11] linear linkers such as cyanide^[12] or rigid structure-directing ligands^[13] have been used to prepare heterometallic complexes. Herein, we describe a new step-by-step approach to synthesize large 3d–3d' heterometallic oxo-bridged clusters. Firstly, we use a preformed Cu^{II} complex, which contains multiple, latent hydroxy binding sites, to target the trapping and encapsulation of an inner metal-oxo core. Secondly, the choice of Cu^{II} as the central ion increases the flexibility further, due to its range of typical coordination environments from [4] to [4+2]. We report two compounds that contain a striking “core-shell” $\{\text{Mn}_{18}\text{Cu}_6\}$ complex as either a hexa- or dication, where the Cu^{II} precursors

encapsulate a hexacapped cuboctahedral manganese oxide $\{\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_6\text{O}_{14}\}$ nanocluster.

The Cu^{II} center is enclosed using the bis-tris propane ligand [2,2'-(propane-1,3-diylidimino)bis[2-(hydroxymethyl)propane-1,3-diol]] (H_6L , Scheme 1) forming the precursor

Scheme 1. Bis-tris propane (H_6L).

complex $[\text{Cu}(\text{H}_6\text{L})\text{Cl}]\text{Cl}\cdot 1.25\text{H}_2\text{O}$ (**1**·1.25 H_2O) (see Supporting Information, Figure S1) in almost quantitative yield (see Experimental). This is then redissolved and utilized in a second reaction to generate the heterometallic complexes: addition of base to a solution of **1**, followed by addition of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ leads to the formation of $[\text{Mn}_{18}\text{Cu}_6\text{O}_{14}(\text{H}_2\text{L})_6\text{Cl}_2(\text{H}_2\text{O})_6]\text{Cl}_6\cdot \text{H}_2\text{O}$ (**2**· H_2O) using $\text{NMe}_4\text{OH}/\text{EtOH}$ or $[\text{Mn}_{18}\text{Cu}_6\text{O}_{14}(\text{H}_2\text{L})_6\text{Cl}_6]\text{Cl}_2\cdot 10\text{H}_2\text{O}\cdot 6\text{CH}_3\text{OH}$ (**3**·10 $\text{H}_2\text{O}\cdot 6\text{CH}_3\text{OH}$) using NEt_3/MeOH . Both compounds can be prepared reproducibly, albeit in low yields, which is not uncommon in the area of high-nuclearity complexes.^[14] We have been unable to obtain these complexes using a range of one-pot reactions and preformation of the Cu^{II} complex appears to be essential.

The structure of the cationic cluster in **2** is based upon a $\{\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_6\text{O}_{14}\}^{20+}$ core, encapsulated by six $\{\text{Cu}(\text{H}_2\text{L})\}^{2-}$ groups. Oxidation states have been confirmed by bond-valence sum (BVS) calculations and by consideration of charge balance/coordination environments. The twelve Mn^{III} and fourteen O^{2-} anions, form a hollow cube (ca. 3.8 Å O–O edge) (Figure 1a). The Mn^{III} cations describe a cuboctahedron, capped on each square face by a Mn^{II} , forming a giant octahedron (Figure 1b). Six faces of this giant octahedron are capped by a Cu^{II} center, which resides off-center, above one of the smaller constituent $\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_2\}$ triangular faces (Figure 1c). The Cu^{II} ions describe a further octahedron, twisted with respect to the $\{\text{Mn}^{\text{II}}_6\}$ octahedron, giving a remarkable level of self-assembly: polyhedral shells of expanding size describing archimedean $\{\text{Mn}^{\text{III}}_{12}\} < \text{platonic } \{\text{Mn}^{\text{II}}_6\} < \text{platonic } \{\text{Cu}^{\text{II}}_6\}$ solids (Figure 2).

