Supramolecular Chemistry

Route to Cluster Helicates**

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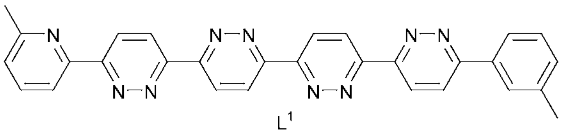
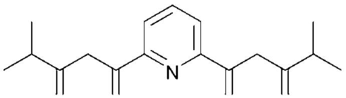
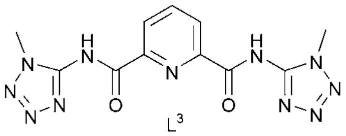
Most supramolecular helicates contain either two or three metal centers, whereas those with four or more remain relatively uncommon.[1,2] Strategies for the construction of metallohelicates with high nuclearity use long organic ligand strands or guest molecules as templating agents, and thus some linear[3] and circular helicates[4] have been reported. In contrast, there are very few examples of discrete multimetallic helicates in which the metal centers are disposed in a polyhedral mode: the pentatopic ligand L^1 forms a quadruply stranded helicate[5] $[Ag_{10}L^1_4]^{10+}$, and related ligands L^2 and L^3 form bis(triple-helical) metal complexes with six ligand strands wrapped around the $[M_8O_2]^{12+}$ metaloxo clusters ($M = Zn^{II}$, Cd^{II}, and Mn^{II}).[6] These helicates are complex



L^1



L^2



L^3

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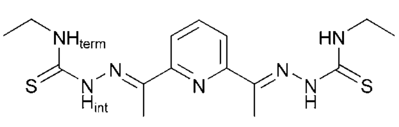
polystranded architectures that do not display metal–metal interactions.

Helicates are being used in the construction of novel materials, devices, and machines with programmed properties and functions, such as luminescence,[7] DNA binding,[8] chirality,[9] magnetic exchange,[3,10] anion binding,[11] metal-ion translocation,[12] or electrochemical structural rearrangement.[13] However, all these possible applications could undergo remarkable development if the extremely important biological, physical, and chemical properties of cluster compounds were considered.[14] Unfortunately, there are no efficient synthetic routes to "cluster helicates".

Herein, we report the first strategy to construct cluster compounds with a helical arrangement of ligands around the central metal core, that is, "cluster helicates". In particular, we describe the use of a ligand that potentially has a dianionic and helicand character and is equipped with two soft donor atoms, which allow the helicate assembly to be controlled through selection of the oxidation state of the metal centers. We therefore designed bis(4-ethyl-3-thiosemicarbazone)-2,6-diacetylpyridine (H_2L) as such a ligand (int = internal, term = terminal), which contains two soft sulfur donor atoms so that it would be an effective moiety to support the self-assembly of metal(II) dinuclear dihelicate complexes.[15] We recently reported the anion-binding properties of this ligand, and its application to the selective colorimetric recognition of fluoride anions in organic solvents.[16]



H_2L

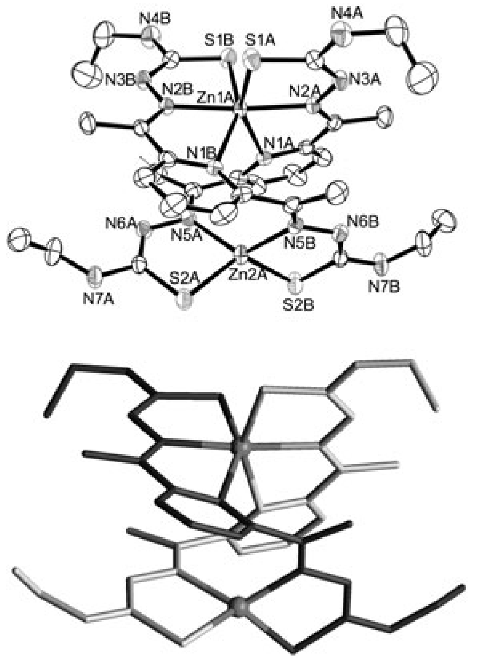


Figure 1. Top: Molecular structure of dihelicate complex $[Zn_2(L)_2]$ (**1**), with the two strands of L labeled as A and B. Thermal ellipsoids are drawn at the 40% probability level, carbon atoms are shown as unshaded ellipsoids, and hydrogen atoms have been omitted for clarity. Bottom: Ball-and-stick representation of **1**, with the two strands of L highlighted in light gray (A) and dark gray (B).

