

Small-ring heterocycles as components of multidentate ligands: some structural studies relating to ring opening

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Abstract Structural studies of seven complexes of ligands derived from various azetidine- and oxetane-containing ligands characterise the difference in reactivity of both free and bound forms of these two four-membered heterocycles. The relatively unreactive azetidine ring is preserved in a variety of transformations, whereas facile opening of the oxetane ring provides a convenient pathway to complexes with pendent functionality.

Keywords Azetidines · Oxetanes · Ring opening · Multidentate ligands · X-ray structures

Dedicated to Professor Leonard F. Lindoy, the “compleat coordination chemist” and master of macrocycles, on the occasion of his 75th birthday.

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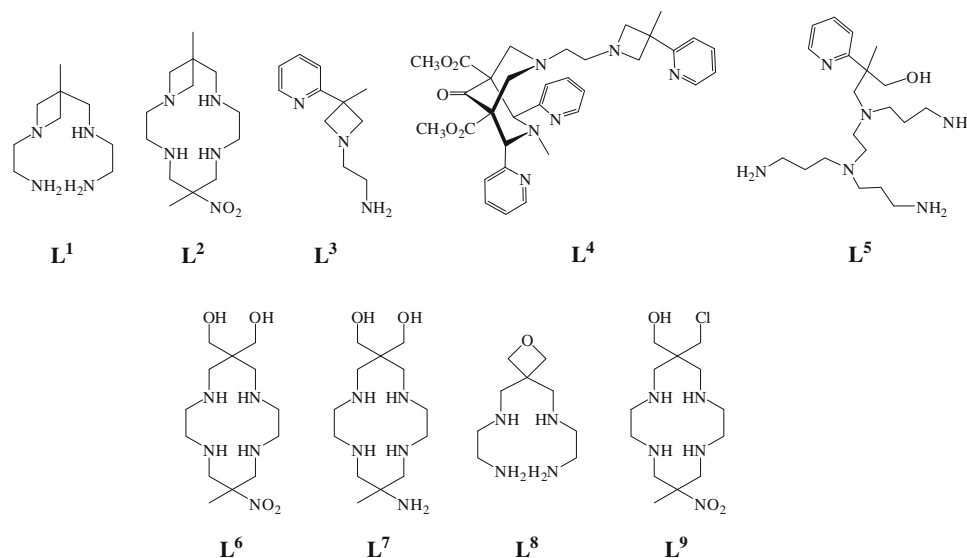
Introduction

The synthetic utility of three- and four-membered heterocyclic rings as molecular constituents is in large part due to the facility of their ring opening reactions [1–6]. This reactivity can be usefully controlled by metal ion binding to the heteroatom [3, 4, 6–14], although any influence that metal ion binding may have when the heteroatom is not directly bound and the ring is simply part of the superstructure of a multidentate ligand is less clear. As part of our studies of the synthesis and applications of azetidine-derived ligands [15–26], we present herein some structural studies bearing on these issues. The ligands from which the various complexes were derived are shown in Fig. 1.

Results and discussion

The ligand L^1 , readily obtained as an intermediate in the reaction of *tris*(hydroxymethyl)ethane derivatives with ethane-1,2-diamine [26], can be converted [24] to the macrocycle L^2 by reaction of its Cu(II) complex with formaldehyde and nitroethane under well-established conditions [27, 28]. We have previously used the complex $[Cu(L^2)]^{2+}$ as a source of the reduced (amino) form of L^2 and characterised that ligand as its Co(III) complex [24]. Here, we describe the crystal structure of the precursor complex itself with thiocyanate as the counter anion. Although the crystal quality was poor, resulting in a structure of less-than-desirable accuracy, the result obtained is useful for comparison with others in the present series. As is rather commonly the case with Cu(II) complexes [15, 16], the crystal lattice contains the metal ion in two coordination environments distinguished by the fact that in one the copper is five-coordinate, being bound to the macrocycle and one thiocyanate anion,

Fig. 1 The ligands L^2 , L^4 , L^5 , L^7 and L^9 structurally characterised in complexes described in the present work, along with some of their precursors characterised previously. Two simple N-monoalkyl derivatives of L^3 are also presently characterised



while in the other it is six-coordinate as a result of coordination of a second thiocyanate. A second thiocyanate anion is rather close to an axial coordination site of the five-coordinate species but in fact seems to be involved in H-bonding to a macrocycle NH (Fig. 2). Such exchange between metal and proton coordination sites is as seen in various other cases [15, 16] and it is rather well known in general that axial interactions of Cu(II) tetra-azamacrocycle complexes may vary greatly in their nature and intensity [29]. Otherwise, the complex is closely similar in form to those of related macrocycles in which the four-membered ring is absent [27–32], the macrocycle here having two five-membered chelate rings in the *gauche* conformation and a chair six-membered chelate ring where the NO_2 substituent is posed axially. The presence of the four-membered ring removes a plane of

symmetry in the macrocycle and renders it chiral [26] even when bound in a form which is essentially the «cyclam *trans*-III» conformation [33], as in the present case, and within the lattice of $\text{Cu}(L^2)(\text{NCS})_2$ each of the two cations lies adjacent to its mirror image (as expected for the space group $P\bar{1}$). While the geometry of the puckered azetidine ring in the bound macrocycle appears to differ significantly from that of azetidine itself in the gas phase [34] or in the crystalline state [35, 36], it is very similar to that in Co(III) complexes of the same ligand [24, 26] and related species [37, 38], and differs only marginally from that in complexes of a variety of metal ions with the tridentate ligand 1-aminoethyl-3-methyl-3-(2'-pyridyl)-azetidine L^3 and its derivatives [15–20] (Table 1; some data for Pd(II) complexes of bidentate azetidines described as «sterically congested» [39] but again resistant to

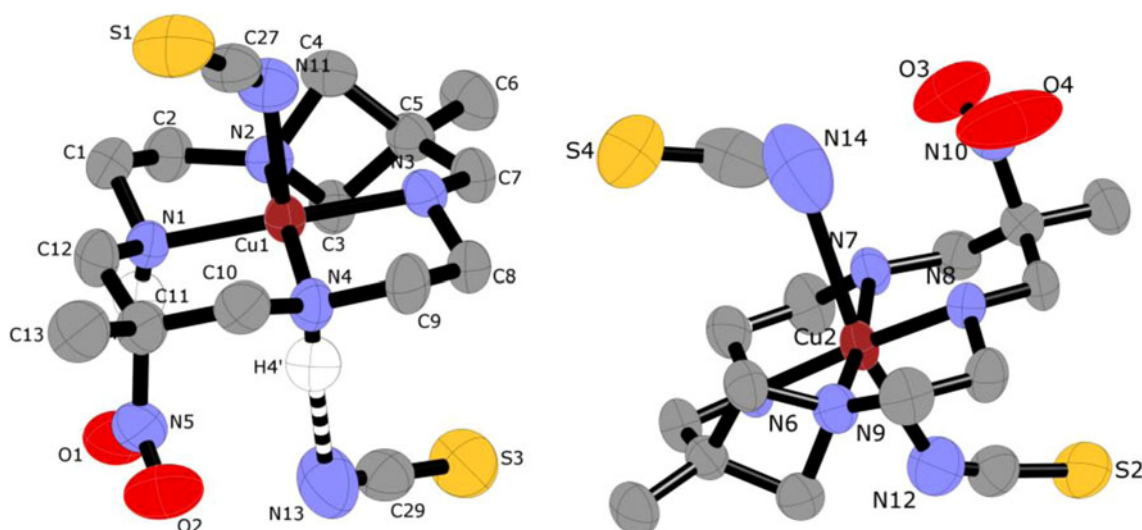


Fig. 2 The two complex ion species present in the crystal lattice of **1**, $\text{Cu}(L^2)(\text{NCS})_2$, showing the different modes of interaction involving the thiocyanate ions

ring opening are also included). Whatever the significance of these differences, it is clear that the bound azetidine unit in $\text{Cu}(\mathbf{L}^1)^{2+}$ and $\text{Cu}(\mathbf{L}^2)^{2+}$ is not activated towards nucleophilic ring opening, since it survives the fairly extensive and vigorous conditions involved in the formation and isolation of the macrocycle complex.