The outer (final) coordination site of each Mn^{II} center is occupied by either a terminal water $\{\text{Mn}(1), \text{Mn}(3)\}$ and symmetry equivalent (s.e.)} or chloride ligand $\{\text{Mn}(2)\}$ and s.e.) (Figure 1b). Each H_2L^{4-} ligand displays the same bonding

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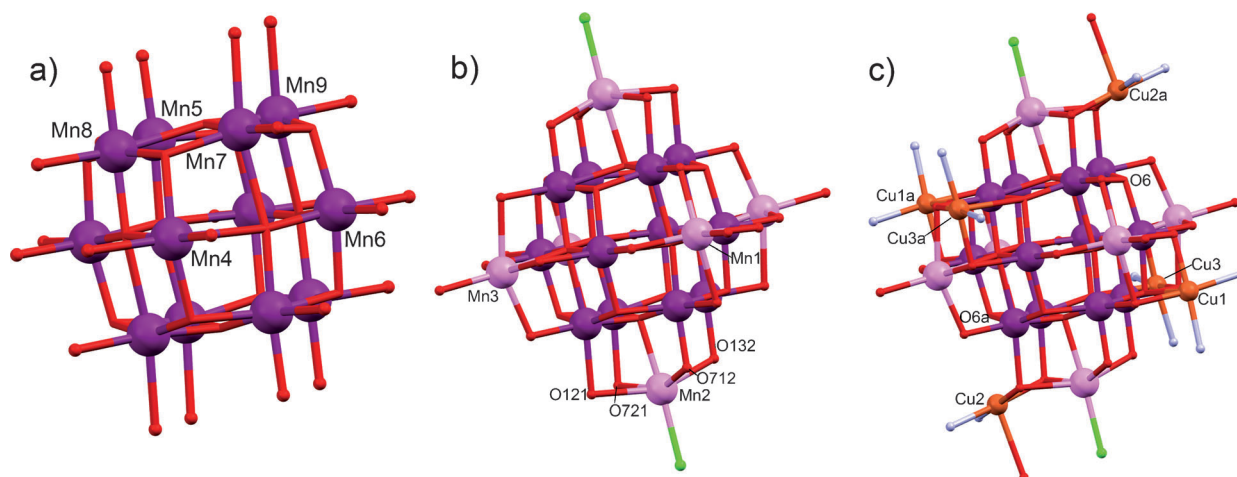


Figure 1. POV-Ray depictions of a) the $\{\text{Mn}^{\text{III}}_{12}\text{O}_{14}\}$ core of **2**, b) expansion to include the Mn^{II} octahedron encapsulating the core, c) the overall heterometallic core of **2**. Mn^{III} , purple; Mn^{II} , pink; Cu^{II} , bronze; Cl, green; O, red (oxide = capped stick, alkoxide = ball and stick); N, blue (C and H atoms omitted for clarity).

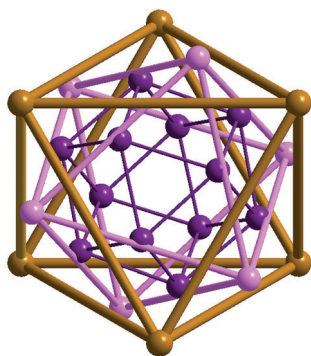


Figure 2. Expanding polyhedral shells $\{\text{Mn}^{\text{III}}_{12}\} < \{\text{Mn}^{\text{II}}_6\} < \{\text{Cu}^{\text{II}}_6\}$ in **2** (colors as previously described).

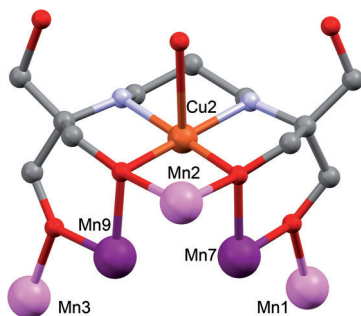


Figure 3. H_2L^{4-} ligand binding mode in **2**; the apical bond of Cu^{II} is pointing outwards from the core, to a H_2O ligand. Colors are as previously described, plus C, gray (H atoms not shown).

