Coordination chemistry of 1,4-bis-carboxymethylcyclam, $H_2(1,4\text{-bcc})$†

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Zinc metal reduction of the cobalt(III) complex $[Co(1,4\text{-bcc})]^+$ (1,4-bcc = 1,4-bis-carboxymethylcyclam) produces the corresponding cobalt(II) complex which crystallises as the coordination polymer $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$. A method has been developed for removal of the cobalt(III) ion from $[Co(1,4\text{-bcc})]^+$ and isolation of the free ligand as its hydrochloride salt, $H_2(1,4\text{-bcc})\cdot 4HCl$. This has been used for the preparation of new metal complexes, and the syntheses and characterisation of the copper(II), nickel(II), zinc(II) and chromium(III) complexes containing the 1,4-bcc ligand are described. X-Ray crystal structures of $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n\cdot 2.5H_2O$, $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n\cdot 0.25MeOH\cdot H_2O$ and $[Cu(1,4\text{-bcc})H]ClO_4$ show the complexes to have the *trans*(O) geometry of the 1,4-bcc ligand, while the structure of $[Cr(1,4\text{-bcc})H_{0.5}](ClO_4)_{1.5}\cdot EtOH$ exhibits the *cis*(O) configuration.

Introduction

As part of our interest in the reactions of ligands coordinated to cobalt(III) we developed a novel route to 1,4-bis-carboxymethylcyclam $H_2(1,4\text{-bcc})$ which contains two N-carboxymethyl substituents, and can be considered to be a derivative of the 14-membered cyclam macrocycle bearing two pendant coordinated α-amino acid groups. We reported the synthesis of the cobalt(III) complex containing this ligand, $[Co(1,4\text{-bcc})]^+$, *via* an intramolecular alkylation reaction (Fig. 1).[1] The *trans*(O) geometry of this complex, which contains the four cyclam nitrogen atoms in the equatorial plane, and the two carboxylate oxygen atoms *trans*, was determined by X-ray crystallography and supported by NMR spectroscopy consistent with C_2 symmetry. We subsequently reported a photochemical decarboxylation of $[Co(1,4\text{-bcc})]^+$ to give a cobalt complex containing a Co–C–N three-membered ring, in which the N atom also comprises part of the cyclam ring.[2]

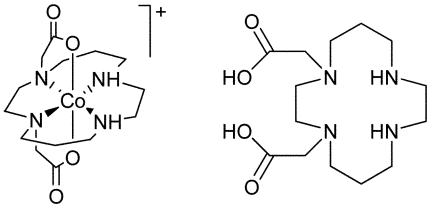

Fig. 1 Sketch of $[Co(1,4\text{-bcc})]^+$ and $H_2(1,4\text{-bcc})$.

The 1,4-bcc ligand was synthesised *via* a reaction occurring within the coordination sphere of a cobalt(III) complex in which the ligands were preorganised for the intramolecular alkylation reaction. The utility of this direct route to the 1,4-bcc ligand, which can be achieved in a one-pot synthesis beginning with $H[Co(edda)Cl_2]$ (edda = *N*,*N*′-ethanediaminediacetate), is increased if the complex can be demetallated to give the free $(1,4\text{-bcc})^{2-}$ ligand, which would then be available for coordination to other metals. In this paper we report the chemical reduction of the cobalt(III) complex $[Co(1,4\text{-bcc})]^+$ to the corresponding cobalt(II) complex, removal of cobalt to obtain the free ligand as the hydrochloride salt $H_2(1,4\text{-bcc})\cdot 4HCl$, and the preparation of copper, nickel, zinc and chromium complexes of 1,4-bcc.

Results and discussion

Reduction of the cobalt(III) complex of 1,4-bcc to cobalt(II)

Non-macrocyclic complexes of cobalt(III) typically exhibit irreversible one-electron reduction in aqueous solution because the kinetic lability of the cobalt(II) complexes formed on reduction leads to aquation and generation of $[Co(H_2O)_6]^{2+}$. As reported previously, $[Co(1,4\text{-bcc})]ClO_4$ exhibits a reversible electrochemical reduction wave in aqueous solution ($E^\circ = -0.29$ V), ascribed to the enhanced kinetic stability imparted by the macrocyclic pendant-arm ligand.[1] This was an indication that chemical reduction of $[Co(1,4\text{-bcc})]ClO_4$ to give a cobalt(II) complex sufficiently inert to be isolable might be able to be achieved.

