

Novel Complexes of Ligands Containing Phenol and Alcohol Groups: From Polynuclear Cluster, 1D Coordination Polymer to 2D Supramolecular Assemblies

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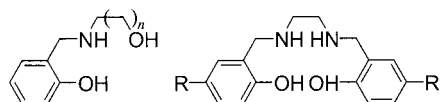
A series of Co^{II} , Cu^{II} , Zn^{II} , Ag^{I} and mixed-valence cobalt complexes **1–9** with tridentate and tetradentate chelating ligands containing oxygen-bridging and hydrogen-bonding groups have been synthesized, four of which have been structurally characterized: $[\text{Co}_6\text{L}_6^1(\text{OH})(\text{H}_2\text{O})_3]\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ (**1**) [$\text{H}_2\text{L}^1 = N$ -(2-hydroxybenzyl)ethanolamine] is a hexanuclear $\text{Co}^{\text{III}}_3\text{Co}^{\text{II}}_3$ complex, with a core of quadruple face-sharing defective cubane-like units; $[\text{CuNaL}^2(\text{ClO}_4)]_\infty$ (**3**) [$\text{H}_2\text{L}^2 = N,N'$ -bis(2-hydroxybenzyl)ethylenediamine] is a μ_3 -phenoxo- and μ_4 -perchlorato-bridged 1D heterometallic $\text{Cu}^{\text{II}}\text{Na}^{\text{I}}$ coordination polymer; the coordination moieties of $[\text{CuL}^3]_4 \cdot 4\text{H}_2\text{O}$ (**6**) [$\text{H}_2\text{L}^3 = N,N'$ -bis(2-hydroxy-5-methylbenzyl)ethylenedi-

amine] form a 2D hydrogen-bonded network structure of monophenoxo-bridged dimeric moieties; and the molecules of $[\text{Ag}(\text{H}_2\text{L}^2)(\text{HL}^2)]$ (**9**) are connected to give an undulated 2D structure, consisting of hydrogen-bonded hexagonal units. The variety of these structures is discussed on the basis of the stereoelectronic preferences of the metal atoms, hydrogen bonds, disposition of the bridging groups, steric effect, and conformational flexibility of the ligands. Variable-temperature magnetic properties of **1** and **6** are also reported.

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Introduction

Assemblies of polynuclear complexes, coordination polymers and hydrogen-bonded supramolecular coordination networks have potential applications and are aesthetically appealing.^[1–3] The assemblies of these frameworks are influenced by factors such as the structures of the ligands and the stereoelectronic preferences of the metal ions.^[4] The assembly of metal atoms with chelating ligands containing endogenous bridging atoms is one promising route to unexpected, interesting coordination structures, wherein the most commonly utilized bridging atoms are from carboxylate functionalities.^[5] In contrast, chelating ligands containing phenol groups have been much less explored.^[6] We demonstrate here the successful construction of various novel coordination architectures, utilizing chelating ligands containing phenol and/or alkoxy groups ($\text{H}_2\text{L}^1 - \text{H}_2\text{L}^3$) (Scheme 1), which have been synthesized by the reduction



Scheme 1. Molecular structures of the ligands (H_2L^1 : $n = 1$, H_2L^2 : $n = 2$, H_2L^3 : $\text{R} = \text{H}$, H_2L^3 : $\text{R} = \text{CH}_3$)

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of the corresponding Schiff bases. The phenol and the alkoxy groups can act as bridging and hydrogen-bonding functionalities. Compared with the corresponding Schiff bases, $\text{H}_2\text{L}^1 - \text{H}_2\text{L}^3$ have greater flexibility and conformational freedom. In addition, the amino groups, which are absent in the Schiff bases, may also affect the structures of the products via intermolecular hydrogen bonds. Consequently, these ligands may be promising for the construction of novel coordination assemblies, and so we have investigated several of their metal complexes. Our interest in ligands containing phenoxy and alkoxy groups also lie in their relevance to the coordination environments of active sites of metalloenzymes.^[7]

Divalent metals with pseudooctahedral coordination preferences, namely, Co^{II} , Cu^{II} and Zn^{II} , have been used for the synthesis of the complexes. For comparison, the soft metal Ag^{I} , which has a tetrahedral preference, has also been used. Thus, a series of Co^{II} , Cu^{II} , Zn^{II} , Ag^{I} and mixed-valence cobalt complexes have been synthesized, four of which have been characterized by X-ray crystal analyses to reveal structures varying from hexanuclear cluster, 1D bimetallic coordination polymers to 2D supramolecular assemblies. The structures of the complexes are discussed on the basis of various structure-directing factors, including the metal coordination preferences, hydrogen bonds, bridging groups, steric effect, and conformational flexibility of the ligands. Variable-temperature magnetic properties of two of the complexes are also reported. The results ob-

tained are valuable for the design and synthesis of further such novel complexes.

Results

Synthesis and Spectroscopic Results: To promote the deprotonation and subsequent coordination of the phenol and the alkoxy groups, complexes **1–8** were synthesized at alkaline pH by the addition of stoichiometric aqueous NaOH solution. For the Ag^I complex (**9**), Ag₂O precipitates upon the addition of NaOH, and the direct reaction of H₂L² with AgNO₃ in methanol resulted in a white precipitate of **9**, which was gradually dissolved by the addition of an excess of concentrated ammoniacal solution. Probably, the coordinated H₂L² is initially displaced by NH₃, which then evaporates to allow H₂L² to reform complex **9**, which gradually crystallized. Attempts to synthesize Ag^I complexes of H₂L¹ and H₂L³ gave only the free ligands, possibly due to the weak coordinating abilities of the ligands and the instability of the resulting complexes.

In the IR spectra of complexes **1–8**, the coordination of the phenol groups is exhibited by the shifting of $\nu(\text{C}-\text{O})$ to higher wavenumbers. For complexes **3–5**, and **7**, the intense bands near 1100 cm⁻¹ show distinct splittings, indicative of coordinated ClO₄⁻.