Further illustration of the stability of the azetidine ring towards nucleophilic opening is provided by the synthesis of the “bispidine” [40] derivative \mathbf{L}^4 starting from 1-(2'-aminoethyl)-3-methyl-3-(2''-pyridyl)-azetidine, \mathbf{L}^3 [15]. Such bispidine ligands may have various applications [40–42] and one issue here is the nature of their coordination to metal ions. In the present case, \mathbf{L}^4 binds to Cu(II) as a hypodentate species [43], with the N of the intact azetidine ring being bound but the N of the 2-pyridyl substituent on this ring being unbound (Fig. 3). As is commonly the case in complexes of bispidine ligands [40], the carbonyl group is present in its hydrated form, i.e. as a gem-diol, this presumably reflecting both strain induced by the coordination and the enhanced electrophilicity of the carbonyl-C within the electric field of the Cu(II) cation. The complex cation is chiral as a result of the *gauche* conformation of the saturated five-membered chelate ring and the lattice may be regarded as containing columns of centrosymmetric pairs (of enantiomers) lying parallel to *a*, with perchlorate anions serving to bridge within the pair via $\text{CH}\cdots\text{O}$ and $\text{OH}\cdots\text{O}$ interactions. The perchlorate ions also form H-bonds to the gem-diol hydroxyl groups, thus linking columns together. Each centrosymmetric, perchlorate-bridged pair in a given column appears to be linked to the next by various $\text{CH}\cdots\text{O}$ interactions. Dimensions of the azetidine ring (Table 1) do not differ dramatically from those in the range defined in various related species (Table 1), and must again be associated with a lack of any significant susceptibility to nucleophilic cleavage, although there is a clear “anomaly” associated with the near-negligible puckering of the four-membered ring. Given that the energy required for a change in the degree of puckering would be expected to be small [34, 44], here this is perhaps a reflection of the fact that the formally uncoordinated pyridine-N appears to be involved in H-bonding to the bound water molecule (Fig. 3), giving a ring which is less constraining than those found in all other cases, where the azetidine-N bridges two true chelate rings. Note also that the steric congestion in certain Pd(II) complexes of bidentate azetidines [39] appears to be largely accommodated also by a flattening of the azetidine ring.

\mathbf{L}^4 is a member of a now quite extensive family of derivatives of \mathbf{L}^3 , although it is a relatively complicated example. Previous studies [15, 16, 18, 19] have been focussed on complexes of \mathbf{L}^3 and its simpler products of various alkylation reactions, and we add herein to this sub-series the structural characterisation of the Zn(II) complexes

of the N-benzyl and N-(4-pyridyl)methyl derivatives of \mathbf{L}^3 , $[\text{Zn}(\text{NBz}-\mathbf{L}^3)\text{Cl}_2]$, **3**, and $[\text{Zn}(\text{N}(4\text{-pm})-\mathbf{L}^3)\text{Cl}_2]$, **4**, both species in which, again, the four-membered ring appears to be insensitive to nucleophiles. The molecular units found within the lattices of these two complexes are shown in Fig. 4, the ligand in the case of **4** being hypodentate in such a mononuclear species because of the substituent position of the introduced pyridine group. In both lattices, sheet-like structures (parallel to the *bc* plane in **3** and to the *ab* plane in **4**) can be identified in which the two enantiomers of the complex alternate. Somewhat surprisingly, in neither case does there appear to be intermolecular H-bonding involving the single NH centre and the lattices appear to be structured via $\text{CH}\cdots\text{Cl}$ and edge-to-face aromatic interactions. Despite the initial impression given by certain views of the lattices, π -stacking does not seem to be of importance in either case. Interestingly, the Zn complex **3** differs from its Cu analogue [18] not only because of the absence of H-bonding in its lattice but because the benzyl substituent adopts an axial, not an equatorial orientation on the five-membered chelate ring, as indeed it does also in the Pd(II) complex [20]. If this preference is not determined by lattice interactions, then rather than reflecting non-existent axial interactions in the Pd(II) case as we have previously argued, it perhaps reflects more subtly differences in axial site interactions resulting from the Zn stereochemistry being close to trigonal bipyramidal while that of Cu is close to square pyramidal.

Nucleophilic ring opening of the azetidine unit of \mathbf{L}^3 has been observed [16] under conditions where direct alkylation appears to lead to quaternisation of the azetidine-N and the same consequence is observed when an excess of acrylonitrile is used to cause multiple Michael additions. At exactly what stage of the overall synthesis of \mathbf{L}^5 , which is complicated by the additional step of reduction of introduced nitrile groups, ring opening occurs has not been established but the formation of an amino-alcohol shows that water (or possibly hydroxide) must have been the attacking nucleophile. In its complex with Cu(II), \mathbf{L}^5 provides another example of a ligand behaving in a hypodentate fashion, only one of the three amino groups added during the synthesis being directly bound to the metal (Fig. 5). The coordination geometry of the metal ion is approximately square pyramidal, the bound alcohol group being axial, and the two pendent 3-ammoniopropyl groups both project below the base. The lattice incorporates a bilayer structure where sheets of cations lie in planes parallel to the *ab* plane, with the pendent groups all lying to one side of a given plane but their orientation alternating from one plane to the next, so that the bilayers can be viewed either as having confronting pendent groups or confronting axial groups. The pendent groups from the two sides are bridged by extensive H-bonding interactions involving both water- and perchlorate-O atoms but they are also linked through an H-bond chain $\text{NH}\cdots\text{OClO}_2\text{O}\cdots$

Table 1 Dimensions of the metal ion (M)/azetidine unit found in crystalline complexes of various multidentate derivatives of the cyclic amine