The next step in the study was the preparation of metal(II) dinuclear dihelicate derivatives containing H_2L. Our experience with this class of complex and the absence of hard donor atoms in the main body of H_2L led us to use Cu^{II} and Zn^{II} ions to prepare these complexes. Electrochemical oxidation[17] of a zinc plate in a conducting solution of H_2L in acetonitrile afforded a yellow solution, from which a pale yellow solid precipitated on concentration. The ESI mass spectrum and elemental analysis of this material are consistent with the formation of the neutral dimeric species $[Zn_2(L)_2]$, which arises from the double deprotonation of H_2L in the electrochemical cell. This complex was also characterized by IR spectroscopy (see Supporting Information).

Recrystallization of this yellow precipitate from acetonitrile by slow evaporation afforded pale yellow crystals of complex **1**, from which its molecular structure was determined by X-ray crystallography (Figure 1).[18,19] Its structure reveals the formation of the common [6+4] double-stranded dihelicate $[Zn_2(L)_2]$ (**1**). A racemic mixture of both enantiomers is observed in the unit cell. One Zn^{II} center is tetracoordinated in a tetrahedral mode by two imine nitrogen atoms and two thiolate sulfur atoms from two different ligands. The other Zn^{II} ion is hexacoordinated in a distorted octahedral mode by two pyridine nitrogen atoms, two imine nitrogen atoms, and two thiolate sulfur atoms. This coordination is achieved by symmetrical intertwining of the two ligand strands along the helical axis (Zn···Zn: 4.26 Å). This behavior is quite similar to that found by us in a zinc(II) dinuclear dihelicate complex containing a similar thiosemicarbazone ligand.[15]

The copper(II) derivative was obtained by treatment of H_2L with copper(II) perchlorate in hot acetonitrile. A dark brown solid was isolated and identified as the discrete complex $[Cu_2(L)_2]\cdot 2\,CH_3CN$ (**2**), which was characterized by elemental analysis, IR spectroscopy, ESI mass spectrometry, and magnetic moment measurements (see Supporting Information). Unfortunately, it was impossible to obtain single crystals suitable for X-ray diffraction studies. However, it is expected that **2** has a double-helical arrangement of ligands around the metal centers as it is structurally analogous to **1**.

Once the ability of H_2L to form dinuclear dihelicate complexes with Cu^{II} and Zn^{II} centers was established, we explored the possibility of increasing the nuclearity of these dinuclear dihelicates to obtain neutral dihelical species with a stoichiometry of M_4L_2 by substitution of the divalent metal centers by metal(I) ions (Figure 2).

It is known that all pure substances fulfill the principle of electroneutrality, and as H_2L has a tendency to form metal complexes in its doubly deprotonated form, two dianionic ligand units can be coordinated by four metal(I) ions to form a neutral $[M_4L_2]$ complex. We believe that the presence of the coordinatively versatile thiolate donor atoms in H_2L is

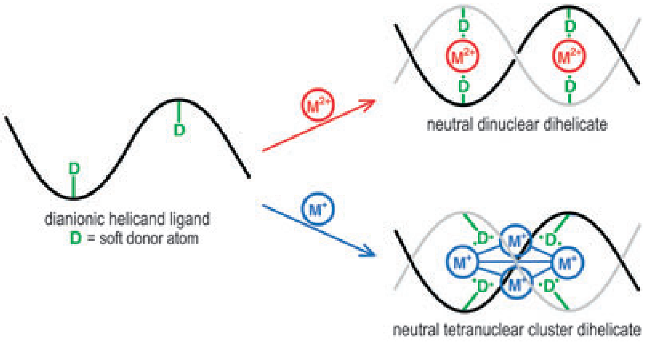


Figure 2. Schematic representation of our synthetic approach to the assembly of "cluster helicates": The substitution of divalent metal centers by metal(I) ions and the use of a dianionic and helicand ligand that contains two soft donor atoms, which can act both as terminal or bridging coordination points depending of the hardness/softness of the metal centers they bind, are the factors that make stabilization of this novel supramolecular motif possible.