Isotropic EPR spectra of complex **3** and **6** in DMF containing four copper hyperfine lines are observed at 300 K (Figure 1), while the spectra at 100 K have axial symmetries, with four hyperfine peaks in the parallel region derived from the coupling of the copper nucleus and the unpaired

electron. The EPR parameters (**3**: $g_{\parallel} = 2.229$, $g_{\perp} = 2.004$, $A_{\parallel} = 186.4$ G, $A_{\text{iso}} = 85.7$ G; **6**: $g_{\parallel} = 2.231$, $g_{\perp} = 2.006$, $A_{\parallel} = 188.7$ G) are indicative of tetragonal coordination environments with $(d_{x^2-y^2})^1$ ground states for complexes **3** and **6**.^[8]

The electronic spectra of the copper and cobalt complexes in DMF (Table 1) exhibit intraligand transitions, and d–d transitions in addition to strong LMCT bands, confirming the coordination of the deprotonated phenoxy groups.

Structural Results: The crystal structure of **1** consists of a discrete [Co₆L₆(OH)(H₂O)₃]²⁺ hexameric entity (Figure 2, a, Table S1 of the Supporting Information; see also the footnote on the first page of this article), two noncoordinated chloride counter anions, and ten water molecules of crystallization. Bond lengths, charge balance considerations

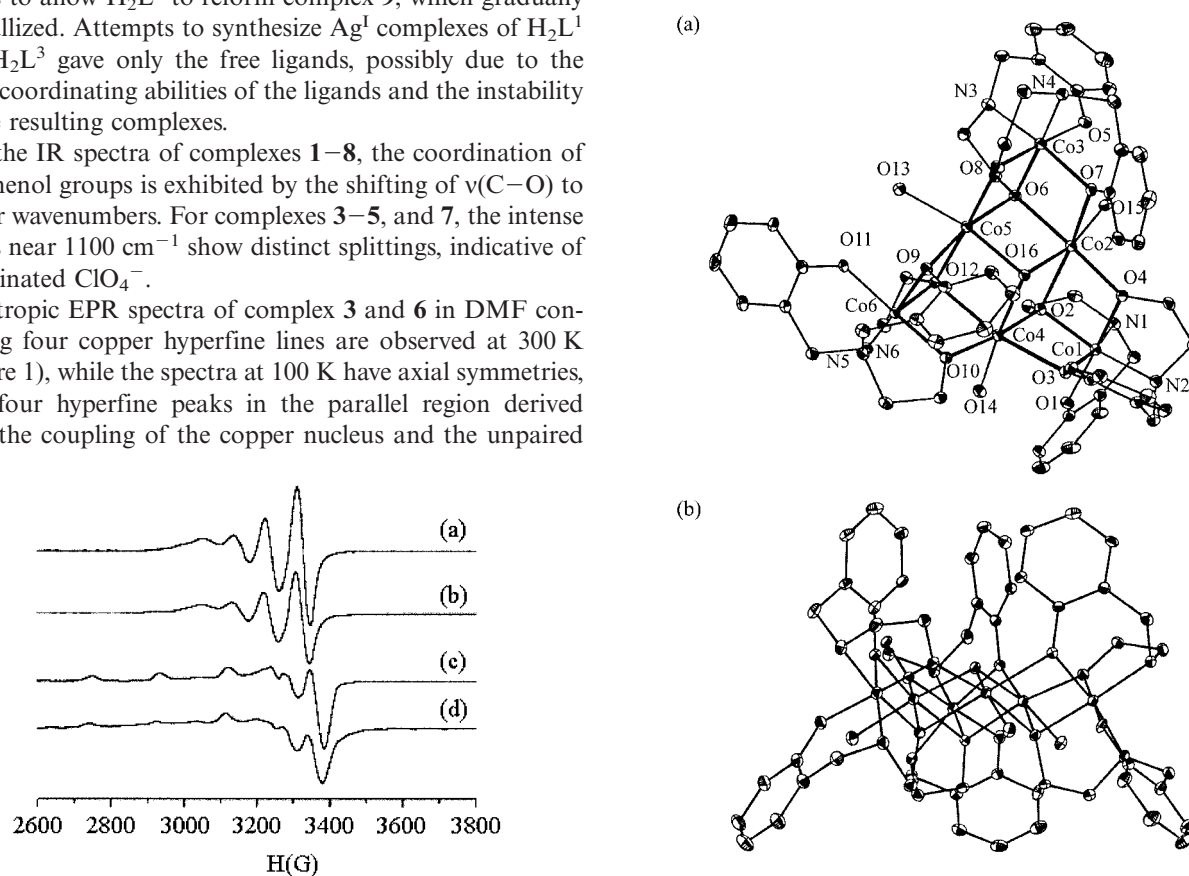


Figure 1. EPR spectra of the complexes in DMF: (a) **3**, 300 K; (b) **6**, 300 K; (c) **3**, 100 K; (d) **6**, 100 K

Figure 2. Complementary views of the structure of **1** showing 20% probability displacement ellipsoids. H atoms have been omitted for clarity

Table 1. Electronic spectra of the complexes in DMF

Complexes $\pi \rightarrow \pi^*$	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) $n \rightarrow \pi^*$	L → M	d → d	
1	264 (9.63×10^3)	290 (5.30×10^3)	358 (1.35×10^3)	598 (100)
3		290 (1.37×10^4)	390 (1.22×10^3)	605 (283)
4		252 (2.46×10^4)	373 (3.01×10^3)	584 (323)
6	268 (6.00×10^3)	286 (5.33×10^3)	340 (704), 398 (781)	598 (296)
7	213 (1.51×10^4)	247 (1.42×10^4)	384 (1.55×10^3)	592 (205)