M	M–N/Å	C–N/Å	C–C/Å	MNC/°	CNC/°	NCC/°	CCC/°	Pucker ^a /°	Temp.; ref. no.
– ^b	–	1.467(2), 1.477(2); 1.464(2), 1.470(2)	1.516(3), 1.517(2); 1.510(3), 1.513(2)	–	88.9(1); 89.4(1)	88.6(1), 89.0(1); 89.4(1), 89.5(1)	85.6(1); 86.0(1)	150.3(2); 154.6(2)	170 K; [35, 36]
– ^c	–	1.477(9)	1.560(9)	–	88.0(8)	–	82(1)	143(2)	333 K; [34]
Co(III) ^d	1.973(5); 1.988(4); 1.995(5)	1.510(7), 1.512(7); 1.519(7), 1.525(7); 1.487(8), 1.534(7)	1.525(8), 1.531(8); 1.514(8), 1.527(8); 1.522(8), 1.522(8)	115.8(3), 116.0(3); 115.2(3), 117.3(4); 115.6(3), 117.0(4)	85.5(4); 85.6(4); 86.0(4)	89.0(4), 89.2(4); 88.5(4), 88.8(4); 88.4(4), 90.1(4)	84.7(5); 84.8(4); 85.7(4)	144.7(5); 144.9(5); 145.5(5)	~298 K; [38]
Co(III)	1.996(8)	1.528(13); 1.536(11)	1.514(13); 1.551(13)	116.1(6); 116.2(6)	86.8(7)	88.2(7); 89.9(7)	86.7(7)	149.6(8)	294 K; [37]
Co(III)	1.990(2)	1.518(3), 1.517(3)	1.542(4), 1.546(4)	111.6(2), 114.8(2)	87.0(2)	87.6(2), 87.7(2)	85.2(2)	142.6(4)	100 K; [26]
Co(III)	1.989(6)	1.524(9), 1.530(9)	1.531(10), 1.545(10)	112.7(4), 115.2(4)	85.7(5)	88.5(5), 88.7(5)	85.0(5)	143.6(9)	100 K; [26]
Co(III)	2.008(9)	1.522(13), 1.529(13)	1.512(14), 1.514(13)	113.1(6), 113.9(6)	85.4(7)	88.8(7), 89.1(7)	86.3(8)	146.3(13)	100 K; [24]
Co(III)	1.966(5)	1.515(7), 1.518(8)	1.525(8), 1.545(7)	112.9(4), 114.8(4)	86.0(4)	88.1(4), 89.0(4)	84.8(4)	143.6(7)	100 K; [24]
Co(III)	1.997(3)	1.505(4), 1.521(4)	1.539(5), 1.546(5)	111.3(2), 115.9(2)	86.7(2)	87.8(2), 88.1(3)	84.7(3)	142.4(4)	100 K; [24]
Co(III)	1.959(5); 1.963(5)	1.495(8), 1.552(8); 1.518(7), 1.521(7)	1.536(8), 1.540(9); 1.544(8), 1.559(7)	108.2(4), 114.1(4); 110.6(3), 114.6(4)	84.7(5); 86.3(4)	89.2(4), 91.2(5); 88.2(4), 88.7(4)	83.7(5); 84.1(4)	142.8(8); 145.4(8)	100 K; [24]
Ni(II)	1.913(2)	1.494(3), 1.504(3)	1.546(3), 1.557(3)	105.9(1), 114.8(1)	88.7(2)	88.2(2), 88.9(2)	85.0(2)	148.0(2)	293 K; [15]
Cu(II) ^e	2.038(3); 2.062(3)	1.493(4), 1.508(4); 1.489(4), 1.506(4)	1.559(5), 1.560(4); 1.550(5), 1.558(4)	106.7(2), 112.7(2); 105.7(2), 113.7(2)	89.0(2), 89.1(2)	88.4(2), 89.2(2); 88.5(2), 89.2(2)	85.1(2); 84.7(2)	149.2(3); 149.6(3)	100 K; [15]
Cu(II) ^e	2.037(4); 2.053(4)	1.487(6), 1.510(6); 1.492(6), 1.501(6)	1.546(6), 1.555(7); 1.560(7), 1.563(7)	105.2(3), 113.9(3); 106.3(3), 113.3(3)	88.9(3); 89.2(3)	88.5(3), 89.0(3); 88.5(3), 88.9(3)	84.6(3); 85.2(3)	148.4(4); 150.0(4)	293 K; [15]
Cu(II) ^e	2.003(3); 2.017(3)	1.491(6), 1.506(5); 1.487(5), 1.493(5)	1.542(7), 1.564(6); 1.537(6), 1.550(6)	103.8(3), 115.6(3); 105.4(2), 114.9(3)	88.9(3); 88.5(3)	88.9(3), 89.2(3); 89.1(3), 89.4(3)	84.7(3); 85.0(3)	149.9(4); 150.4(4)	293 K; [15]
Cu(II)	2.039(2)	1.488(4), 1.503(3)	1.547(4), 1.559(4)	108.3(2), 111.2(2)	89.3(2)	88.3(2), 89.3(2)	85.2(2)	150.5(3)	293 K; [15]
Cu(II)	1.998(1)	1.505(2), 1.505(2)	1.549(2), 1.553(2)	110.3(1), 111.1(1)	88.6(1)	88.7(1), 88.9(1)	85.3(1)	149.4(2)	100 K; [15]
Cu(II)	1.995(3)	1.500(5), 1.518(5)	1.561(6), 1.573(6)	103.5(3), 116.1(3)	89.8(3)	88.2(3), 88.4(3)	85.6(3)	150.0(4)	100 K; [16]