essential in satisfying the coordination requirements of the four metal(I) ions and then in stabilizing the [M_4L_2] cluster. Furthermore, these thiolate atoms can act either as terminal or bridging coordination points depending on the degree of hardness/softness of the metal centers to which they bind: as the hardness of the metal ion increases, the tendency of the thiolate sulfur atom to act as a μ_1 donor increases. Therefore, monothiolate ligands that act as μ_2 or μ_3 bridges between soft acids are very common in transition-metal chemistry.[20] Moreover, the ability of thiourea sulfur atoms to act as bridges between either Cu^I or Ag^I ions in the formation of high-nuclearity [M_6L_6] cluster complexes has been recently reported by Dilworth and co-workers.[21] Finally, if two L^{2-} units can stabilize a neutral [M_4L_2] complex, we expect that this [M_4L_2] complex will have a double-helical microarchitecture, since H_2L can form dihelicates. Therefore, we expect H_2L, which potentially has dianionic and helicand character, to be a good building block for the construction of tetranuclear cluster dihelicates.

Treatment of H_2L with [$Cu(CH_3CN)_4$]PF_6 in hot acetonitrile and recrystallization of the resulting brown solid from acetonitrile afforded single crystals of [$Cu_4(L)_2$]$\cdot$4CH_3CN (**3**), which were studied by X-ray diffraction.[22] This complex was further characterized by IR spectroscopy and ESI mass spectrometry (see Supporting Information). In the ESI mass spectrum, a base peak corresponding to [$Cu_4(L)_2+H$]$^+$ was observed, thus confirming that the [4+2] complex is the main species in solution.

ORTEP and ball-and-stick representations of the structure of **3** are shown in Figure 3 (selected bond angles and distances are given in the Supporting Information). The structure comprises four Cu^I ions and two doubly deprotonated thiosemicarbazone ligands and is solvated with four molecules of acetonitrile. Each Cu^I center occupies a three-coordinate distorted trigonal environment, in which they are bound by two thiolate sulfur atoms from different ligands and one imine nitrogen atom. Thus, both ligands act as bis-bidentate N_2S_2 donors. The pyridine nitrogen atoms of the two L^{2-} units remain uncoordinated. The distortion from an ideal trigonal geometry at all the Cu^I centers is shown by the angles between the nitrogen, copper, and sulfur atoms, which range from 83.95° to 146.73° (see Supporting Information).

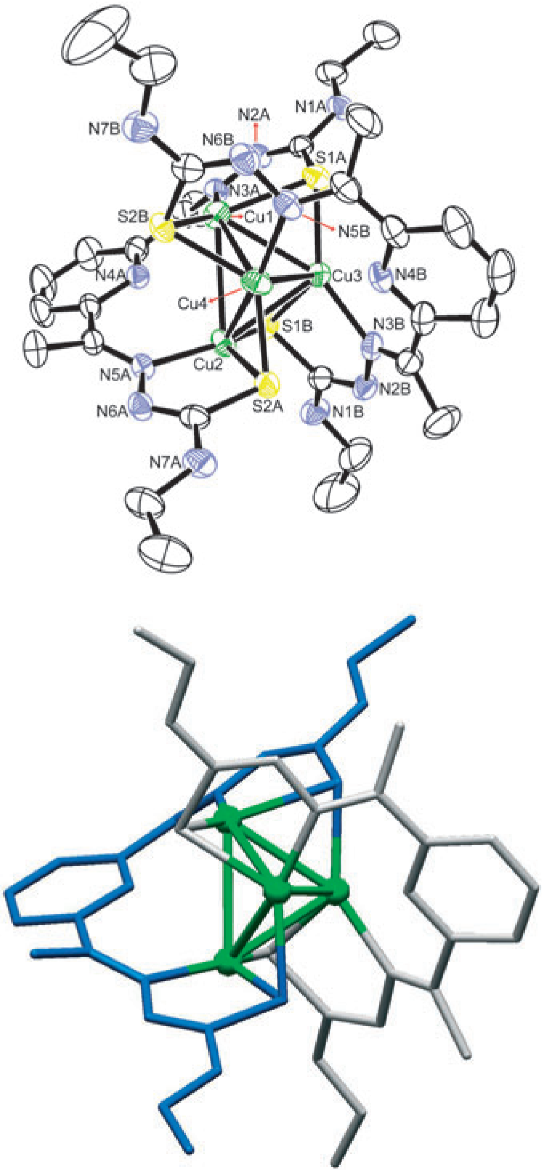


Figure 3. Top: Molecular structure of the neutral tetranuclear cluster helicate complex [$Cu_4(L)_2$]$\cdot$4CH_3CN (**3**), with the two strands of L labeled as A and B. Thermal ellipsoids are drawn at the 40% probability level, carbon atoms are shown as unshaded ellipsoids, and hydrogen atoms and solvent molecules have been omitted for clarity. Bottom: Ball-and-stick representation of **3**, with the two strands of L colored in blue (A) and gray (B), and the Cu_4 core shown in green.