A solution of $[Co(1,4\text{-bcc})]ClO_4$ in 1.0 mol L^{-1} HCl solution was placed in a vial with a piece of amalgamated zinc, and the vial was sealed and allowed to stand at room temperature. After approximately two days the colour of the solution had changed from the deep red characteristic of the cobalt(III) complex to pale yellow, and yellow crystals had formed on the surface of the zinc amalgam. The resulting complex was characterised by X-ray crystallography. It was not characterised further as the crystals are air-sensitive and reform the cobalt(III) complex as evidenced by a colour change from yellow back to red after standing in air for 15 min. NMR spectroscopy did not prove useful for characterising the paramagnetic cobalt(II) complex.

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The molecular structure determination shows that the crystal is a coordination polymer comprised of chains of the neutral cobalt(II) complex Co(1,4-bcc) linked through zinc dichloride moieties which are coordinated to the carboxylate oxygen atoms of the 1,4-bcc ligand carboxylate groups (Fig. 2), giving an overall composition $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$. The zinc atoms, each bonded to two chloro and two carboxylate oxygen atoms, have approximate tetrahedral geometry. The chemical reduction of $[Co(1,4\text{-bcc})]ClO_4$ could also be achieved using aluminium amalgam, as evidenced by a change in colour of the reaction mixture from red to yellow under the same conditions that produced the polymeric complex with zinc, although no crystalline product was obtained. It is possible that the zinc ion plays an important role in stabilising the solid state structure of the cobalt(II) complex.

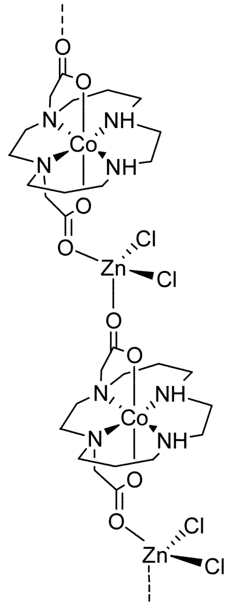

Fig. 2 Sketch of $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$.

Isolation of the free 1,4-bcc ligand

Removal of the cobalt centre from $[Co(1,4\text{-bcc})]ClO_4$ was achieved by heating a solution of the complex with excess potassium cyanide under nitrogen in deoxygenated water, in the presence of a stoichiometric amount of $[Co(H_2O)_6]^{2+}$. This method was developed by Sargeson for removal of cobalt from the encapsulating bicyclic hexamine ligand, sar.[3] The solution changed colour from red, to pale green, to yellow, and finally became almost colourless upon heating at reflux temperature overnight. The initial green colour is attributed to the formation of the $[Co(CN)_5]^{3-}$ ion,[4] which acts as the reductant, forming $[Co(CN)_6]^{3-}$ and the yellow cobalt(II) complex Co(1,4-bcc). Demetallation of the cobalt(II) complex in the presence of excess cyanide ion releases the free 1,4-bcc ligand and forms further $[Co(CN)_5]^{3-}$. The process can be summarised by eqns (1)–(3).

$$[Co^{II}(H_2O)_6]^{2+} + 5\,CN^- \rightarrow [Co^{II}(CN)_5]^{3-} + 6\,H_2O \tag{1}$$

$$[Co^{II}(CN)_5]^{3-} + [Co^{III}(1,4\text{-bcc})]^+ + CN^- \rightarrow Co^{II}(1,4\text{-bcc}) + [Co^{III}(CN)_6]^{3-} \tag{2}$$

$$Co^{II}(1,4\text{-bcc}) + 6\,H_2O \rightarrow [Co^{II}(H_2O)_6]^{2+} + 1,4\text{-bcc}^{2-} \tag{3}$$

After exposure of the reaction mixture to air, concentrated hydrochloric acid was added (**CAUTION:** generation of HCN gas) to produce the hydrochloride salt $H_2(1,4\text{-bcc})\cdot 4HCl$ which was then separated from the cobalt by-products using cation exchange chromatography. White, solid $H_2(1,4\text{-bcc})\cdot 4HCl$ was isolated from the eluent, and although it could not be recrystallised due to its high solubility and hygroscopic nature, the material obtained after the ion-exchange chromatography proved by NMR spectroscopy and elemental analysis to be pure enough to use in subsequent reactions.