and magnetic measurements (vide infra) reveal that the three inner cobalt atoms are Co^{II} , and the outer ones are Co^{III} . Each Co^{III} has an N_2O_4 ligation, namely the two phenoxo, two alkoxo and two amino groups of two $\text{fac}-(\text{L}^1)^{2-}$ ligands. The phenoxo and alkoxo groups of the $(\text{L}^1)^{2-}$ ligands, together with a μ_3 -hydroxo ligand, bridge the six cobalt atoms, resulting in, apparently, the first Co_6O_{10} face-sharing quadruple defective cubane-like complex. The whole hexameric entity adopts a crown shape (Figure 2, b), with the three phenyl rings at the upper rim tilted inward, and the phenyl rings at the lower rim tilted outward. According to the "Harris" notation,^[9] the upper $(\text{L}^1)^{2-}$ and lower $(\text{L}^1)^{2-}$ ligands are involved in $32_{12}2_{13}1_1$ and $31_{13}2_{12}3_{11}$ bridging modes, respectively (Figure 3). The $\text{Co}^{\text{III}}-\text{N}$ and $\text{Co}^{\text{III}}-\text{O}$ distances are in the ranges 1.944(7)–1.980(7) and 1.862(5)–1.956(5) Å, respectively. The $\text{Co}^{\text{II}}-\text{O}$ distances are in the range 1.991(5)–2.286(5) Å, and the $\text{Co}^{\text{II}}-\text{O}-\text{Co}^{\text{II}}$ angles are 94.44(19)–107.8(3)°, with $\text{Co}^{\text{II}}\cdots\text{Co}^{\text{II}}$ separations of 3.240, 3.253 and 3.270 Å, respectively.

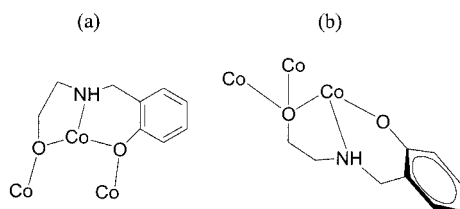


Figure 3. Bridging modes of $(\text{L}^1)^{2-}$ in complex 1

Table 2. Selected bond lengths and angles for 3

Bond lengths (Å)			
$\text{Cu}(1)-\text{O}(2)$	1.914(3)	$\text{Cu}(1)-\text{O}(1)$	1.924(4)
$\text{Cu}(1)-\text{O}(6)$	2.640(5)	$\text{Cu}(1)-\text{O}(3)^{[\text{a}]}$	2.672(5)
$\text{Cu}(1)-\text{N}(2)$	2.005(5)	$\text{Cu}(1)-\text{N}(1)$	2.007(4)
$\text{Na}(1)-\text{O}(1)$	2.433(4)	$\text{Na}(1)-\text{O}(6)$	2.450(5)
$\text{Na}(1)-\text{O}(2)$	2.616(4)	$\text{Na}(2)-\text{O}(3)^{[\text{b}]}$	2.327(5)
$\text{Na}(2)-\text{O}(2)$	2.453(4)	$\text{Na}(2)-\text{O}(1)$	2.569(4)
Bond angles (°)			
$\text{O}(2)-\text{Cu}(1)-\text{O}(1)$	84.4(2)	$\text{O}(2)-\text{Cu}(1)-\text{N}(2)$	95.6(2)
$\text{O}(1)-\text{Cu}(1)-\text{N}(2)$	175.7(2)	$\text{O}(2)-\text{Cu}(1)-\text{N}(1)$	176.4(2)
$\text{O}(1)-\text{Cu}(1)-\text{N}(1)$	93.9(2)	$\text{N}(2)-\text{Cu}(1)-\text{N}(1)$	86.4(2)
$\text{O}(1)-\text{Na}(1)-\text{O}(1)^{[\text{b}]}$	180.0	$\text{O}(1)-\text{Na}(1)-\text{O}(6)^{[\text{b}]}$	96.66(14)
$\text{O}(1)^{[\text{b}]}-\text{Na}(1)-\text{O}(6)^{[\text{b}]}$	83.34(14)	$\text{O}(1)-\text{Na}(1)-\text{O}(2)$	83.34(14)
$\text{O}(1)^{[\text{b}]}-\text{Na}(1)-\text{O}(6)$	96.66(14)	$\text{O}(6)^{[\text{b}]}-\text{Na}(1)-\text{O}(6)$	180.000(1)
$\text{O}(1)-\text{Na}(1)-\text{O}(2)$	61.28(12)	$\text{O}(1)^{[\text{b}]}-\text{Na}(1)-\text{O}(2)$	118.72(12)
$\text{O}(6)^{[\text{b}]}-\text{Na}(1)-\text{O}(2)$	105.80(13)	$\text{O}(6)-\text{Na}(1)-\text{O}(2)$	74.20(13)
$\text{O}(1)-\text{Na}(1)-\text{O}(2)^{[\text{b}]}$	118.72(12)	$\text{O}(1)^{[\text{b}]}-\text{Na}(1)-\text{O}(2)^{[\text{b}]}$	78.91(14)
$\text{O}(6)^{[\text{b}]}-\text{Na}(1)-\text{O}(2)^{[\text{b}]}$	74.20(13)	$\text{O}(6)-\text{Na}(1)-\text{O}(2)^{[\text{b}]}$	105.80(13)
$\text{O}(2)-\text{Na}(1)-\text{O}(2)^{[\text{b}]}$	180.0	$\text{O}(3)^{[\text{b}]}-\text{Na}(2)-\text{O}(3)^{[\text{a}]}$	180.000(1)
$\text{O}(3)^{[\text{b}]}-\text{Na}(2)-\text{O}(2)$	96.6(2)	$\text{O}(3)^{[\text{b}]}-\text{Na}(2)-\text{O}(2)^{[\text{c}]}$	83.4(2)
$\text{O}(3)^{[\text{a}]}-\text{Na}(2)-\text{O}(2)$	83.4(2)	$\text{O}(3)^{[\text{a}]}-\text{Na}(2)-\text{O}(2)^{[\text{c}]}$	96.6(2)
$\text{O}(2)-\text{Na}(2)-\text{O}(2)^{[\text{c}]}$	180.000(1)	$\text{O}(3)^{[\text{b}]}-\text{Na}(2)-\text{O}(1)^{[\text{c}]}$	78.91(14)
$\text{O}(3)^{[\text{a}]}-\text{Na}(2)-\text{O}(1)^{[\text{c}]}$	101.09(14)	$\text{O}(2)-\text{Na}(2)-\text{O}(1)^{[\text{c}]}$	118.28(11)
$\text{O}(2)^{[\text{c}]}-\text{Na}(2)-\text{O}(1)^{[\text{c}]}$	61.72(11)	$\text{O}(3)^{[\text{b}]}-\text{Na}(2)-\text{O}(1)$	101.09(14)
$\text{O}(3)^{[\text{a}]}-\text{Na}(2)-\text{O}(1)$	78.91(14)	$\text{O}(2)-\text{Na}(2)-\text{O}(1)$	61.72(11)
$\text{O}(2)^{[\text{c}]}-\text{Na}(2)-\text{O}(1)$	118.28(11)	$\text{O}(1)^{[\text{c}]}-\text{Na}(2)-\text{O}(1)$	180.0

[a] Symmetry transformations used to generate equivalent atoms: $-1 + x, y, z$. [b] $2 - x, 2 - y, 2 - z$. [c] $1 - x, 2 - y, 2 - z$.