The four metal centers form a {Cu_4S_4} central core, with each thiolate sulfur atom bridging two Cu^I ions. The two ligands span the tetrahedral core of metal centers and intertwine to give a double-helix structure. A racemic mixture of both enantiomers is observed in the unit cell. The double deprotonation of the ligand on coordination is evident from the observed bond lengths in the cluster (see Supporting

Information). The C_{thio}–S_{thio} bond lengths increased from 1.656–1.668 Å in H_2L to 1.764–1.771 Å in **3** while the N_{int}–C_{thio} bond lengths decreased from 1.367–1.368 Å to 1.282–1.294 Å, thus indicating that the N_{int}=C_{thio}–S_{thio} resonance form predominates in the complex. This assumption is confirmed by the C_{thio}–N_{term} bond lengths in **3** (1.346–1.366 Å), as they indicate the single nature of the bonds.

The four Cu^I ions in this unique neutral dihelicate are located in the vertex of a distorted tetrahedron. This distortion is clearly revealed by the Cu···Cu distances. Interestingly, the distances between the "bridged" Cu^I ions are shorter (2.672–2.706 Å) than those between the "unbridged" Cu^I ions (2.881–2.883 Å). Currently, there is extended controversy over the existence of Cu···Cu interactions in Cu^I cores, such as those found in the present case.[23] The distances between the metal centers are close to the sum of the van der Waals radii for two copper atoms (2.80 Å)[24] and are in agreement with the proposed existence of Cu···Cu interactions.[25] These interactions would mean that the coordination number of the Cu^I ions in **3** should increase from 3 to 6.

To confirm our approach to the preparation of cluster dihelicates, we synthesized another metal(I) derivative using this ligand. Electrochemical oxidation of a silver plate in a conducting solution of H_2L in acetonitrile yielded a yellow solution from which a yellow solid precipitated upon concentration. Recrystallization of this solid from dimethyl sulfoxide (DMSO) afforded single crystals of $[Ag_4(L)_2]\cdot 4\,DMSO$ (**4**), which were characterized by X-ray diffraction.[26] This complex was also characterized by IR spectroscopy and ESI mass spectrometry (see Supporting Information): the ESI mass spectrum showed a base signal corresponding to $[Ag_4(L)_2+H]^+$, thus confirming the presence of **4** in solution.

ORTEP and ball-and-stick representations of **4** are shown in Figure 4 (selected bond angles and distances are given in the Supporting Information). The asymmetric unit of this complex comprises two doubly deprotonated ligands, four Ag^I ions, and four unbound DMSO molecules. The Ag^I complex has a similar connectivity to the Cu^I analogue **3**, with the two ligands wrapped around the tetranuclear central Ag^I core to give a double-stranded helical structure. The trigonal coordination geometries of the four metal centers are very distorted, as illustrated by the range of angles between the N, S, and Ag atoms (75.94°–157.45°). Moreover, the C_{thio}–S_{thio} bond lengths are in the range of 1.754–1.774 Å, the N_{int}–C_{thio} bond lengths lie in the range 1.267–1.321 Å, and the C_{thio}–N_{term} bond lengths lie in the range 1.302–1.382 Å, thus indicating a less regular geometry in this complex relative to the Cu^I analogue. Both left- and right-handed helicates are present in the unit cell at 50% occupancy.