The ^1H NMR spectrum of $H_2(1,4\text{-bcc})\cdot 4HCl$ comprises six signals corresponding to the six hydrogen environments of the molecule, which has C_2 symmetry (Fig. 1). Broadening of some peaks was observed, indicative of a dynamic process involving conformational change of the flexible 14-membered macrocycle. A sharper spectrum was obtained by warming the sample to 338 K. Seven signals are observed in the ^{13}C NMR spectrum, corresponding to the seven different carbon environments.

Preparation of copper, nickel, zinc and chromium complexes of 1,4-bcc

Copper complexes of 1,4-bcc were prepared using two different metal salts, copper(II) chloride and copper(II) acetate. In each case, addition of the copper salt to an aqueous solution of $H_2(1,4\text{-bcc})\cdot 4HCl$ at pH 5 resulted in an immediate colour change from the pale blue copper salt to an intense dark blue solution, indicative of replacement of the aqua ligands in the salt by the stronger field amine ligands present in 1,4-bcc. The two copper(II) salts each gave rise to crystalline products containing the Cu(1,4-bcc) complex, both of which were characterised by X-ray crystallography. However, the composition of the crystals was different for the two salts, with the product derived from copper acetate giving crystals containing Cu(1,4-bcc) monomers, whereas the product resulting from copper chloride crystallised as a coordination polymer, $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$. This polymer differs from the related $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$ polymer in several ways. Firstly, the Cu(1,4-bcc) complexes are linked through square planar $CuCl_2(O)_2$ centres, in contrast to the tetrahedral $ZnCl_2(O)_2$ moieties. Secondly, two types of $CuCl_2(O)_2$ groups alternate within the polymer chain. In the first type, the copper atom is bonded to two C=O oxygen atoms of neighbouring Cu(1,4-bcc) groups, as observed for zinc in $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$. The second type, however, shows a much more unusual coordination mode in which the $CuCl_2(O)_2$ group is bonded to the carboxylate Cu–O oxygen atoms that are also directly bonded to copper in the two adjacent Cu(1,4-bcc) complexes. The coordination environments around the three different types of copper atoms in $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$ are illustrated in Fig. 3.

The copper 1,4-bcc complex in $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$ and Cu(1,4-bcc) is an isomer of the previously reported complex Cu(1,8-bcc),[5] which contains the two pendant carboxymethyl arms on opposite rather than adjacent nitrogen atoms within the cyclam ring. The UV-visible spectrum of [Cu(1,4-bcc)] exhibits one d–d band at 591 nm, which is comparable to other copper(II) complexes with N_4O_2 coordination spheres; Cu(1,8-bcc) ($\lambda_{max} = 565$ nm)[5] and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ($\lambda_{max} = ca.$ 600 nm).[4] Observation of the

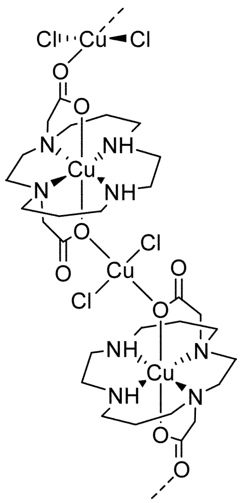

Fig. 3 Sketch of $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$.

$[M + H^+]$ ion in the high-resolution mass spectrum of Cu(1,4-bcc) with the isotope pattern expected for copper provided additional characterisation for both of these complexes.