mode $\eta^3:\eta^3:\eta^2:\eta^2:\eta^1:\eta^1:\mu_6$ (Figure 3) and each Cu^{II} center is bridged to a Mn^{II} and two Mn^{III} centers via two μ_3 ligand alkoxide arms (Figures 1c and 3). The Cu^{II} centers are best described as distorted [4+1] coordinate, with the apical bond (ca. 2.6 Å) to either a core oxide anion [for $\text{Cu}(1)$, $\text{Cu}(3)$] or an (outer) water ligand [for $\text{Cu}(2)$]. Hence, four $\{\text{CuN}_{2(\text{eq})}\text{O}_{2(\text{eq})}\text{O}_{(\text{ax})}\}$ pyramids point towards the core and

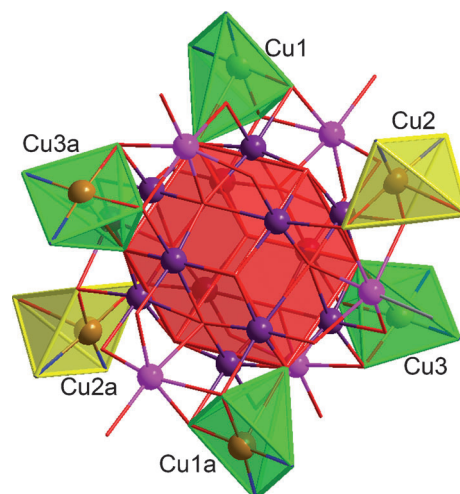


Figure 4. Differing coordination environments of the Cu^{II} cations; yellow pyramids indicate Cu^{II} centers where the apical bond points away from the core, green pyramids have the apical Cu^{II} bond pointing to the core. Red cube represents the core Mn^{III} -oxide cube. $\text{Cu}1\text{a} = \text{Cu}1\{1.5-x, 0.5-y, 1-z\}$.

two point away (Figure 4) and the coordinative flexibility of the Cu^{II} center (i.e. the direction of the Cu^{II} axial bonds) modulates the shape of the $\{\text{Mn}_{18}\text{Cu}_6\}$ complex. For $\text{Cu}(1)$ and $\text{Cu}(3)$ there is an additional (outer) weak interaction with a lattice chloride anion {2.9808(1), 2.959(3) Å} and for $\text{Cu}(2)$ an additional (inner) weak interaction with a cube corner oxide anion {O(6), 2.986(3) Å} (Figure 1c).

Compound **3** contains a similar $\{\text{Mn}_{18}\text{Cu}_6\}$ complex, as a dication, where the core structure is largely the same as for compound **2** (Figure S2 and Tables S5 and S6). However, in this case, each Mn^{II} center is equivalent and has a terminal chloride ligand (cf. either Cl^- or H_2O in **2**) (Figure 5). If we describe each Cu^{II} center as [4+1] as in **2**, then each apical ligand (ca. 2.6 Å) bonds to a core oxide anion (cf. two of these were to an {outer} water ligand in **2**, that is, pointing away

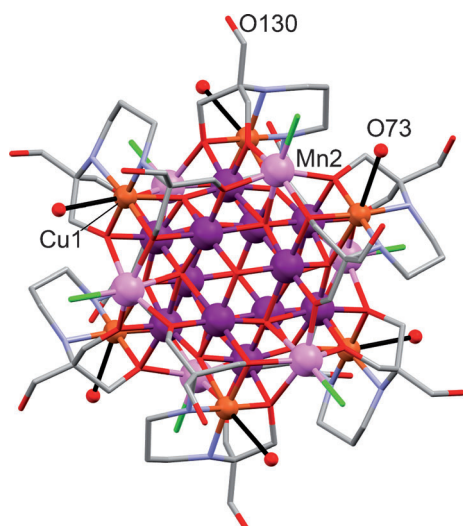


Figure 5. **3**, viewed along the three-fold axis. Bonds to oxygen atoms of neighboring clusters, utilized in forming a 3D net are shown as solid black lines.