The four Ag^I ions form a distorted tetrahedron (Figure 5). The intermetallic Ag···Ag distances range from 2.909 to 3.086 Å between the sulfur-bridged Ag^I ions and from 3.219 to 3.235 Å between the unbridged Ag^I ions. All these distances are significantly shorter than the sum of the van der Waals radii for two silver atoms (van der Waals radius for Ag = 3.44 Å)[24] and may suggest the existence of metal–metal interactions.[27] The possible existence of these interactions implies that the coordination number of the Ag^I ions in **4**

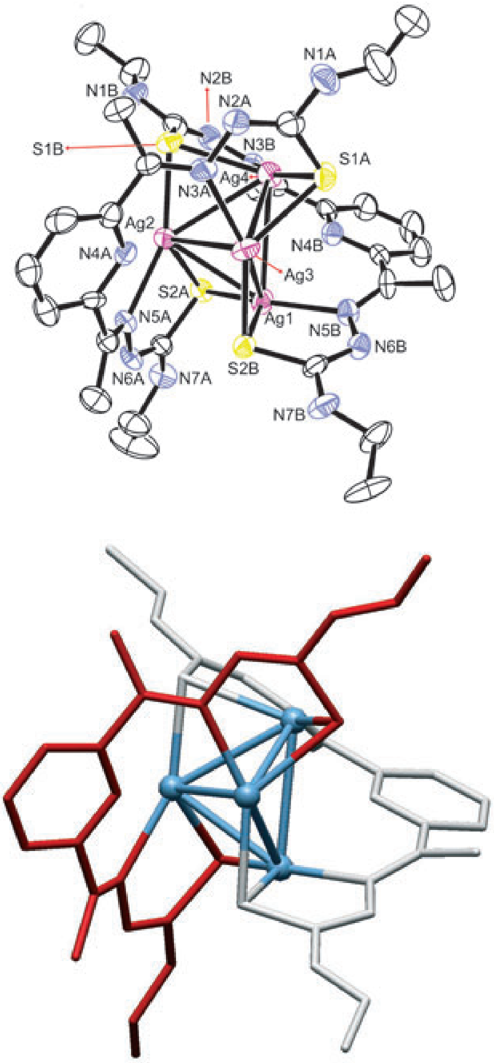


Figure 4. Top: Molecular structure of the neutral tetranuclear cluster helicate complex $[Ag_4(L)_2]\cdot 4\,DMSO$ (**4**), with the two strands of L labeled as A and B. Thermal ellipsoids are drawn at the 40% probability level, carbon atoms are shown as unshaded ellipsoids, and hydrogen atoms and solvent molecules have been omitted for clarity. Bottom: Ball-and-stick representation of **4**, with the two strands of L colored in red (A) and light gray (B), and the Ag_4 core shown in light blue.

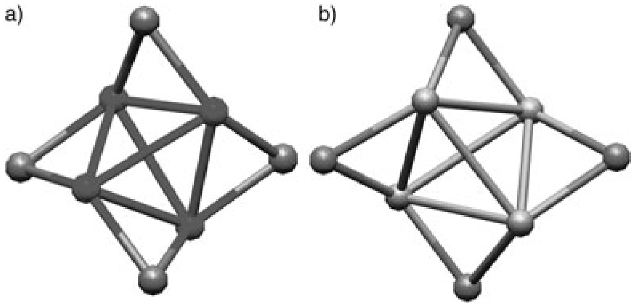


Figure 5. Ball-and-stick representation of the central $\{M_4S_4\}$ core of a) $[Cu_4(L)_2]\cdot 4\,CH_3CN$ (**3**) and b) $[Ag_4(L)_2]\cdot 4\,DMSO$ (**4**).

should increase from 3 to 6, which is unusual for this metal ion.

To our knowledge, complexes **3** and **4** are the first examples of double-stranded helicates in which the helical axis is composed of a polyhedron of metal ions. Moreover, there are few reports of structurally characterized copper(I) thiosemicarbazone complexes[21,28] and, surprisingly, the structure of only one silver(I) thiosemicarbazone complex has been determined,[21] although the stoichiometries of these coordination compounds were first reported in the early 1980s.[29]

In conclusion, we have prepared dinuclear dihelicates and tetranuclear cluster dihelicates and demonstrated that self-assembly of their building blocks can be controlled. This control can be achieved by using a dianionic helicand ligand that is equipped with two soft donor atoms and by selection of the oxidation state of the metal centers. We believe that this synthetic approach could provide new perspectives on the preparation of complex, stable, and reproducible metallosupramolecular architectures with high nuclearity and programmed properties. Our synthetic approach to the preparation of "cluster helicates" seems to be extendable to other systems, as our ongoing research has produced new examples of metal(I) tetranuclear cluster dihelicate complexes using different bis(thiosemicarbazone) ligands.