The asymmetric unit of 3 (Table 2) consists of one Cu^{II} , one $(\text{L}^2)^{2-}$, one ClO_4^- anion and two partially occupied Na^1 atoms lying on the special positions of the inversion centers with occupation factors of 50%. Thus, 3 can be understood as a 1:1 adduct of CuL^2 with NaClO_4 , wherein $(\text{L}^2)^{2-}$ coordinates with Cu^{II} as a tetradentate ligand in the equatorial plane. The neighboring CuL^2 units are arranged in an alternating up/down-up/down mode, and act as neutral ligands to coordinate Na^1 atoms via the phenoxo O atoms, affording an infinite zigzag arrangement of alternating Cu^{II} and Na^1 centers along the a axis (Figure 4). The final coordination polymer involves phenoxo and perchlorato groups in the unusual μ_3 - and μ_4 -bridging modes, respectively, and the final coordination geometries around Cu^{II} and Na^1 are elongated octahedral and irregular octahedral, respectively. This appears to be the first coordination polymer of H_2L^2 .^[10]

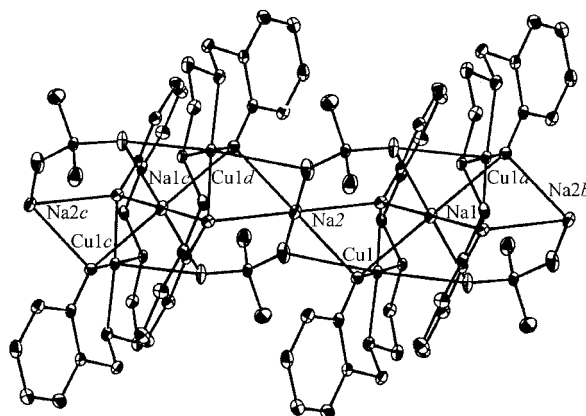


Figure 4. One-dimensional linear structure of 3, showing the atom labeling scheme at the 20% probability level with H atoms omitted for clarity

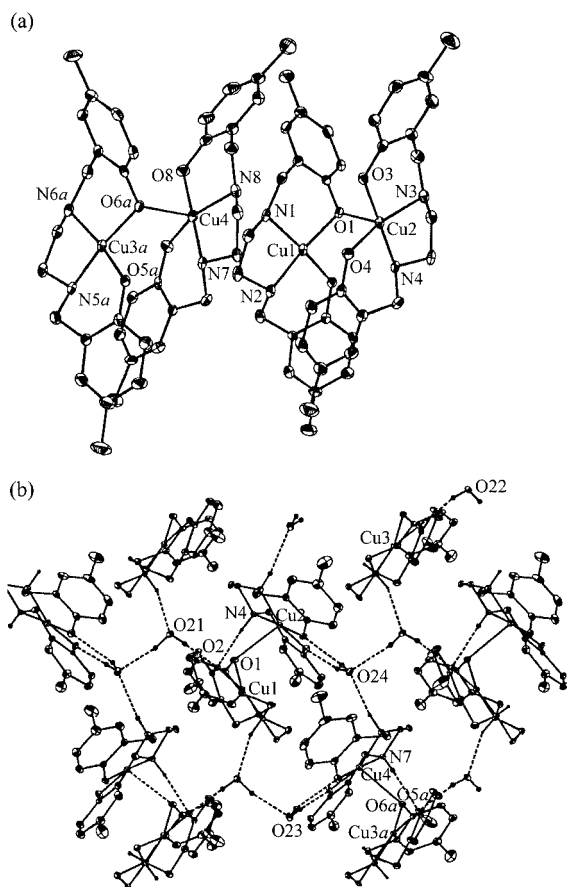
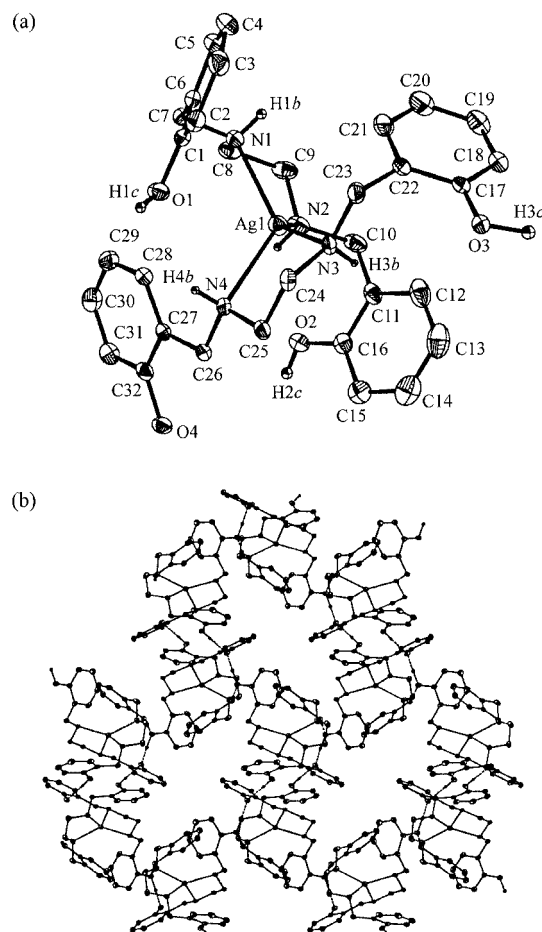
The asymmetric unit of crystal 6 (Table 3) consists of four crystallographically independent, and chemically similar, CuL^3 moieties and four water molecules of crystallization. In each CuL^3 moiety, the tetradentate $(\text{L}^3)^{2-}$ ligand is coordinated in the basal plane of Cu^{II} . The four CuL^3 units are connected into two dimers via axial monophenoxo bridging, with $\text{Cu}-\text{O}$ bridging distances of 2.562(2) and 2.490(3) Å, and $\text{Cu}-\text{O}-\text{Cu}$ angles of 98.49(10) and 103.56(10)°, respectively. The dimers are further connected by multiple hydrogen bonds, i.e., every two water molecules are connected via hydrogen bonds to form a structural unit, which in turn connects the amino and the phenoxo functionalities to form a 2D sheet approximately along the ab plane (Figure 5). In the final structure, half of the water molecules are quadruple-connecting, and the other half are triple-connecting. Interestingly, a nearly planar six-membered ring is formed by $\text{Cu}(4)$, $\text{O}(7)$, $\text{O}(8)$, and the water molecule via hydrogen bonds.