from the core). These structural changes result in a more compact core with higher symmetry (S_6). If we describe the Cu^{II} centers as distorted [4+2] instead, the second axial position is occupied by the oxygen atom of a CH_2OH ligand arm on an adjacent molecule (Cu1-O73' ca. 2.75 Å) (Figure S3) and each $\{\text{Mn}_{18}\text{Cu}_6\}$ cluster is connected to six nearest neighbor clusters via double $\{\text{Cu-OCCN-Cu}'\}$ bridges ($\text{Cu}\cdots\text{Cu}'$ ca. 6.2 Å), creating a 3D network (Figure 6, S4). Hence, the subtle change to the reaction conditions also induces a new level of self-assembly of the $\{\text{Mn}_{18}\text{Cu}_6\}$ complexes in **3**; this is not possible in **2**, due to the presence of the two centers (Cu2 and s.e.) with H_2O ligands.

The largest heterometallic 3d-based cluster is a mixed-valent $\{\text{Cu}_4^{\text{I}}\text{Cu}_{13}^{\text{II}}\text{Mn}_4^{\text{II}}\text{Mn}_{12}^{\text{III}}\text{Mn}_{12}^{\text{IV}}\}$ cluster, prepared from Cu powder, $\text{Mn}(\text{OAc})_2$ and triethanolamine in DMF.^[15]

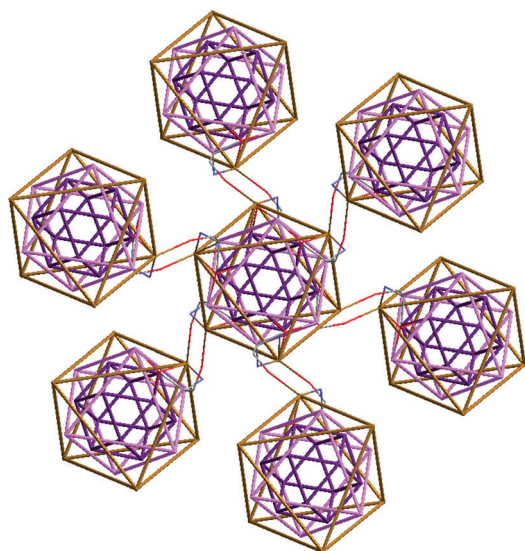


Figure 6. Pseudo-octahedral arrangement of $\{\text{Mn}_{18}\text{Cu}_6\}$ clusters in the extended structure, linked by Cu-OCCN-Cu bridges.

Further high-nuclearity Mn/Cu complexes include: $\{\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}_8\}$ and $\{\text{Mn}^{\text{II}}_5\text{Cu}^{\text{II}}_4\}$ ^[11] or $\{\text{Mn}^{\text{III}}_6\text{Cu}^{\text{II}}_{10}\}$ and $\{\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4\text{Cu}^{\text{II}}_8\}$.^[16] However, none of these one-pot reactions result in either similar metal ion topologies or oxidation levels to those found in **2** and **3**. Interestingly, the $\{\text{Mn}^{\text{III}}_{12}\}$ core structure of the $\{\text{Mn}_{18}\text{Cu}_6\}$ complexes is related to the smaller Mn-oxo clusters, $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_6\text{O}_8(\text{OEt})_6(\text{O}_2\text{CPh})_{12}]$ ^[17] and $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_{12}(\mu_4\text{-O})_8(\mu_4\text{-Cl})_6(t\text{Bu-PO}_3)_8]$ ^[18] where the central position is occupied by a Mn^{IV} or a Mn^{II} cation, respectively (cf. empty in **2** and **3**). Hence, our approach may provide a more general route to trap and build upon stable metal-oxo core architectures: here trapping a $\{\text{Mn}^{\text{III}}_{12}\}$ core and adding $\{\text{Mn}^{\text{II}}_6\}$ and $\{\text{Cu}^{\text{II}}_6\}$ shells.

