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Heterometallic Complexes

Directed Synthesis of $\{Mn_{18}Cu_6\}$ Heterometallic Complexes**

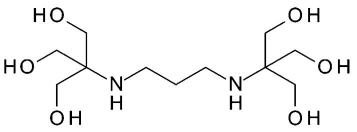
*Victoria A. Milway, Floriana Tuna, Andrew R. Farrell, Laura E. Sharp, Simon Parsons, and Mark Murrie**

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" $\{Mn_{18}Cu_6\}$ complex as either a hexa- or dication, where the Cu^{II} precursors encapsulate a hexacapped cuboctahedral manganese oxide $\{Mn^{III}_{12}Mn^{II}_6O_{14}\}$ nanocluster.

The Cu^{II} center is enclosed using the bis-tris propane ligand {2,2′-(propane-1,3-diyldiimino)bis[2-(hydroxymethyl)-propane-1,3-diol] (H_6L, Scheme 1) forming the precursor complex $[Cu(H_6L)Cl]Cl\cdot1.25\,H_2O$ (**1**$\cdot1.25\,H_2O$) (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 $MnCl_2\cdot4\,H_2O$ leads to the formation of $[Mn_{18}Cu_6O_{14}(H_2L)_6Cl_2(H_2O)_6]Cl_6\cdot H_2O$ (**2**$\cdot H_2O$) using NMe_4OH/EtOH or $[Mn_{18}Cu_6O_{14}(H_2L)_6Cl_6]Cl_2\cdot10\,H_2O\cdot6\,CH_3OH$ (**3**$\cdot10\,H_2O\cdot6\,CH_3OH$) 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.



Scheme 1. Bis-tris propane (H_6L).

The structure of the cationic cluster in **2** is based upon a $\{Mn^{III}_{12}Mn^{II}_6O_{14}\}^{20+}$ core, encapsulated by six $\{Cu(H_2L)\}^{2-}$ 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 $\{Mn^{II}Mn^{III}_2\}$ triangular faces (Figure 1c). The Cu^{II} ions describe a further octahedron, twisted with respect to the $\{Mn^{II}_6\}$ octahedron, giving a remarkable level of self-assembly: polyhedral shells of expanding size describing archimedian $\{Mn^{III}_{12}\}$ < platonic $\{Mn^{II}_6\}$ < platonic $\{Cu^{II}_6\}$ solids (Figure 2).

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

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[*] Dr. V. A. Milway, A. R. Farrell, L. E. Sharp, Dr. M. Murrie
WestCHEM, School of Chemistry, University of Glasgow
Glasgow G12 8QQ (UK)
E-mail: mark.murrie@glasgow.ac.uk
Dr. F. Tuna
EPSRC National UK EPR Facility, School of Chemistry and Photon Science Institute, The University of Manchester
Manchester M13 9PL (UK)
Prof. S. Parsons
EaStCHEM School of Chemistry, The University of Edinburgh
Edinburgh, EH9 3JJ (UK)

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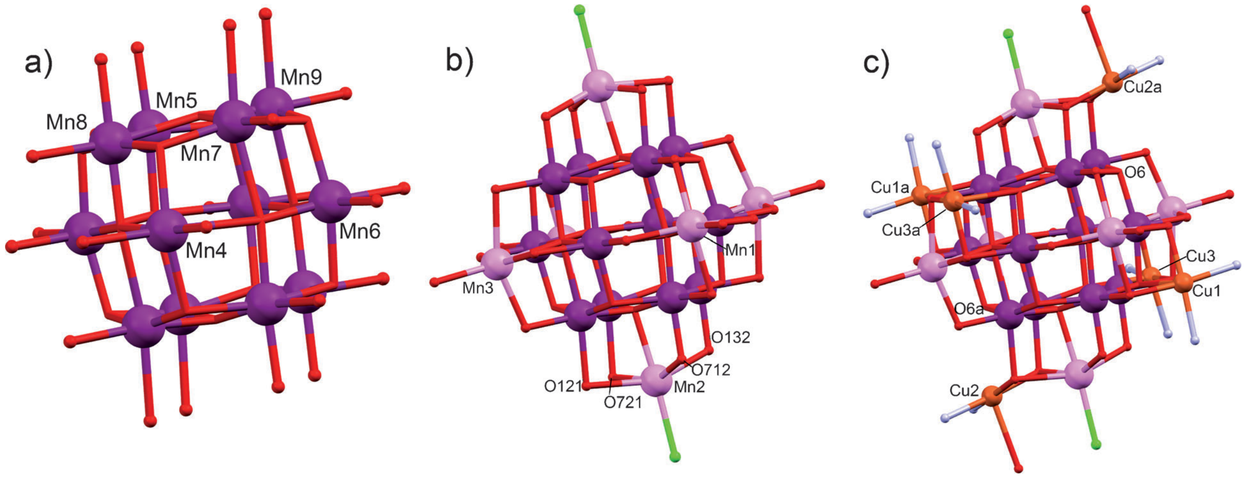