In the crystal structure of the Ag^{I} complex 9 (Figure 6, and Table 4), Ag^{I} is coordinated with four N atoms from two L^2 ligands, with one ligand in the protonated H_2L^2 form, and the other in mono-deprotonated $(\text{HL}^2)^-$. The noncoordinated phenol and phenolate groups are involved

Table 3. Selected bond lengths and angles for **6**

Bond lengths (Å)			
Cu(1)–O(1)	1.911(2)	Cu(1)–O(2)	1.913(2)
Cu(1)–N(1)	1.989(3)	Cu(1)–N(2)	2.005(3)
Cu(2)–O(3)	1.925(2)	Cu(2)–O(4)	1.952(3)
Cu(2)–N(4)	2.016(3)	Cu(2)–N(3)	2.019(3)
Cu(3)–O(5)	1.918(2)	Cu(3)–O(6)	1.919(2)
Cu(3)–N(5)	1.990(3)	Cu(3)–N(6)	1.994(3)
Cu(4)–O(8)	1.923(3)	Cu(4)–O(7)	1.953(2)
Cu(4)–N(8)	2.009(3)	Cu(4)–N(7)	2.027(3)
Cu(4)–O(6) ^[a]	2.490(2)	Cu(2)–O(1)	2.562(3)
Bond Angles (°)			
O(1)–Cu(1)–O(2)	88.88(10)	O(1)–Cu(1)–N(1)	94.06(11)
O(2)–Cu(1)–N(1)	169.22(11)	O(1)–Cu(1)–N(2)	167.52(12)
O(2)–Cu(1)–N(2)	92.85(11)	N(1)–Cu(1)–N(2)	86.52(12)
O(3)–Cu(2)–O(4)	89.01(10)	O(3)–Cu(2)–N(4)	177.63(12)
O(4)–Cu(2)–N(4)	162.48(12)	O(3)–Cu(2)–N(3)	93.81(11)
O(4)–Cu(2)–N(3)	92.12(11)	N(4)–Cu(2)–N(3)	85.74(12)
O(5)–Cu(3)–O(6)	89.52(10)	O(5)–Cu(3)–N(5)	93.57(11)
O(6)–Cu(3)–N(5)	166.20(11)	O(5)–Cu(3)–N(6)	167.66(11)
O(6)–Cu(3)–N(6)	93.90(11)	N(5)–Cu(3)–N(6)	85.93(12)
O(8)–Cu(4)–O(7)	89.23(11)	O(8)–Cu(4)–N(8)	94.19(12)
O(7)–Cu(4)–N(8)	160.38(11)	O(8)–Cu(4)–N(7)	177.69(11)
O(7)–Cu(4)–N(7)	92.40(11)	N(8)–Cu(4)–N(7)	84.81(12)
Cu(4)–O(6) ^[a] –Cu(3) ^[a]	103.56(11)	Cu(2)–O(1)–Cu(1)	98.49(10)

^[a] Symmetry transformations used to generate equivalent atoms: $x, -1 + y, z$.

Figure 5. Molecular structure and 2-D sheet of complex **6**, approximately along the *ab* planeFigure 6. Molecular structure and undulated 2-D sheet of complex **9**, approximately along the *bc* planeTable 4. Selected bond lengths and angles for **9**

Bond lengths (Å)			
Ag1–N3	2.298(3)	Ag1–N2	2.331(2)
Ag1–N1	2.410(2)	Ag1–N4	2.424(2)
Bond Angles (deg)			
N3–Ag1–N2	135.88(11)	N3–Ag1–N1	130.47(9)
N2–Ag1–N1	76.48(9)	N3–Ag1–N4	77.94(8)
N2–Ag1–N4	118.59(9)	N1–Ag1–N4	124.34(8)

in intermolecular hydrogen bonds, resulting in an undulated 2D network of hexagonal units; each corner of the hexagons is occupied by an Ag^I atom. Interestingly, the hydrogen bond O3...H...O4A [O3...O4A 2.444(3) Å, bond angle of 173.56°] can be regarded as a (–)CAHB type; such strong bonds have been observed mostly in systems containing carboxylate and carboxylic acid molecules.^[11] Their occurrence between the phenolate and the phenol groups is rather unusual.

Magnetic Studies: The magnetic behavior of **1** and **6** was studied. With the decreasing of temperature, the observed $\chi_M T$ for **1** (Figure S1, see Supporting Information) gradually decreases from 8.47 (300 K) to 3.02 cm³·mol^{–1}·K at 5 K, which is characteristic of an antiferromagnetically cou-

pled Co^{II} moiety, and is consistent with the crystal structure (vide supra). For **6**, however, $\chi_{\text{M}}T$ (Figure S2, Supporting Information) increases slowly from 0.633 (300 K) to a maximum of $0.737 \text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ at 9 K, and then decreased to $0.730 \text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ at 5 K, indicating a net weak ferromagnetic interaction between the Cu^{II} centers due to the coexistence of ferro- and antiferromagnetic interactions, which can be assigned to interactions within the dimers with the bridging angles of 98.49° and 103.56° (vide supra), respectively.