Structurally closest to **2** and **3** is perhaps the polyoxo-metalate anion $[\text{Ti}_{12}\text{Nb}_6\text{O}_{44}]^{10-}$, which also has an empty central cavity, in which Ti^{IV} and Nb^{V} take the place of Mn^{III} and Mn^{II} , respectively.^[19] Comparisons can also be drawn with Pd^0 clusters: $[\text{Pd}_{23}(\text{CO})_{20}(\text{PET})_{10}]$ consists of a centered cuboctahedral $\{\text{Pd}_{13}\}$ core, with square faces capped by Pd atoms in the sites occupied by the six Mn^{II} in $\{\text{Mn}_{18}\text{Cu}_6\}$.^[20] The resulting $\{\text{Pd}_{19}\}$ giant octahedron is capped on four of its eight faces by additional Pd atoms, in positions close to those occupied by Cu^{II} in **2** and **3**.

The core of **2** is observed by ESI-MS (Figure S5, Table S7). All labile aquo ligands are lost and ion-pairs are observed for $\{[\text{Cu}^{\text{II}}_6\text{Mn}^{\text{II}}_6\text{Mn}^{\text{III}}_{12}(\text{H}_2\text{L})_6\text{O}_{14}\text{Cl}_2]\text{Cl}_3\}^{3+}$ (m/z 1146.7) and $\{[\text{Cu}^{\text{II}}_6\text{Mn}^{\text{II}}_6\text{Mn}^{\text{III}}_{12}(\text{H}_2\text{L})_6\text{O}_{14}\text{Cl}_2]\text{Cl}_4\}^{2+}$ (m/z 1737.5) and some fragmentation of the parent ion is observed, $[\text{Cu}(\text{H}_5\text{L})]^+$ (m/z 344.1). The solution stability provides further potential for using these reaction systems to probe heterometallic cluster assembly.

The bridging in **2** is complex and each metal cation is bridged to between three and eight others, via single oxygen bridges. Bridging angles range from 88.28–107.83°. The overall picture is similar for **3**, except that the higher symmetry of the molecule results in a minimum of four bridging connections to neighboring metal ions. The majority of the bridging angles are large, and as a result, we would expect antiferromagnetic coupling to dominate; which proves to be the case (Figure S6). Magnetization vs. field data (Figure S7) suggests a large number of excited states with similar energies, and a poorly defined ground state. AC measurements do not show any evidence of frequency dependence; this is unsurprising as the Jahn–Teller axes of the Mn^{III} centers are nearly perpendicular, leaving little net magnetic anisotropy.

Using our step-by-step approach, starting with a pre-formed Cu^{II} complex, we can trap and encapsulate manganese oxide nanoclusters. Reactions changing the anion (Cl^-), precursor (Cu^{II}) and core metal ion (Mn) are all underway, in order to assemble new heterometallic clusters and to explore the self-assembly of high-nuclearity complexes.

Experimental Section

All reagents and solvents were obtained from commercial suppliers and used without further purification.

Synthesis of **1**: H_6L (5.70 g, 20.2 mmol) and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (5.28 g, 31.0 mmol) were combined in ethanol (120 mL) and heated to 60 °C.

A dark green solution formed, followed by precipitation of a pale blue solid (15 mins). The mixture was heated for 5 h. After cooling, the blue precipitate $[\text{Cu}(\text{H}_6\text{L})\text{Cl}]\text{Cl}\cdot 1.25\text{H}_2\text{O}$ ($1\cdot 1.25\text{H}_2\text{O}$) was collected by filtration and washed with ethanol. Yield 8.63 g, 96%. IR: $\tilde{\nu}$ = 3140, 3018, 2943, 1470, 1428, 1307, 1263, 1114, 1077, 1064, 1011, 761 cm^{-1} . Elemental analysis ($\text{C}_{11}\text{H}_{26}\text{N}_2\text{O}_6\text{CuCl}_2\cdot 1.25\text{H}_2\text{O}$) [%], found: C 30.01, H 6.50, N 6.38; calcd: C 30.07, H 6.54, N 6.38. Single crystals suitable for X-ray study were obtained by recrystallization from ethanol yielding $1\cdot 0.5\text{EtOH}$ (see Supporting Information).