The reaction of nickel(II) acetate with an aqueous solution of $H_2(1,4\text{-bcc})\cdot4HCl$ proceeded along similar lines to the copper complexes, with a colour change from light blue $Ni(O_2CCH_3)_2\cdot4H_2O$ to lavender Ni(1,4-bcc) at pH 5. This colour change is indicative of substitution of H_2O ligands in the nickel coordination sphere by amine ligands with a higher ligand field strength.[4] Ni(1,4-bcc) was characterised by elemental analysis, and UV-visible and IR spectroscopy. Two of the three d–d bands expected for octahedral nickel(II) complexes are observed at 562 and 358 nm.

The zinc complex of 1,4-bcc was obtained from heating zinc acetate with $H_2(1,4\text{-bcc})\cdot4HCl$ in aqueous solution (pH 5) at 70–80 °C for 4 h. Although crystals suitable for X-ray crystallography were not obtained for Zn(1,4-bcc), the $^{13}C\{^1H\}$ NMR spectrum obtained for this complex is similar to that observed for $[Co(1,4\text{-bcc})]^+$, exhibiting seven resonances for the 14 carbon atoms in the complex, indicative of C_2 symmetry and consistent with the same *trans*(O) geometry observed for the cobalt(III), cobalt(II) and copper(II) complexes. The resonances observed in the ^1H NMR spectrum of Zn(1,4-bcc) are very similar to those observed for $[Co(1,4\text{-bcc})]^+$ (number of peaks, coupling constants and chemical shifts). The NMR resonances for the zinc complex are generally shifted by a small amount to higher field, relative to the cobalt(III) complex. Zinc(II) is a larger ion bearing a lower formal charge than Co(III) and thus exerts less of an electron-withdrawing effect on the 1,4-bcc ligand. Overall, the similarities between the spectra of the zinc(II) and cobalt(III) 1,4-bcc complexes suggest that they are structurally analogous.

Coordination of chromium(III) by 1,4-bcc proved to be more difficult than for the other metals discussed above. The kinetic inertness and oxophilicity of the Cr(III) centre may act to retard the complexation reaction. The optimum conditions for the formation of $[Cr(1,4\text{-bcc})]ClO_4$ resulted from heating at reflux temperature for 20 h an aqueous solution (pH 4) of $H_2(1,4\text{-bcc})\cdot4HCl$ with excess $Cr(ClO_4)_3\cdot6H_2O$. The use of a stoichiometric amount of the chromium salt or a lower pH gave poorer yields. As the reaction progressed the colour changed from blue to pink.

The complex was characterised by high resolution mass spectrometry, and UV-visible and IR spectroscopy. X-ray crystallography demonstrated that the 1,4-bcc ligand coordinates to chromium with a *cis*(O)-N_4O_2 coordination sphere (Fig. 4), in contrast to the *trans*(O) arrangement observed or deduced for the cobalt(III), cobalt(II), zinc(II) and copper(II) metal complexes. The observation of two symmetrical d–d bands in the UV-visible spectrum of $[Cr(1,4\text{-bcc})]^+$ and two C=O stretching frequencies in the IR spectrum are consistent with this geometry.[6] The chromium complex exhibiting the *cis*(O) configuration is most likely the kinetic product resulting from coordination of chromium(III) by the 1,4-bcc ligand. The long reaction time and harsher conditions required for the formation of $[Cr(1,4\text{-bcc})]^+$ (relative to zinc(II), nickel(II) and copper(II)) are a consequence of the kinetic inertness characteristic of chromium(III).

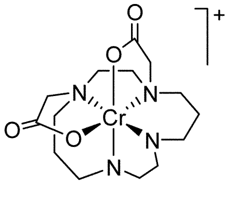

Fig. 4 Sketch of $[Cr(1,4\text{-bcc})]^+$.