Discussion

The unsymmetrical tridentate ligand H_2L^1 contains both phenol and alkoxy groups. It forms the hexanuclear cluster **1**, with both the phenoxy and alkoxy groups involved in bridging. A few polynuclear clusters have also been reported for similar tridentate unsymmetrical ligands.^[12,13] While the number of polynuclear transition metal complexes reported continues to grow rapidly, some nuclearities remain rare. Only a few hexanuclear cobalt complexes containing N or O donors have been reported,^[14] along with some larger cobalt cages^[15] and a number of hexanuclear cobalt-chalcogen clusters.^[16] The occurrence of complex **1** may be related to the properly disposed bridging functionalities from the $(\text{L}^1)^{2-}$ ligand and the suitable chelate ring size. In contrast to the *fac*-coordination mode of $(\text{L}^1)^{2-}$ in **1**, in the related tetranuclear cubane Cu^{II} complex $[\text{Cu}_4\text{L}'_4]$ [$\text{L}' = N$ -(2-hydroxybenzyl)propanolamine, Scheme 1],^[12] the two O atoms from $(\text{L}')^{2-}$ occupy the *trans* positions in the basal plane of the square pyramidal coordination polyhedron of Cu^{II} , which can be ascribed to the tendency for the six-membered chelate ring in $[\text{Cu}_4\text{L}'_4]$ to span a larger distance, as compared to the corresponding five-membered ring in complex **1**. In $[\text{Cu}_4\text{L}'_4]$, all the alkoxy groups act as μ_3 -bridges, with the phenoxy groups at the *trans* positions not involved in bridging. In contrast, the neighboring alkoxy and phenoxy groups in complex **1** are involved in more complicated bridging modes (vide supra), resulting in the larger nuclearity.

Considering the distances between the O, N, and Cl^- atoms, the water molecules, and the chlorides, form complicated hydrogen-bond networks with the amino, phenoxy, and alkoxy groups of the $(\text{L}^1)^{2-}$ ligands. These multiple hydrogen bonds may contribute to the stability of the complex, and thus the crystal structure can readily be determined at room temperature. For the polynuclear Cu^{II} complex of $(\text{L}^1)^{2-}$, the crystal structure cannot be obtained due to its efflorescence during measurement.^[8] In the Zn^{II} complex $[\text{ZnHL}^1\text{Cl}]$ (**2**), the alkoxy group is not deprotonated, even if an excess of NaOH is added, which can be ascribed to the weaker coordination of Zn^{II} , as compared to Co^{II} and Cu^{II} . The positive charge of Zn^{II} is balanced by a chloride, in addition to the deprotonated phenoxy group.

In contrast to H_2L^1 , the tetradentate ligand H_2L^2 has an additional phenyl ring, and H_2L^3 has a further two methyl groups on the two phenyl rings – severe steric hindrance

can be anticipated if similar polynuclear clusters of these two ligands are formed. Thus, the 1D heterometallic coordination polymer and the weak axial monophenoxo-bridged binuclear moieties are seen for **3** and **6**, respectively. For $[\text{CoL}^2\text{NaClO}_4]\cdot\text{CH}_3\text{OH}$ (**4**), $[\text{ZnL}^2\cdot\text{NaClO}_4]\cdot\text{H}_2\text{O}$ (**5**), and $[\text{CoL}^3\text{NaClO}_4]\cdot 1.5\text{H}_2\text{O}$ (**7**), structures similar to that of **3** may also be assigned.

For the complex of H_2L^2 with the soft Ag^{I} atom, which prefers a tetrahedral coordination, the ligand acts in bidentate mode in complex **9** via coordination of the N atoms. H_2L^2 is usually a tetradentate ligand,^[10] but the unusual bidentate coordination mode can be rationalized by the tendency of Ag^{I} to coordinate with N rather than O atoms, and by the tetrahedral preference of four-coordinate Ag^{I} , which cannot be satisfied without great strain if the ligand coordinates in a tetradentate mode. Thus, the 1:2 complex $[\text{Ag}(\text{H}_2\text{L}^2)(\text{HL}^2)]$ is formed, irrespective of the molar ratio of the reagents, and the noncoordinated phenol groups are involved in intermolecular hydrogen bonds, resulting in an undulated 2D network.

The rich coordination modes of the ligands can also be related to their conformational flexibility, as evidenced by the large values of 36.9° , 52.0° and 84.9° for the dihedral angles between the two mean planes through the aromatic rings of the same ligands in complexes **3**, **6**, and **9**, respectively. In contrast to the approximately planar trinuclear salen adduct $[\text{Cu}(\text{salen})]_2\text{NaClO}_4$,^[17] the totally different arrangement in complex **3** provides a perfect match between the coordination environment provided by the donor atoms of $(\text{L}^2)^{2-}$ and the pseudooctahedral coordination preferences of the Cu^{II} and Na^{I} centers, and, also, the positive and the negative charges are exactly balanced. This perfect match gives extreme thermal stability to the novel coordination polymer: no weight loss was observed for **3** until about 328°C . These subtle matching factors are delicate, and extremely sensitive to the structures of the ligands. As for H_2L^2 , similar complexes with other divalent metals, namely, the Co^{II} complex $[\text{CoL}^2]\cdot\text{NaClO}_4\cdot\text{CH}_3\text{OH}$ (**4**) and the Zn^{II} complex $[\text{ZnL}^2\cdot\text{NaClO}_4]\cdot\text{H}_2\text{O}$ (**5**) were also obtained; however, for H_2L^3 , only the corresponding Co^{II} complex $[\text{CoL}^3\text{NaClO}_4]\cdot 1.5\text{H}_2\text{O}$ (**7**) was obtained. No NaClO_4 is included in the Cu^{II} and Zn^{II} complexes of H_2L^3 .