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[18] Crystal structure analysis of **1**: X-ray diffraction data were collected from a yellow prismatic crystal ($\approx 0.35 \times 0.20 \times 0.20\,\text{mm}^3$) by means of a Smart CCD-1000 BRUKER diffractometer using graphite-monochromatized $\text{Mo}_{\text{K}\alpha}$ radiation ($\lambda = 0.71073$ Å) from a fine-focus sealed-tube source. Crystal data for $C_{30}H_{42}N_{14}S_4Zn_2$: $M_r = 857.76$, $T = 298(2)$ K, monoclinic $C2/c$, $a = 16.6419(8)$, $b = 15.9953(8)$, $c = 15.1626(7)$ Å, $\beta = 109.7820(10)°$, $V = 3798.0(3)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.500\,\text{g}\,\text{cm}^{-3}$, $\mu = 1.526\,\text{mm}^{-1}$, 12634 measured reflections, 4524 independent reflections ($R_{\text{int}} = 0.0475$), 4524 independent reflections with $I_O > 2\sigma(I_O)$, 231 parameters refined, GOF = 1.077, $R_1 = 0.0482$ ($I_O > 2\sigma(I_O)$) and 0.0876 (for all data), $R_{2w} = 0.0840$ ($I_O > 2\sigma(I_O)$) and 0.0961 (for all data), max./min. residual electron density 0.350/−0.551 e Å^{-3}.[26b]

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[22] Crystal structure analysis of **3**: X-ray diffraction data were collected from a brown prismatic crystal ($\approx 0.48 \times 0.32 \times 0.19\,\text{mm}^3$) by means of a Smart CCD-1000 BRUKER diffractometer using graphite-monochromatized $\text{Mo}_{\text{K}\alpha}$ radiation ($\lambda = 0.71073$ Å) from a fine-focus sealed-tube source. Crystal data for $C_{38}Cu_4H_{54}N_{18}S_4$: $M_r = 1145.40$, $T = 293$ (2) K, monoclinic $P2(1)/c$, $a = 22.509(5)$, $b = 15.037(3)$, $c = 16.051(3)$ Å, $\beta = 108.143(4)°$, $V = 5162.8(18)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.368\,\text{g}\,\text{cm}^{-3}$, $\mu = 1.827\,\text{mm}^{-1}$, 31220 measured reflections, 10535 independent reflections ($R_{\text{int}} = 0.0471$), 10535 independent reflections with $I_O > 2\sigma(I_O)$,

557 parameters refined, GOF = 1.006, $R_1 = 0.0529$ ($I_O > 2\sigma(I_O)$) and 0.1187 (for all data), $R_{2w} = 0.1777$ ($I_O > 2\sigma(I_O)$) and 0.2147 (for all data), max./min. residual electron density 0.946/−0.544 e Å^{-3}.[26b]

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[26] a) Crystal structure analysis of **4**: X-ray diffraction data were collected from a yellow prismatic crystal ($\approx 0.46 \times 0.30 \times 0.18$ mm^3) by means of a Smart CCD-1000 BRUKER diffractometer using graphite-monochromatized Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) from a fine-focus sealed-tube source. Crystal data for $Ag_4C_{38}H_{66}N_{14}O_4S_8$: $M_r = 1471.01$, $T = 293$ (2) K, monoclinic $P2(1)/c$, $a = 22.910(5)$, $b = 15.600(3)$, $c = 16.550(3)$ Å, $\beta = 107.74(3)°$, $V = 5633.6(19)$ Å^3, $Z = 4$, $\rho_{calc} = 1.711$ g cm^{-3}, $\mu = 1.706$ mm^{-1}, 15892 measured reflections, 8169 independent reflections ($R_{int} = 0.0452$), 8169 independent reflections with $I_O > 2\sigma(I_O)$, 616 parameters refined, GOF = 1.092, $R_1 = 0.0680$ ($I_O > 2\sigma(I_O)$) and 0.1041 (for all data), $R_{2w} = 0.2057$ ($I_O > 2\sigma(I_O)$) and 0.2342 (for all data), max./min. residual electron density 1.401/−0.879 e Å^{-3}. All the crystal structures were solved by direct methods and refined by full-matrix least-square procedures on F^2 using SHELX-97 software.[19] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at calculated positions. b) CCDC 265393 (**1**), 265394 (**3**), and 265395 (**4**) 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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