X-Ray crystallography

Two of the complexes, Cu(1,4-bcc) and $[Cr(1,4\text{-bcc})]ClO_4$ crystallised with a molecule and half a molecule, respectively, of $HClO_4$ associated with each metal complex, and the formulae of the crystallographically determined species are $[Cu(1,4\text{-bcc})H]ClO_4$ and $[Cr(1,4\text{-bcc})H_{0.5}](ClO_4)_{1.5}$. The molecular structures of $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$, $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$ and the cation of $[Cr(1,4\text{-bcc})H_{0.5}](ClO_4)_{1.5}$ are shown in Fig. 5–7. The molecular structure of the copper complex $[Cu(1,4\text{-bcc})H]ClO_4$ which was also determined by X-ray crystallography is isostructural to the copper 1,4-bcc moiety in the coordination polymer $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$

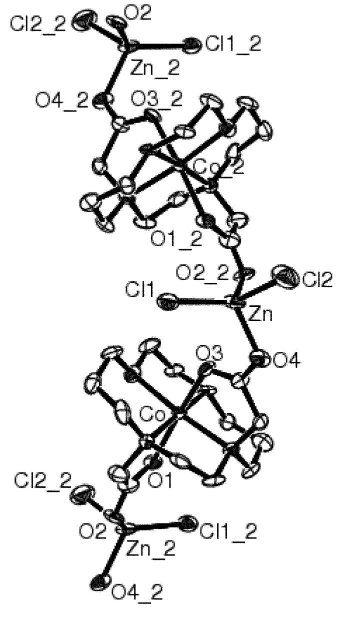

Fig. 5 Polymeric chain structure of $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$.

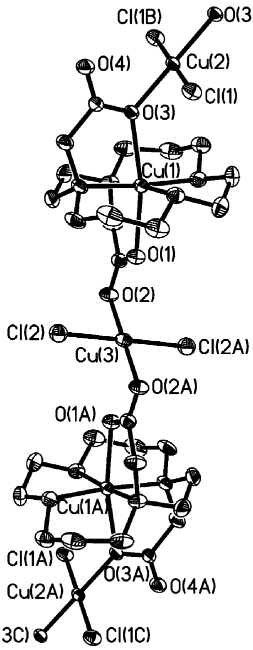

Fig. 6 Polymeric chain structure of $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$.

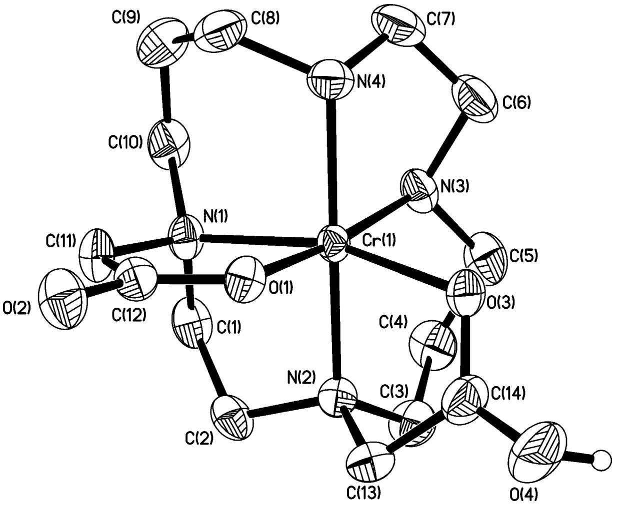

Fig. 7 Molecular structure of the cation of $[Cr(1,4\text{-bcc})H_{0.5}](ClO_4)_{1.5}$. The proton on O(4) has an occupancy of 0.5.

and is not shown as a separate figure. Crystal data for all four complexes, and significant bond lengths and angles together with those for the cobalt(III) cation $[Co(1,4\text{-bcc})]^{+1}$ are given in Tables 1 and 2. Two independent molecules occur in the unit cell for $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$ and thus two sets of data are given for this complex in Table 2.