Figure 1. POV-Ray depictions of a) the $\{\mathrm{Mn^{III}}_{12}\mathrm{O}_{14}\}$ core of **2**, b) expansion to include the $\mathrm{Mn^{II}}$ octahedron encapsulating the core, c) the overall heterometallic core of **2**. $\mathrm{Mn^{III}}$, purple; $\mathrm{Mn^{II}}$, pink; $\mathrm{Cu^{II}}$, bronze;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

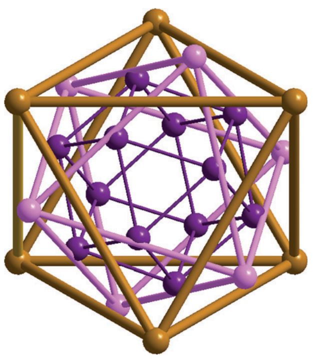

Figure 2. Expanding polyhedral shells $\{\mathrm{Mn^{III}}_{12}\} < \{\mathrm{Mn^{II}}_6\} < \{\mathrm{Cu^{II}}_6\}$ in **2** (colors as previously described).

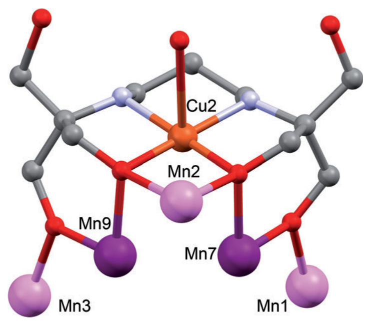

Figure 3. $\mathrm{H_2L^{4-}}$ ligand binding mode in **2**; the apical bond of Cu2 is pointing outwards from the core, to a $\mathrm{H_2O}$ ligand. Colors are as previously described, plus C, gray (H atoms not shown).

mode $\eta^3:\eta^3:\eta^2:\eta^2:\eta^1:\eta^1:\mu_6$ (Figure 3) and each $\mathrm{Cu^{II}}$ center is bridged to a $\mathrm{Mn^{II}}$ and two $\mathrm{Mn^{III}}$ centers via two μ_3 ligand alkoxide arms (Figures 1 c and 3). The $\mathrm{Cu^{II}}$ centers are best described as distorted [4+1] coordinate, with the apical bond (ca. 2.6 Å) to either a core oxide anion {for Cu(1), Cu(3)} or an (outer) water ligand {for Cu(2)}. Hence, four $\{\mathrm{CuN_{2(eq)}O_{2(eq)}O_{(ax)}}\}$ pyramids point towards the core and two point away (Figure 4) and the coordinative flexibility of the $\mathrm{Cu^{II}}$ center (i.e. the direction of the $\mathrm{Cu^{II}}$ axial bonds) modulates the shape of the $\{\mathrm{Mn_{18}Cu_6}\}$ complex. For Cu(1) and Cu(3) there is an additional (outer) weak interaction with a lattice chloride anion {2.9808(1), 2.959(3) Å} and for Cu(2) an additional (inner) weak interaction with a cube corner oxide anion {O(6), 2.986(3) Å} (Figure 1 c).

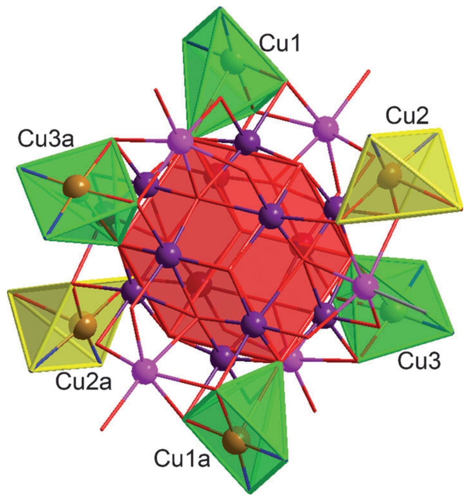

Figure 4. Differing coordination environments of the $\mathrm{Cu^{II}}$ cations; yellow pyramids indicate $\mathrm{Cu^{II}}$ centers where the apical bond points away from the core, green pyramids have the apical $\mathrm{Cu^{II}}$ bond pointing to the core. Red cube represents the core $\mathrm{Mn^{III}}$-oxide cube. Cu1a = Cu1{1.5−*x*, 0.5−*y*, 1−*z*}.