Conclusions

Various novel coordination assemblies can be successfully obtained by altering the ligands and metal atoms. For metal atoms with octahedral coordination preferences, with increasing steric hindrance and the decreasing bridging ability of the ligands, the structures of the products vary from polynuclear cluster and 1D heterometallic coordination polymer to weak axial monophenoxo-bridged binuclear moieties. For the soft Ag^{I} atom, which prefers tetrahedral coordination, H_2L^2 coordinates bidentately via the N atoms to give a 1:2 complex. These results provide further insight into the subtle structure-directing factors of metal complexes, including the metal coordination preferences, the

disposition of the bridging groups, the conformational flexibility, the hydrogen bonds, and the steric effect of the ligands. This work may be valuable in our aim to design and synthesize novel complexes; for example, coordination assemblies could arise by modifying the aliphatic chains or the phenyl rings of the ligands or by adding further donor groups into the phenyl rings.

Experimental Section

Physical Measurements: IR spectra were recorded with a Bruker Vector-22 spectrometer (KBr Disc.). UV-Vis spectra were obtained with a Shimadzu UV-Vis 2401 PC spectrophotometer. EPR measurements were performed with a Bruker ER200D-SRC spectrometer at X-band (9.46 GHz). Microanalyses of C, H and N were carried out with a GmbH VarioEL elemental analyzer. Magnetic susceptibility data were collected with a Quantum Design Squid magnetometer in the temperature range 5–300 K. The data were corrected for the diamagnetism of the sample holder and for diamagnetic contributions with Pascal's constants.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of the material should be used and it should be handled with extreme care.

5-Methylsalicylaldehyde was prepared by the reaction of *p*-cresol and CHCl_3 in aqueous ethanol according to the Reimer–Tiemann procedure. $\text{H}_2\text{L}^1\cdot\text{HCl}\cdot 1.5\text{H}_2\text{O}$ was synthesized by the method reported earlier;^[8] H_2L^2 was prepared by a similar method., and H_2L^3 was prepared in analogues fashion starting from 5-methylsalicylaldehyde and ethylenediamine.

$[\text{Co}_6\text{L}_6(\text{OH})(\text{H}_2\text{O})_3]\text{Cl}_2\cdot 10\text{H}_2\text{O}$ (1): $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (100 mg, 0.40 mmol), $\text{H}_2\text{L}^1\cdot\text{HCl}\cdot 1.5\text{H}_2\text{O}$ (89 mg, 0.40 mmol), aqueous NaOH (0.3 mL, 4 M, 1.2 mmol), and a few drops of H_2O_2 were added successively to methanol (100 mL). The resulting solution was then boiled under reflux for 3 h, and concentrated in vacuo. The so-obtained microcrystalline brown solid was collected and washed with diethyl ether and dried (yield 97 mg, 87%). $\text{C}_{54}\text{H}_{93}\text{Cl}_2\text{Co}_6\text{N}_6\text{O}_{26}$: calcd. C 38.91, H 5.62, N 5.04; found C 38.69, H 5.63, N 4.89. IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ 3386 br. (H_2O), 3190 s (N–H), 1596 s, 1567 m, 1483 s, 1448 s, 1304 m, 1284 s (C–O), 1270 vs (C–O), 882 m, 759 s, 685 s, 630 m, 602 w, 535 w.

$[\text{ZnHL}^1\text{Cl}]$ (2): A solution of $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (149 mg, 0.40 mmol), $\text{H}_2\text{L}^1\cdot\text{HCl}\cdot 1.5\text{H}_2\text{O}$ (89 mg, 0.40 mmol), and aqueous NaOH (0.2 mL, 4 M, 0.8 mmol) was boiled under reflux for 4 h, and then concentrated in vacuo. The resulting colorless solid was collected and washed with diethyl ether and dried (yield 91 mg, 85%). $\text{C}_9\text{H}_{12}\text{ClNO}_2\text{Zn}$: calcd. C 40.48, H 4.53, N 5.25; found C 40.59, H 4.75, N 5.06. IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3260 m (N–H), 2922 w, 2859 w, 1597 s, 1569 m, 1483 s, 1453 s, 1277 s (C–O), 1086 s, 1021 s, 874 m, 760 s, 623 m, 592 w, 528 w.

$[\text{CuNaL}^2(\text{ClO}_4)]_\infty$ (3): The microcrystalline brown solid complex **3** was prepared by a procedure similar to that of **2**, starting from $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (0.142 g, 0.40 mmol), H_2L^2 (117 mg, 0.40 mmol), and NaOH (0.2 mL, 4 M, 0.8 mmol) (yield 170 mg, 93%). $\text{C}_{16}\text{H}_{18}\text{ClCuN}_2\text{NaO}_6$: calcd. C 42.12, H 3.98, N 6.14; found C 42.04, H 4.01, N 5.88. IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3263 s (N–H), 3059 w, 2884 w, 1597 w, 1566 w, 1483 s, 1451 s, 1290 s, 1270 s (C–O), 1116 s, 1108 s, 1088 s, 1055 m, 1038 m, 992 m, 958 w, 926 w, 883 m, 858 w, 755 s, 729 m, 626 s, 596 w, 570 m, 530 w, 408 w.

$[\text{CoL}^2\text{NaClO}_4]\cdot\text{CH}_3\text{OH}$ (4): $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (100 mg, 0.40 mmol), H_2L^2 (117 mg, 0.40 mmol), aqueous NaOH (0.2 mL, 4 M, 0.8 mmol) and NaClO_4 (49 mg, 0.40 mmol) were added successively to methanol (50 mL). The resulting solution was boiled under reflux for 4 h, and then concentrated in vacuo to give a yellowish green powder that was collected and washed with diethyl ether and dried (yield 153 mg, 79%). $\text{C}_{17}\text{H}_{22}\text{ClCoN}_2\text{NaO}_7$: calcd. C 42.21, H 4.58, N 5.79; found C 42.63, H 4.67, N 5.77. IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3424 br., 3226 m (N–H), 2927 m, 1598 s, 1481 s, 1451 s, 1399 m, 1272 s (C–O), 1116 s, 1106 s, 1085 s, 881 m, 759 s, 625 m, 594 w, 508 w.