Table 1 continued

M	M–N/Å	C–N/Å	C–C/Å	MNC/°	CNC/°	NCC/°	CCC/°	Pucker ^a /°	Temp.; ref. no.
Cu(II) ^c	2.013(2); 2.036(2)	1.505(3), 1.506(3), 1.498(3), 1.501(3)	1.554(4), 1.561(4), 1.547(3), 1.558(4)	108.6(2), 111.2(2), 109.4(2), 109.5(2)	88.9(2); 89.3(2)	89.0(2), 89.3(2), 88.7(2), 89.2(2)	85.2(2); 85.5(2)	151.0(3); 151.3(3)	100 K; [16]
Cu(II)	2.003(2)	1.495(3), 1.499(3)	1.552(4), 1.559(3)	110.1(2), 111.9(2)	89.1(2)	88.7(2), 89.1(2)	84.9(2)	149.7(3)	100 K; [16]
Cu(II) ^c	1.987(5); 1.989(5)	1.491(10), 1.501(9); 1.500(11), 1.507(11)	1.530(12), 1.547(13); 1.555(13), 1.569(14)	103.6(4), 113.5(4); 103.3(4), 114.2(5)	88.4(6); 88.1(7)	88.5(5), 89.5(5); 89.3(6), 89.6(6)	84.0(8); 85.4(7)	148.7(9); 149.7(9)	293 K; [16]
Cu(II) ^c	2.000(3); 2.028(3)	1.493(4), 1.499(4), 1.485(5), 1.509(4)	1.537(5), 1.551(5); 1.541(5), 1.549(4)	106.0(2), 115.1(2); 109.3(2), 111.0(2)	88.8(2); 88.8(3)	89.0(2), 89.2(2); 89.0(3), 89.2(3)	85.2(3); 85.3(2)	150.5(3); 150.6(3)	293 K; [16]
Cu(II) ^d	2.002(5); 2.016(5)	1.502(8), 1.504(8); 1.491(8), 1.494(9)	1.546(8), 1.572(9); 1.491(8), 1.494(9)	103.7(4), 114.6(4); 105.8(4), 111.8(4)	89.1(5); 90.0(5)	89.0(5), 87.9(5); 89.0(5), 88.7(5)	85.1(5); 84.7(5)	148.4(7); 150.6(7)	100 K; [16]
Cu(II)	2.065(2)	1.493(3), 1.503(3)	1.560(3), 1.563(3)	105.1(1), 112.4(1)	89.5(1)	88.4(2), 88.6(2)	84.9(2)	148.7(3)	100 K; [16]
Cu(II) ^c	2.041(7); 2.043(6)	1.477(9), 1.553(12); 1.499(8), 1.507(9)	1.522(12), 1.535(10); 1.546(9), 1.547(9)	100.6(5), 117.2(5); 108.2(4), 111.7(4)	86.8(5); 89.5(5)	88.4(6), 90.7(6); 88.1(5), 88.3(5)	85.9(6); 86.3(5)	149.9(9); 150.4(9)	100 K; [18]
Cu(II)	2.006(5)	1.495(7), 1.513(8)	1.531(9), 1.544(9)	109.5(4), 110.7(4)	88.2(5)	89.1(5), 89.2(5)	85.8(5)	150.6(8)	100 K; [18]
Cu(II)	2.004(3)	1.495(5), 1.505(5)	1.545(5), 1.559(5)	107.9(2), 112.1(2)	89.0(2)	88.0(2), 88.9(2)	85.2(3)	148.4(5)	293 K; [19]
Cu(II) ^c	2.040(2); 2.047(2)	1.505(3), 1.505(4); 1.494(3), 1.497(4)	1.552(4), 1.558(4); 1.548(4), 1.551(4)	107.9(2), 111.5(2); 107.0(2), 113.0(2)	89.0(2); 88.9(2)	89.0(2), 88.7(2); 88.9(2), 89.1(2)	85.4(2); 85.1(2)	150.3(3); 150.1(3)	100 K; [19]
Cu(II) ^c	1.976(7); 1.986(7)	1.500(1), 1.505(10); 1.513(10), 1.523(10)	1.543(10), 1.567(11); 1.535(10), 1.578(10)	109.7(5), 110.6(5); 109.2(5), 110.3(5)	87.0(6); 88.8(6)	88.6(5), 89.3(5); 89.5(6), 90.7(6)	85.1(6); 84.4(6)	149.8(1); 149.8(1)	293 K; Present work, 1
Cu(II)	2.022(3)	1.515(3), 1.519(4)	1.554(4), 1.558(4)	112.7(2), 121.9(2)	89.2(2)	91.9(2), 92.0(2)	86.4(2)	173.0(5)	293 K; Present work, 2
Zn(II)	2.121(1)	1.491(2), 1.506(2)	1.557(2), 1.558(2)	108.6(1), 112.8(1)	89.4(1)	89.7(1), 90.2(1)	85.2(1)	155.2(2)	100 K; [19]
Zn(II)	2.089(2)	1.499(2), 1.504(3)	1.553(3), 1.554(3)	109.1(1), 112.2(1)	88.9(1)	89.3(1), 89.6(1)	85.3(1)	152.3(3)	100 K; [19]
Zn(II)	2.109(1)	1.497(2), 1.509(2)	1.552(3), 1.557(2)	109.8(1), 110.2(1)	89.3(1)	89.6(1), 89.8(1)	85.6(1)	154.9(2)	150 K; Present work, 3
Zn(II)	2.111(2)	1.496(2), 1.504(3)	1.554(3), 1.560(3)	107.7(1), 115.2(1)	89.3(1)	89.5(2), 90.0(2)	85.2(2)	154.2(3)	150 K; Present work, 4
Pd(II)	2.018(6)	1.503(8), 1.506(9)	1.538(9), 1.559(9)	107.6(4), 112.2(4)	88.0(5)	89.0(5), 89.8(5)	84.9(5)	149.2(8)	293 K [17]

Table 1 continued

M	M–N/Å	C–N/Å	C–C/Å	MNC/°	CNC/°	NCC/°	CCC/°	Pucker ^a /°	Temp.; ref. no.
Pd(II)	2.020(3)	1.497(4),	1.551(4),	109.5(2),	88.6(2)	88.6(2)	85.2(2)	149.3(4)	100 K [20]
		1.510(4)	1.551(5)	110.0(2)		89.1(2)			
Pd(II)	2.031(2)	1.498(3),	1.544(5),	105.0(2),	88.6(2)	88.4(2),	85.8(2)	149.8(5)	293 K [20]
		1.512(3)	1.545(3)	113.9(2)		88.8(2)			
Pd(II)	2.075(4)	1.518(5),	1.555(6),	107.8(2),	88.5(3)	90.4(3),	85.9(3)		293 K; [39]
		1.526(5)	1.563(6)	118.7(3)		90.4(3)			
Pd(II)	2.042(2)	1.507(4),	1.550(4),	109.8(2),	89.5(2)	90.3(2),	86.5(2)		296 K; [39]
		1.531(4)	1.570(4)	113.4(2)		90.2(3)			

^a Defined as the angle subtended at the centroid of the C–C diagonal by the N and C atoms of the other diagonal

^b Data for the parent ligand azetidine in the crystalline state; two inequivalent molecules are present in the lattice

^c Gas phase measurements on azetidine by electron diffraction [38]

^d Three inequivalent units present in the lattice

^e Two inequivalent units present in the lattice

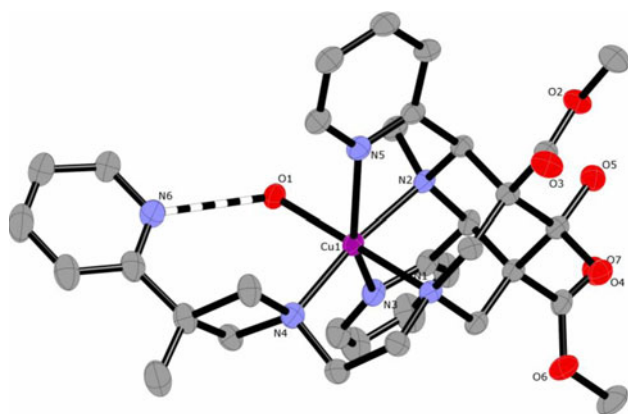


Fig. 3 The cation present in the crystal lattice of **2**, [Cu(L⁴)(OH₂)](ClO₄)₂, showing the large “chelate” ring formed by H-bonding of the pendent pyridine-N to coordinated water

·H₂O···O-alcohol through to the face behind. The strong H-bond donor capacity of the bound alcohol is reflected in the short contact to lattice water, where O···O is 2.652(6) Å (and a similarly strong interaction is seen in the lattice of the complex of L⁷; see ahead).