Compound **3** contains a similar $\{\mathrm{Mn_{18}Cu_6}\}$ 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 $\mathrm{Mn^{II}}$ center is equivalent and has a terminal chloride ligand (cf. either $\mathrm{Cl^-}$ or $\mathrm{H_2O}$ in **2**) (Figure 5). If we describe each $\mathrm{Cu^{II}}$ 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

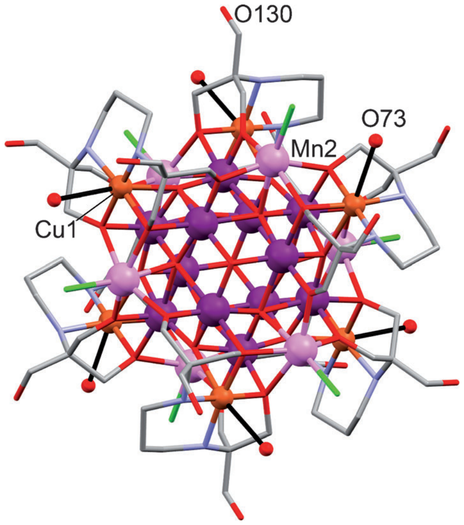

Figure 5. **3**, viewed along the three-fold axis. Bonds to oxygen atoms of neighboring clusters, utilized in forming a 3D net are shown as solid black lines.

from the core). These structural changes result in a more compact core with higher symmetry (S_6). If we describe the $\mathrm{Cu^{II}}$ centers as distorted [4+2] instead, the second axial position is occupied by the oxygen atom of a $\mathrm{CH_2OH}$ ligand arm on an adjacent molecule (Cu1–O73′ ca. 2.75 Å) (Figure S3) and each $\{\mathrm{Mn_{18}Cu_6}\}$ cluster is connected to six nearest neighbor clusters via double {Cu-OCCN-Cu′} bridges (Cu···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 $\{\mathrm{Mn_{18}Cu_6}\}$ complexes in **3**; this is not possible in **2**, due to the presence of the two centers (Cu2 and s.e.) with $\mathrm{H_2O}$ ligands.

The largest heterometallic 3d-based cluster is a mixed-valent $\{\mathrm{Cu^{I}_4Cu^{II}_{13}Mn^{II}_4Mn^{III}_{12}Mn^{IV}_{12}}\}$ cluster, prepared from Cu powder, $\mathrm{Mn(OAc)_2}$ and triethanolamine in DMF.[15]

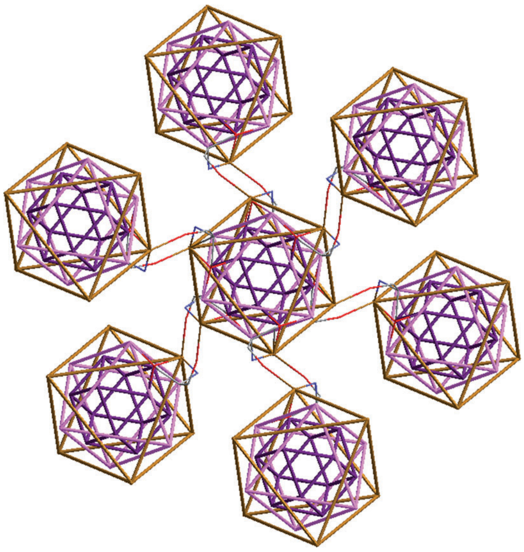

Figure 6. Pseudo-octahedral arrangement of $\{\mathrm{Mn_{18}Cu_6}\}$ clusters in the extended structure, linked by Cu-OCCN-Cu bridges.

Further high-nuclearity Mn/Cu complexes include: $\{\mathrm{Mn^{II}Cu^{II}_8}\}$ and $\{\mathrm{Mn^{II}_5Cu^{II}_4}\}$[11] or $\{\mathrm{Mn^{III}_6Cu^{II}_{10}}\}$ and $\{\mathrm{Mn^{III}_8Mn^{IV}_4Cu^{II}_8}\}$.[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 $\{\mathrm{Mn^{III}_{12}}\}$ core structure of the $\{\mathrm{Mn_{18}Cu_6}\}$ complexes is related to the smaller Mn-oxo clusters, $[\mathrm{Mn^{IV}Mn^{III}_6Mn^{II}_6O_8(OEt)_6(O_2CPh)_{12}}]$[17] and $[\mathrm{Mn^{II}Mn^{III}_{12}(\mu_4\text{-}O)_8(\mu_4\text{-}Cl)_6(\mathit{t}Bu\text{-}PO_3)_8}]$[18] where the central position is occupied by a $\mathrm{Mn^{IV}}$ or a $\mathrm{Mn^{II}}$ 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 $\{\mathrm{Mn^{III}_{12}}\}$ core and adding $\{\mathrm{Mn^{II}_6}\}$ and $\{\mathrm{Cu^{II}_6}\}$ shells.