$[\text{ZnL}^2\text{NaClO}_4]\cdot\text{H}_2\text{O}$ (5): Complex **5** was prepared by a procedure similar to that of **3**, using $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ instead of $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (yield 173 mg, 91%). $\text{C}_{16}\text{H}_{20}\text{ClN}_2\text{NaO}_7\text{Zn}$: calcd. C 40.36, H 4.23, N 5.88; found C 40.23, H 4.34, N 6.05. IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3440 br., 3254 m (N–H), 2922 m, 1597 s, 1481 s, 1452 s, 1366 m, 1272 s (C–O), 1110 s, 1039 s, 928 m, 877 m, 760 s, 733 m, 623 m, 591 m.

$[\text{CuL}^3]\cdot 4\text{H}_2\text{O}$ (6): The microcrystalline green solid complex **6** was prepared by a procedure similar to that of **3**, using H_2L^3 instead of H_2L^2 (yield 128 mg, 84%). $\text{C}_{72}\text{H}_{96}\text{Cu}_4\text{N}_8\text{O}_{12}$: calcd. C 56.90, H 6.37, N 7.37; found C 56.69, H 6.07, N 7.01. IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3443 br. (H_2O), 3256 s (N–H), 2919 m, 1642 w, 1488 vs, 1290 s, 1272 s (C–O), 1254 s (C–O), 1122 s, 1093 s, 1055 s, 998 w, 957 w, 863 m, 818 s, 796 s, 635 m, 500 m.

Single crystals of **1**, **3**, and **6** were grown by slow evaporation of their methanol solutions.

$\text{CoL}^3\text{NaClO}_4\cdot 1.5\text{H}_2\text{O}$ (7): Complex **7** is a yellowish green powder that was prepared by a procedure similar to that of **4**, using H_2L^3 instead of H_2L^2 (yield 158 mg, 78%). $\text{C}_{36}\text{H}_{50}\text{Cl}_2\text{Co}_2\text{N}_4\text{Na}_2\text{O}_{15}$: calcd. C 42.66, H 5.53, N 4.97; found C 42.69, H 5.21, N 5.36. IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3442 br., 3226 m (N–H), 2919 m, 1612 s, 1487 s, 1272 s (C–O), 1118 s, 1108 s, 1082 s, 1046 s, 969 w, 927 w, 798 m, 625 m, 517 m.

$[\text{ZnL}^3]\cdot 2\text{H}_2\text{O}$ (8): Complex **8** was prepared by a procedure similar to that of **7**, using H_2L^3 instead of H_2L^2 (yield 128 mg, 80%). $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_4\text{Zn}$: calcd. C 54.08, H 6.55, N 7.01; found C 54.24, H 6.24, N 7.05. IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3408 br., 3253 m (N–H), 2916 m, 2859 m, 1611 s, 1488 s, 1269 s (C–O), 1127 m, 1047 m, 825 s, 790 s, 756 m, 726 w, 531 w, 492 m.

$[\text{Ag}(\text{H}_2\text{L}^2)(\text{HL}^2)]$ (9): A solution of AgNO_3 (68 mg, 0.40 mmol) in H_2O (5 mL) was added to a solution of H_2L^2 (117 mg, 0.40 mmol) in methanol (5 mL). The resultant precipitate was redissolved by the addition of concentrated ammoniacal solution (5 mL). The resulting solution was then filtered and left in a P_2O_5 desiccator in a dark place to slowly evaporate. Single crystals were obtained after several days in 35% yield (91 mg). $\text{C}_{32}\text{H}_{39}\text{AgN}_4\text{O}_4$: calcd. C 58.99, H 6.03, N 8.60; found C 58.80, H 5.78, N 8.31. IR (KBr pellet, cm^{-1}): $\tilde{\nu}$ = 3300 m (N–H), 2922 m, 2857 m, 1595 s, 1454 s, 1385 m, 1329 w, 1251 s (C–O), 1186 m, 876 m, 829 m, 752 s, 504 m.

X-ray Crystallography: All measurements were made with a Rigaku RAXIS-IV image plate area detector with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections [$I > 2.00\sigma(I)$] and variable parameters. All calculations were performed by using the SHELX-97 software package.^[18] A summary of the crystal data is presented in Table 5.

Table 5. Details of X-ray structure determinations

Complexes	1	3	6	9
Empirical formula	C ₅₄ H ₉₃ Cl ₂ Co ₆ N ₆ O ₂₆	C ₁₆ H ₁₈ ClCuN ₂ NaO ₆	C ₇₂ H ₉₆ Cu ₄ N ₈ O ₁₂	C ₃₂ H ₃₉ AgN ₄ O ₄
Formula mass	1666.85	456.30	1519.73	651.54
Crystal System	triclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>T</i> (K)	293(2)	291(2)	291(2)	291(2)
<i>a</i> (Å)	15.363(3)	7.456(2)	20.524(4)	11.395(2)
<i>b</i> (Å)	16.161(3)	11.283(2)	12.765(3)	13.044(3)
<i>c</i> (Å)	14.981(3)	11.326(2)	28.181(6)	21.277(4)
α (°)	91.54(3)	78.15(3)	90.00	90.00
β (°)	106.17(3)	89.07(3)	98.64°	95.00(3)
γ (°)	96.85(3)°	88.32(3)°	90.00	90.00
<i>V</i> (Å ³)	3539.7(12)	932.0(3)	7299(3)	3150.5(11)
<i>Z</i>	2	2	4	4
<i>D</i> _{calcd.} (Mg/m ³)	1.541	1.626	1.383	1.374
μ (mm ⁻¹)	1.528	1.374	1.214	0.681
No. of reflns. [<i>I</i> > 2 σ (<i>I</i>)]	7703	1757	7318	4585
Final <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0842	0.0683	0.0736	0.0424
<i>wR</i> ₂ (all data)	0.2550	0.1703	0.1098	0.0767
Goodness of fit	1.064	1.080	1.032	1.031

CCDC-183121 to -183124 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/cont/retrieving.html [or from the Cambridge Crystallographic Data center, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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