An advantage of the construction of macro(poly)cyclic ligands by the use of nitroalkanes is that the nitro substituent thereby introduced can be readily converted to a good donor amino group [27, 28, 45]. The extensively developed chemistry of the «diammac» ligands [46–48] of this type shows, for example, that binding of the additional amino groups¹ can suffice to force their associated six-

¹ Where the coordination preferences of the metal ion are such that this binding is not favoured, the ligand, bound quadridentate in a square-planar species, appears to prefer the common, cyclam-like conformation where both six-membered chelate rings adopt the chair conformation [33]

membered chelate ring into a boat conformation and this is again observed in the complex [Co(L⁷)]Cl₂·ClO₄·H₂O. More interesting in this particular case, however, is that the crystal structure (Fig. 6), again of marginal quality but acceptable for the purposes of the present comparisons, shows that one of the hydroxyl groups of the hydroxymethyl substituents is also bound in a similar manner and that despite the fact that the presence of two hydroxymethyl groups means that coordination equivalent to that of either *syn*- or *anti*-diammac species is possible, it is that equivalent to that of the less common *syn*-diammac which is observed. Thus, the pendent-O and -N donors occupy adjacent (*cis*) positions in the coordination sphere of the cobalt atom. This may be a consequence of the presence of one more atom in the chelate ring involving the hydroxyl donor, although it must be noted that Co(III) complexes of a closely related macrocycle where the two hydroxymethyl groups of L⁴ are replaced by H and (non-coordinating) OH have been characterized [31] in forms where the pendent amino group is bound *cis* to a sixth unidentate ligand and that the true equilibrium distribution of isomers in any of these systems has not been established. Other isomers may have been present in the trace species observed during chromatography of the Co/L⁷ reaction products but clearly the isolated species is at least the kinetically strongly preferred form of the complex.

The binding of but one of the geminal hydroxymethyl groups to the metal is a means of discrimination which might be exploited for selective reactions which are overall equivalent to opening of the oxetane ring of a species such as L⁸ by a reagent other than water. An index of the degree of discrimination between the hydroxy centres induced by coordination of L⁷ in [Co(L⁷)]Cl₂·ClO₄·H₂O is the difference in H-bond contacts to chloride ion acceptors (O(1)···Cl(2) 2.85(2); O(2)···Cl(3) 3.09(2) Å) and of course

Fig. 4 The molecular units present in the lattices of **3** (left) and **4** (right)

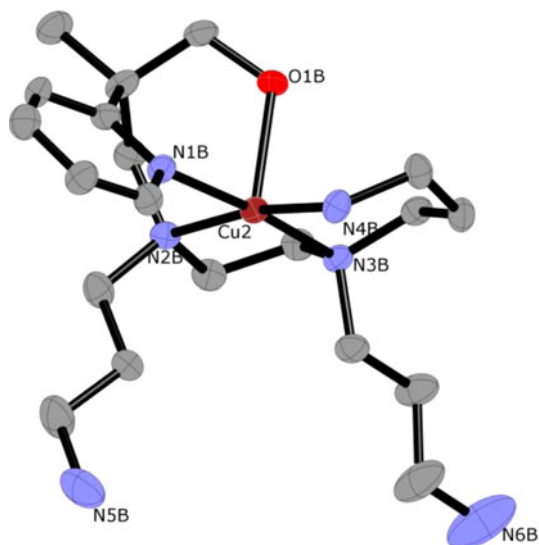
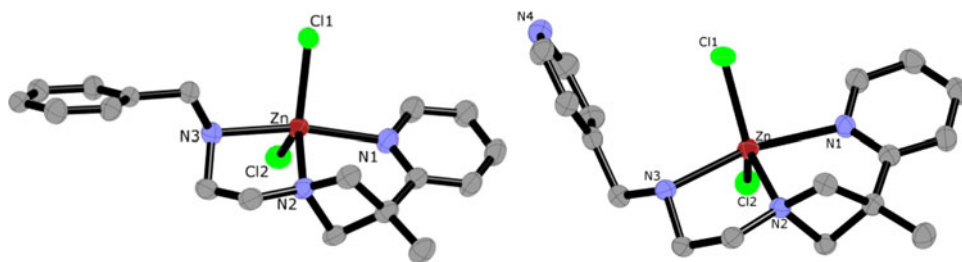


Fig. 5 The cation present in the crystal lattice of **5**, $[\text{Cu}(\text{L}^5\text{H}_2)](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$, showing the two ammoniopropyl groups pendent to one side of the Cu(II) coordination plane

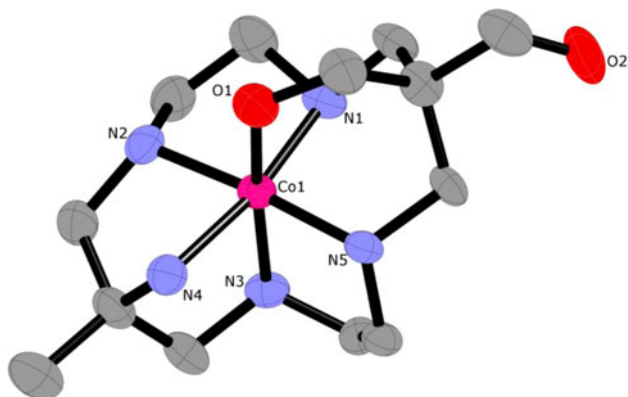


Fig. 6 The cation present in the crystal lattice of **6**, $[\text{Co}(\text{L}^7)]\text{Cl}_2 \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$, showing the adjacent coordination of pendent amino and hydroxyl groups

a large difference in the acidity of the bound and free hydroxyl groups would be anticipated [49].

That an oxetane ring which is pendent to a bound macrocycle may be reactive is shown by the structure of $[\text{Cu}(\text{L}^9)\text{Cl}(\text{OH}_2)]\text{PF}_6$. In addition to formation of a

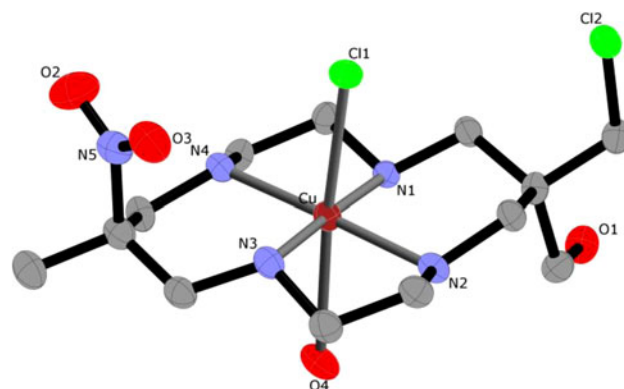


Fig. 7 The cation present in the crystal lattice of **7**, $[\text{Cu}(\text{L}^9)\text{Cl}(\text{OH}_2)]\text{PF}_6$

macrocyclic ring, the reaction conducted on $[\text{Cu}(\text{L}^8)]^{2+}$ results effectively in ring opening of the oxetane by chloride ion. (It is conceivable that the chloromethyl group could result from reaction of an initially-formed *bis*(hydroxymethyl) species with HCl during the purification procedures but such a reaction was not observed during macrocycle formation from the true *bis*(hydroxymethyl)tetramine [23]. This is in stark contrast to the analogous treatment of the bound azetidine complex $[\text{Cu}(\text{L}^2)]^{2+}$, where no evidence was detected of ring opening reactions. The crystallisation of a single isomer of $[\text{Cu}(\text{L}^9)\text{Cl}(\text{OH}_2)]\text{PF}_6$ is somewhat remarkable, especially given the common co-crystallisation of Cu(II) complexes [15, 16, 50], and quite possibly other isomers are present in the total mixture in solution. The cation present in the lattice (Fig. 7) has the macrocycle in the cyclam “*trans*-III” conformation, with the nitro substituent in an axial site of its six-membered chelate ring and oriented so that H-bonding of one oxygen to a macrocycle NH is possible. The nitro group lies to the same side of the mean plane of the macrocycle as the coordinated chloride ion and the chloromethyl substituent apparently produced by nucleophilic ring opening of the oxetane unit initially present in L^8 . The water ligand and the hydroxymethyl group produced by the ring opening lie to the other side. These dispositions enable the formation of infinite helical chains of the cations about axes parallel to *c*, the principal linking

interaction being H-bonding between the chloride and aqua ligands on adjacent complexes ($\text{Cl}\cdots\text{O}$ 3.157(4) Å), though H-bonding of the hydroxymethyl group adjacent to the water ligand to the same chloride must be a bolstering force ($\text{Cl}\cdots\text{O}$ 3.263(4) Å).