Structurally closest to **2** and **3** is perhaps the polyoxometalate anion $[\mathrm{Ti_{12}Nb_6O_{44}}]^{10-}$, which also has an empty central cavity, in which $\mathrm{Ti^{IV}}$ and $\mathrm{Nb^{V}}$ take the place of $\mathrm{Mn^{III}}$ and $\mathrm{Mn^{II}}$, respectively.[19] Comparisons can also be drawn with $\mathrm{Pd^0}$ clusters: $[\mathrm{Pd_{23}(CO)_{20}(PEt)_{10}}]$ consists of a centered cuboctahedral $\{\mathrm{Pd_{13}}\}$ core, with square faces capped by Pd atoms in the sites occupied by the six $\mathrm{Mn^{II}}$ in $\{\mathrm{Mn_{18}Cu_6}\}$.[20] The resulting $\{\mathrm{Pd_{19}}\}$ giant octahedron is capped on four of its eight faces by additional Pd atoms, in positions close to those occupied by $\mathrm{Cu^{II}}$ 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 $\{[\mathrm{Cu^{II}_6Mn^{II}_6Mn^{III}_{12}(H_2L)_6O_{14}Cl_2]Cl_3}\}^{3+}$ (*m*/*z* 1146.7) and $\{[\mathrm{Cu^{II}_6Mn^{II}_6Mn^{III}_{12}(H_2L)_6O_{14}Cl_2]Cl_4}\}^{2+}$ (*m*/*z* 1737.5) and some fragmentation of the parent ion is observed, $[\mathrm{Cu(H_5L)}]^+$ (*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 $\mathrm{Mn^{III}}$ centers are nearly perpendicular, leaving little net magnetic anisotropy.

Using our step-by-step approach, starting with a preformed $\mathrm{Cu^{II}}$ complex, we can trap and encapsulate manganese oxide nanoclusters. Reactions changing the anion ($\mathrm{Cl^-}$), precursor ($\mathrm{Cu^{II}}$) 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**: $\mathrm{H_6L}$ (5.70 g, 20.2 mmol) and $\mathrm{CuCl_2{\cdot}2\,H_2O}$ (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 $[Cu(H_6L)Cl]Cl\cdot 1.25\,H_2O$ ($\mathbf{1}\cdot 1.25\,H_2O$) 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 ($C_{11}H_{26}N_2O_6CuCl_2\cdot 1.25\,H_2O$) [%], 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 $\mathbf{1}\cdot 0.5\,EtOH$ (see Supporting Information).

Synthesis of **2**: $\mathbf{1}\cdot 1.25\,H_2O$ (109 mg, 0.263 mmol) was dissolved in hot ethanol (60 mL at 60 °C). $NMe_4OH\cdot 5\,H_2O$ (166 mg, 0.842 mmol) was added, and immediately dissolved, resulting in a clear royal blue solution, which was heated for 30 min. $MnCl_2\cdot 4\,H_2O$ (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 $[Mn_{18}Cu_6O_{14}(H_2L)_6Cl_2(H_2O)_6]Cl_6\cdot H_2O$ 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 ($C_{66}H_{144}N_{12}O_{56}Cu_6Mn_{18}Cl_8$, **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**: $\mathbf{1}\cdot 1.25\,H_2O$ (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. $MnCl_2\cdot 4\,H_2O$ (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 $[Mn_{18}Cu_6O_{14}(H_2L)_6Cl_6]Cl_2\cdot 10\,H_2O\cdot 6\,CH_3OH$ 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 ($C_{66}H_{144}N_{12}O_{50}Cu_6Mn_{18}Cl_8\cdot 4.5H_2O\cdot 4CH_3OH$, $\mathbf{3}\cdot 4.5\,H_2O\cdot 4\,CH_3OH$) [%], 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 ($\mathbf{3}\cdot 4.5\,H_2O\cdot 4\,CH_3OH$) [%], 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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