Synthesis of **2**: $1\cdot 1.25\text{H}_2\text{O}$ (109 mg, 0.263 mmol) was dissolved in hot ethanol (60 mL at 60 °C). $\text{NMe}_4\text{OH}\cdot 5\text{H}_2\text{O}$ (166 mg, 0.842 mmol) was added, and immediately dissolved, resulting in a clear royal blue solution, which was heated for 30 min. $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (166 mg, 0.837 mmol) was added, resulting in an immediate color change to dark gray, followed by formation of a precipitate. The mixture was heated for 4 h, and the precipitate (108 mg) was removed by filtration. Black crystals of $[\text{Mn}_{18}\text{Cu}_6\text{O}_{14}(\text{H}_2\text{L})_6\text{Cl}_2(\text{H}_2\text{O})_6]\text{Cl}_6\cdot \text{H}_2\text{O}$ formed in the filtrate over 1 month (ca. 6 mg, 4%) (see Supporting Information). IR: $\tilde{\nu}$ = 3351, 3262, 3212, 2921, 2864, 1634, 1455, 1426, 1393, 1260, 1154, 1100, 1079, 1027, 925, 791, 761 cm^{-1} . Elemental analysis ($\text{C}_{66}\text{H}_{144}\text{N}_{12}\text{O}_{56}\text{Cu}_6\text{Mn}_{18}\text{Cl}_8$, **2**) [%], found: C 21.81, H 4.08, N 4.60; calcd: C 21.72, H 3.97, N 4.61. MS (ESI⁺, *m/z*): 344.1, 1146.7, 1737.5 (see Table S7).

Synthesis of **3**: $1\cdot 1.25\text{H}_2\text{O}$ (108 mg, 0.259 mmol) was dissolved in methanol (30 mL). NEt_3 (0.07 mL, 0.502 mmol) was added, and immediately dissolved, resulting in a clear royal blue solution which was stirred at ambient temperature for 30 min. $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (110 mg, 0.557 mmol) was added, resulting in an immediate color change to blue-black. The solution was heated for 3 h, and filtered. Black crystals of $[\text{Mn}_{18}\text{Cu}_6\text{O}_{14}(\text{H}_2\text{L})_6\text{Cl}_6]\text{Cl}_2\cdot 10\text{H}_2\text{O}\cdot 6\text{CH}_3\text{OH}$ formed in the filtrate over 3 weeks (ca. 4 mg, 3%) (see Supporting Information). IR: $\tilde{\nu}$ = 3361, 3234, 3215, 2947, 2868, 1622, 1458, 1429, 1390, 1262, 1156, 1101, 1084, 1061, 1026, 940, 932, 793, 720 cm^{-1} . Elemental analysis ($\text{C}_{66}\text{H}_{144}\text{N}_{12}\text{O}_{50}\text{Cu}_6\text{Mn}_{18}\text{Cl}_8\cdot 4.5\text{H}_2\text{O}\cdot 4\text{CH}_3\text{OH}$, **3** $\cdot 4.5\text{H}_2\text{O}\cdot 4\text{CH}_3\text{OH}$) [%], found: C 22.39, H 4.59, N 4.62; calcd: C 22.38, H 4.21, N 4.47. A further 17 mg microcrystalline black solid was collected from the solution after removal of the single crystals. IR, as above. Elemental analysis ($3\cdot 4.5\text{H}_2\text{O}\cdot 4\text{CH}_3\text{OH}$) [%], found: C 22.31, H 4.59, N 4.60. Total yield; 21 mg, 18%.

CCDC 907989 (**1**), 907990 (**2**), and 907991 (**3**) 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.

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