Conclusions

At present, there appear to be no exceptions to the generalisation that N-coordination of azetidines (unless deprotonated [9]) results in negligible activation towards nucleophilic attack. In other words, N-coordination of azetidines, as for aziridines [7–14], can be used as a form of protection of the ring, in particular against proton-catalysed reactions [38] as well as against activation by alkylation [1–6, 16] or tosylation, it being well-established that N-tosyl azetidines are susceptible to Lewis-acid-catalysed ring opening [2, 4, 51]. As we have noted previously [15–26], even tertiary azetidine-N is a good donor and it is a species resistant to oxidative reactions (generating imines) which sometimes complicate the reactions of polyamine complexes.

In contrast to simple azetidine complexes, those of oxetanes show significant reactivity towards nucleophiles and ring-opening reactions of bound oxetanes are attracting increasing interest for synthesis [3]. In the present study of reactions of the ligand L^8 , it is unclear at which stage ring opening may have occurred and, given that it is unlikely that coordination of the ether-O to Cu would have occurred, it is possible that acid catalysis may have played some role. What can be said, nonetheless, is that it should be possible to use a pendent oxetane ring on a metal complex to readily provide functionality suitable for the introduction of sophisticated substituents. Note that even in the case where the ring opening might produce just a *bis*(hydroxymethyl) unit, the structure of $[\text{Co}(\text{L}^7)]\text{Cl}_2\cdot\text{ClO}_4\cdot\text{H}_2\text{O}$ shows that metal ion coordination can be used to distinguish between the two groups.

Experimental

Reagents and procedures

All basic chemicals were purchased from Aldrich Chemical Co. and used as received. Ion exchange chromatography was conducted in glass columns under gravity flow using SP-Sephadex C25 (Na^+ form) or Dowex 50Wx2 (H^+ form) cation-exchange resins. Electronic absorption spectra were measured on a SCINCO S-2100 diode-array spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance Digital 400 instrument.

Synthesis

$[\text{Cu}(\text{L}^2)](\text{SCN})_2$

Aqueous formaldehyde (35%, 2.7 g), triethylamine (1.6 g) and nitroethane (0.5 g) were added to a solution of $[\text{Cu}(\text{L}^1)](\text{ClO}_4)_2$ [24] (1.0 g) in methanol (100 mL) and the mixture heated at reflux for 48 h. Acetic acid (15 mL) was added after cooling and the solution was evaporated to near dryness under reduced pressure before being diluted with water (200 mL) and absorbed on a column of Dowex 50Wx2 (H^+ form) cation exchange resin. The column was washed with water (200 mL) and 0.5 mol L^{-1} HCl (500 mL), then eluted with 3 mol L^{-1} HCl to give one pink band. The eluate was evaporated to dryness under reduced pressure, giving a reddish-violet residue. Yield, 1.1 g. This was dissolved in the minimum amount of ethanol, NaSCN added, and diethyl ether added by vapour diffusion to provide violet crystals suitable for a structure determination. Anal. calcd for $[\text{Cu}(\text{L}^2)](\text{SCN})_2 = \text{C}_{15}\text{H}_{27}\text{CuN}_7\text{O}_2\text{S}_2$: C 38.74, H 5.85, N 21.08; Found: C 38.8, H 6.0, N 21.1%. Visible spectrum (in water): $\lambda_{\text{max}} = 512$ nm, $\log \epsilon_{\text{max}} = 2.14$; ~ 625 nm (sh), $\log \epsilon_{\text{max}} = 1.62$.

$[\text{Cu}(\text{L}^4)(\text{OH}_2)](\text{ClO}_4)_2$

Aqueous formaldehyde (0.51 g, 35%) and L^3 [15] (0.48 g) were added successively to a solution of the bispidine precursor 3-methyl-2,4-bis(2-pyridyl)-5,6-bis(methoxycarbonyl)piperidone [52] (1.0 g) in THF (8 mL) and the mixture was heated at 60 °C for 4 h. The resulting dark brown solution was evaporated under reduced pressure to give a dark green oil. This was dissolved in methanol (20 mL), $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.36 g) added and the mixture stirred at room temperature for 1 h before the solvent was removed under reduced pressure. The sticky, blue-green residue was dissolved in water (20 mL) and filtered to remove insoluble brown-black material. The filtrate was applied to SP-Sephadex C-25 (Na^+ form) and the resin column eluted with 0.5 mol L^{-1} NaCl to reveal three components. The first was simply Cu(II) aqua-ion and the third a minor green species which could only be removed using saturated NaCl solution and which was not further characterised. The eluate containing the second, major blue component was collected and evaporated to dryness under reduced pressure. The residue was extracted with ethanol and the largely insoluble NaCl filtered out. Addition of excess LiClO_4 to the filtrate followed by slow evaporation provided blue crystals suitable for a structure determination. Anal. Calcd for $[\text{Cu}(\text{L}^7)(\text{OH}_2)](\text{ClO}_4)_2 = \text{C}_{33}\text{H}_{42}\text{Cl}_2\text{CuN}_6\text{O}_{15}$: C 44.18, H 4.72, N 9.37. Found: C 43.90, H 4.68, N 9.33%. Visible spectrum (in CH_3CN): $\lambda_{\text{max}} = 640$ nm, $\log \epsilon_{\text{max}} = 1.93$; $\lambda_{\text{max}} = 690$ nm, $\log \epsilon_{\text{max}} = 1.98$.

$[Zn(NBz-L^3)Cl_2]$

$[Cu(NBz-L^3)Cl_2]$ [19] (0.50 g) was dissolved in water (20 mL), Zn powder (1.0 g) added and the mixture was stirred for 12 h at room temperature, then filtered through Celite and the filtrate taken to dryness under reduced pressure, giving a white powder. Yield, 0.40 g. An ethanolic solution of the complex was slowly evaporated to provide colourless crystals suitable for a structure determination. Anal. Calcd for $[Zn(NBz-L^3)Cl_2] = C_{18}H_{23}Cl_2N_3Zn$: C 51.76, H 5.55, N 10.06. Found: C 52.1, H 5.46, N 10.1%.

 $[Zn(N(4-pm)-L^3)Cl_2]$

A solution of L^1 (0.70 g) [15] and pyridine-4-aldehyde (0.41 g) in ethanol (5 mL) was heated at 60 °C under nitrogen for 2 h. $NaBH_4$ (0.50 g) was added to the cooled brown solution, which was then stirred for 6 h at room temperature before addition of 2 mol L⁻¹ HCl (10 mL). The mixture was evaporated to dryness under reduced pressure, the residue dissolved in 2 mol L⁻¹ NaOH (50 mL) and the product extracted into $CHCl_3$ (3 × 50 mL). The combined extracts were dried over anhydrous Na_2SO_4 and evaporated to yield a brown oil (0.90 g). This was dissolved in methanol (100 mL) and $CuCl_2 \cdot 2H_2O$ (0.54 g) added to form the Cu(II) complex. The violet solution was evaporated to dryness under reduced pressure, the residue dissolved in water (200 mL) and the solution absorbed onto SP-Sephadex C-25. Elution with 0.3 mol L⁻¹ NaCl gave one violet band and, after evaporation of the eluate to dryness, the complex was extracted into ethanol. Evaporation of this extract provided the crude Cu(II) complex (1.0 g), which was converted into the Zn(II) complex following the same procedure as described above for compound **3**. Again, slow evaporation of an ethanolic solution provided colorless crystals suitable for a structure determination. Anal. Calcd for $[Zn(N(4-pm)-L^3)Cl_2] = C_{17}H_{22}Cl_2N_4Zn$: C 48.77, H 5.30, N 13.38. Found: C 48.5, H 5.43, N 13.4%.

 $[Cu(L^5H_2)](ClO_4)_4 \cdot 2H_2O$

Acetic acid (1.0 g) was added to a solution of L^3 (1.14 g) in acrylonitrile (10.0 g) and the mixture was heated at 70 °C for 24 h under nitrogen. On cooling, the excess nitrile was evaporated off to give a yellow oil. This was mixed with water (50 mL) and extracted with chloroform (3 × 50 mL). The combined extracts were backwashed with water (3 × 50 mL), dried over Na_2SO_4 , then evaporated down to a viscous oil (0.98 g). The whole product was used for the next reaction without purification. It was dissolved in water/methanol (2:1 v/v; 20 mL) and Raney-Ni (3.0 g) added. A solution of $NaBH_4$ (3.0 g) in 8 mol L⁻¹ NaOH (20 mL) was

slowly added under vigorous stirring and the final mixture was stirred at room temperature for another 12 h before reaction was quenched by the addition of HCl (2 mol L⁻¹, 10 mL). NaOH (2 mol L⁻¹, 100 mL) was added to the residue obtained by evaporation to dryness under vacuum and the product extracted from this into chloroform (3 × 50 mL). The combined extracts were backwashed with water, dried over Na_2SO_4 and then evaporated down to give a yellow oil. Yield, 1.23 g. The crude ligand (1.23 g) and $CuCl_2 \cdot 2H_2O$ (0.70 g) were dissolved in methanol (50 mL) and stirred for 0.5 h. The blue solution was evaporated to dryness under reduced pressure and the residue dissolved in water (100 mL) before absorption onto SP-Sephadex C-25. Elution with 0.3 mol L⁻¹ NaCl removed firstly some residual Cu(II) aqua-ion and some trace violet components before a major violet band. The major band eluate was evaporated to dryness under reduced pressure and the complex separated from the bulk of the NaCl present by extraction into ethanol. Evaporation of the ethanol extract gave a violet powder. Yield, 0.71 g. Crystals suitable for a structure determination were obtained by slow evaporation of an aqueous solution after addition of $LiClO_4$. Anal. calc. for $C_{20}H_{46}Cl_4CuN_6O_{19}$: C, 27.30; H, 5.27; N, 9.55. Found: C 27.1, H 5.32, N, 9.47%. Visible spectrum (in water): $\lambda_{max} = 544$ nm, $\log \epsilon_{max} = 2.17$; ~610 nm (sh.), $\log \epsilon_{max} = 2.03$.

 $[Co(L^7)]Cl_2 \cdot ClO_4 \cdot H_2O$

Under vigorous stirring, Zn powder (5.0 g) was added to a solution of $[Cu(L^6)](ClO_4)_2$ [23] (2.6 g) in water (200 mL) and 2 mol L⁻¹ HCl (20 mL) then added dropwise. After 2 h, the mixture was filtered and the colourless filtrate diluted with water (200 mL), and absorbed onto Dowex 50Wx2 (H^+ form). After washing the column with water (200 mL) and 1 mol L⁻¹ HCl (300 mL), the protonated polyamine was eluted with 4 mol L⁻¹ HCl. The eluate was evaporated to dryness under reduced pressure, giving a white powder (1.8 g). This was used to prepare the cobalt complex without further purification. Thus, the hydrochloride salt (1.8 g) was suspended in methanol (50 mL) and NaOH (0.76 g in 20 mL methanol) added. $CoCl_2 \cdot 6H_2O$ (0.95 g) was then added and the mixture aerated for 12 h. The final brown solution was acidified with acetic acid (10 mL) and evaporated to dryness under reduced pressure. The residue was dissolved in water (100 mL) and the red solution adsorbed onto Dowex 50Wx2. After washing the column with water (200 mL), then 0.5 mol L⁻¹ HCl (200 mL), elution with 2 mol L⁻¹ HCl removed four very minor bands ahead of a single major, orange component. The eluate from the major band was evaporated to dryness under reduced pressure, giving a reddish-orange residue (1.9 g). This was dissolved in the minimum amount of water, $LiClO_4$ added, and ethanol added

Table 2 Crystal data and structure refinement details

Compound	1 [Cu(L ¹)(NCS) ₂]	2 [Cu(L ⁴)(OH ₂)](ClO ₄) ₂	3 [Zn(NBz-L ³)Cl ₂]
Chemical formula	C ₁₅ H ₂₇ CuN ₇ O ₂ S ₂	C ₃₃ H ₄₂ Cl ₂ CuN ₆ O ₁₅	C ₁₈ H ₂₃ Cl ₂ N ₃ Zn
<i>M</i> /g mol ⁻¹	465.10	897.17	417.66
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	11.075(2)	17.912(4)	9.6353(5)
<i>b</i> /Å	12.156(2)	10.620(2)	8.3641(2)
<i>c</i> /Å	15.474(3)	19.496(4)	23.8394(11)
α /°	93.66(3)	90	90
β /°	95.68(3)	91.23(3)	92.216(2)
γ /°	91.97(3)	90	90
<i>V</i> /Å ³	2067.0(7)	3707.8(13)	1919.8(1)
<i>Z</i>	4	4	4
<i>D</i> _{calc} /g cm ⁻³	1.495	1.607	1.445
μ /mm ⁻¹	1.284 ^a	0.814 ^a	1.562
<i>F</i> (000)	972	1860	864
<i>T</i> /K	293(2)	293(2)	150(2)
Reflections collected	8654	15402	56789
Independent reflections	8654	8239	3643
“Observed” reflections (<i>I</i> > 2σ(<i>I</i>))	6184	7320	3177
<i>R</i> _{int}	0.153	0.068	0.036
Parameters refined	492	312	219
<i>R</i> ₁	0.136	0.063	0.0239
<i>wR</i> ₂	0.457	0.173	0.0628
<i>S</i>		1.036	1.037
Flack parameter			
Complex	4 [Zn(N(4-pm)L ³)Cl ₂]	5 [Cu(L ⁵ H ₂)](ClO ₄) ₄ ·2H ₂ O	
Chemical formula	C ₁₇ H ₂₂ Cl ₂ N ₄ Zn	C ₂₀ H ₄₆ Cl ₄ CuN ₆ O ₁₉	
<i>M</i> /g mol ⁻¹	418.66	879.97	
Crystal system	Orthorhombic	Monoclinic	
Space group	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>	
<i>a</i> /Å	10.0178(5)	16.1182(5)	
<i>b</i> /Å	18.3142(4)	12.0495(8)	
<i>c</i> /Å	20.1207(10)	31.178(2)	
α /°	90	90	
β /°	90	97.995(3)	
γ /°	90	90	
<i>V</i> /Å ³	3691.5(3)	7150.4(7)	
<i>Z</i>	8	8	
<i>D</i> _{calc} /g cm ⁻³	1.507	1.635	
μ /mm ⁻¹	1.626	0.994	
<i>F</i> (000)	1728	3656	
<i>T</i> /K	150(2)	100(2)	
Reflections collected	73478	222692	
Independent reflections	3504	13501	
“Observed” reflections (<i>I</i> > 2σ(<i>I</i>))	2842	9299	
<i>R</i> _{int}	0.023	0.044	
Parameters refined	218	925	
<i>R</i> ₁	0.0287	0.0896	

Table 2 continued

Complex	4 [Zn(N(4-pm)L ³)Cl ₂]	5 [Cu(L ⁵ H ₂)](ClO ₄) ₄ ·2H ₂ O
<i>wR</i> ₂	0.0677	0.2625
<i>S</i>	1.018	1.101
Complex	6 [Co(L ⁷)]Cl ₂ ·ClO ₄ ·H ₂ O	7 [Cu(L ⁴)](OH ₂)Cl]PF ₆
Chemical formula	C ₁₃ H ₃₃ Cl ₃ CoN ₅ O ₇	C ₁₃ H ₃₀ Cl ₂ CuF ₆ N ₅ O ₄ P
<i>M</i> /g mol ⁻¹	599.85	599.83
Crystal system	Monoclinic	Hexagonal
Space group	<i>C2/c</i>	<i>P6₁</i>
<i>a</i> /Å	33.336(7)	10.0382(7)
<i>b</i> /Å	7.9130(16)	10.0382(7)
<i>c</i> /Å	19.271(4)	38.788(2)
<i>α</i> /°	90	90
<i>β</i> /°	114.48(3)	90
<i>γ</i> /°	90	120
<i>V</i> /Å ³	4626.5(16)	3384.9(4)
<i>Z</i>	12	6
<i>D</i> _{calc} /g cm ⁻³	1.535	1.766
<i>μ</i> /mm ⁻¹	1.131 ^b	1.356
<i>F</i> (000)	2224	1842
<i>T</i> /K	293(2)	100(2)
Reflections collected		45762
Independent reflections	6687	4275
“Observed” reflections (<i>I</i> > 2σ(<i>I</i>))	4063	3941
<i>R</i> _{int}	0.185	0.041
Parameters refined	497	291
<i>R</i> ₁	0.1122	0.0572
<i>wR</i> ₂	0.3070	0.1431
<i>S</i>	1.074	1.072

^a Synchrotron λ 0.77000 Å^b Synchrotron λ 0.69996 Å

by vapour diffusion to produce reddish orange, needle-like crystals suitable for a structure determination. Anal. calcd for [Co(L⁷)]Cl₂·ClO₄·H₂O = C₁₃H₃₃Cl₃CoN₅O₇: C 29.09, H 6.20, N 13.05. Found: C 29.5, H 6.0, N 13.2%. Visible spectrum (in water): λ_{max} = 485 nm, log ε_{max} = 2.08.

[Cu(L⁹)Cl(OH₂)]PF₆

A solution of [Cu(L⁸)]Cl₂ [23] (2.0 g) in methanol (100 mL) was heated at reflux for 48 h after addition of formaldehyde (35%, 5.1 g), nitroethane (0.9 g), and triethylamine (3.0 g). After cooling, acetic acid (15 g) was added and the solution evaporated to dryness under reduced pressure. The residue was dissolved in water (200 mL) and absorbed onto Dowex 50W-x2 (H⁺ form). Elution with 3 mol L⁻¹ HCl after washing with water (200 mL) and 0.5 mol L⁻¹ HCl (500 mL) gave one pink

band. The eluate was evaporated to dryness under reduced pressure to give a blue powder (2.1 g). This was dissolved in the minimum amount of water, excess NH₄PF₆ added and ethanol then added by vapour diffusion to provide pink crystals suitable for a structure determination. Anal. calcd for [Cu(L⁶)Cl(OH₂)]PF₆ = C₁₃H₃₀Cl₂CuF₆N₅O₄P: C 26.03, H 5.04, N 11.68. Found: C 26.4, H 5.2, N 11.7%. Visible spectrum (in water): λ_{max} = 511 nm, log ε_{max} = 1.90; ~615 nm (sh), log ε_{max} = 1.37.

Crystallography

The data for compounds **3**, **4** and **7** were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer [53] using graphite-monochromated Mo-Kα radiation (λ 0.71073 Å). Each crystal was introduced in a glass capillary with a protecting “Paratone-N” oil (Hampton

Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. The data (φ - and ω -scans) were processed with HKL2000 [54]. The structures were solved by direct methods with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97 [55]. Absorption effects were corrected empirically with the program SCALEPACK [54]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were found on Fourier-difference maps and all the others were introduced at calculated positions; all were treated as riding atoms with a displacement parameter equal to 1.2 (OH, OH₂, NH, CH, CH₂) or 1.5 (CH₃) times that of the parent atom.

The data for compounds **1**, **2**, **5** and **6** were collected at 293(2) K using an ADSC Quantum 210 collector at Beamline 4A MXW of the Pohang Light Source. The unit cell determinations and data collections were done using 0.77 Å radiation with a detector-to-crystal distance of 6.0 cm. Preliminary cell constants and an orientation matrix were determined from 36 sets of frames collected at scan intervals of 5° with an exposure time of 1 s per frame. The data were processed with HKL2000 [53] and reflections were indexed using the automated indexing routine of DENZO. A total of 8654, 15402, 222692, and 6687 reflections for compounds **1**, **2**, **5** and **6**, respectively, were obtained by collecting 72 sets of frames with 5° scans and an exposure time of 1 s per frame. These highly redundant data sets were corrected for Lorentz and polarisation effects and a (negligible) correction for crystal decay applied. The space groups were assigned using the program XPREP (version 6.13, Bruker-AXS). The structures were solved by direct methods and refined on F^2 by full-matrix least-squares procedures. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in the structure factor calculations at idealised positions using a riding model but the positions were not refined. The structure of **1** was refined as corresponding to a racemic twin.

Crystal data and structure refinement parameters are given in Table 2. The molecular plots were drawn with SHELXTL [55]. CCDC reference numbers are 799125–799131.

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