The complexes $[Co(1,4\text{-bcc})]^+$, $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$, $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$ and $[Cu(1,4\text{-bcc})H]^+$ all contain the $[M(1,4\text{-bcc})]^{n+}$ ligand in the *trans*(O) configuration, in which the four nitrogen atoms of the cyclam ligand occupy equatorial sites, with the two pendant carboxylate oxygen atoms in the axial sites. A different geometry is observed for $[Cr(1,4\text{-bcc})]^+$ which exists in the *cis*(O) configuration, with the cyclam ligand folded and the two oxygen atoms occupying *cis* coordination sites. The four complexes with the *trans*(O) geometry have the *R*,*R*,*S*,*S* (or enantiomeric) configuration at the cyclam nitrogen atoms, with the six- and five-membered chelate rings in the chair and gauche conformations, respectively. Each complex has overall C_2 molecular symmetry, although this can only be observed in solution by NMR spectroscopy for the diamagnetic $[Co(1,4\text{-bcc})]^+$ complex.

In each of the five complexes reported here (including *cis*(O)-$[Cr(1,4\text{-bcc})]^+$) the metal-tertiary nitrogen distances (M–N1, M–N2) are longer than those to the secondary nitrogen atoms (M–N3, M–N4). Within the cyclam macrocycle, the N–M–N angles for the six-membered chelate rings (N2–M–N3, N1–M–N4) are a little larger than 90° (*ca.* 92–95°) while those for the five-membered chelate rings (N1–M–N2, N3–M–N4) are typically less than 90° (*ca.* 81–89°), typical of cyclam complexes. The N–M–O angles (five-membered chelate ring) range from *ca.* 78 to 81.5°, and are all smaller than the N–M–N angles (with the exception of the cobalt(III) complex) perhaps reflecting the reduced conformational flexibility arising from the sp^2 hybridised carboxylate carbon present in the ring. The exception arises for the complex containing the smallest metal ion, Co(III) in $[Co(1,4\text{-bcc})]^+$, for which the N–Co–O angles are close to 87°, comparable to the five-membered ring N–Co–N angles. All four of the *trans*(O) complexes show O–M–O angles reduced from 180°, ranging from 178.04(12)° for $[Co(1,4\text{-bcc})]^+$ to 162.59(6)° for Cu(1,4-bcc). The cobalt(III) complex which has the O–Co–O angle closest to 180° also contains the smallest metal ion in the series.

Ionic radii for the relevant ions with coordination number 6 are, in increasing order: Co^{3+} (low spin), 0.685 Å; Cr^{3+}, 0.755 Å; Co^{2+} (low spin), 0.79 Å; Cu^{2+}, 0.87 Å; Co^{2+} (high spin), 0.885 Å.[6] The average metal-oxygen distances follow this order, increasing from 1.890 Å for $[Co(1,4\text{-bcc})]^+$ to 2.379 Å for Cu(1,4-bcc). The order does not correlate so well for the M–N distances presumably due to the more constrained nature of the N donors in the macrocycle compared to the O donors of the pendant carboxylate groups. A direct comparison of the effect of oxidation state can be made by comparing the metal coordination spheres in the cobalt(III) and cobalt(II) complexes $[Co(1,4\text{-bcc})]^+$ and $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$, respectively. As expected for the larger Co(II) ion, the Co–N and Co–O distances are significantly longer in the Co(II) complex (Table 2). In the cobalt(III) complex, the Co–O distances are significantly shorter than the Co–N distances, whereas for the cobalt(II) complex the Co–N and Co–O bond lengths are similar. This lengthening of the axial Co–O bonds in the d^7 cobalt(II) complex may be indicative of a small Jahn–Teller distortion.

The two copper complexes $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$ and Cu(1,4-bcc) both contain the same copper(II) 1,4-bcc moiety. The Cu–N bond lengths and most of the bond angles are not significantly different between the two complexes. The Cu–O distances show some differences, with both of those observed for Cu(1,4-bcc) longer than those measured for $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$. This is most marked for Cu–O(3) which is 0.065 Å longer for the monomeric complex. In the coordination polymer, O(3) exists in a unique environment where it bridges between two copper atoms, six-coordinate copper in the 1,4-bcc complex, and four-coordinate copper in the square-planar copper chloride linkers. The two copper 1,4-bcc complexes can be compared to the structure of the isomeric Cu(1,8-bcc) complex, in which the Cu–N and Cu–O bonds average 2.054(5) and 2.263(3) Å, respectively.[5,7]

Table 1 Crystal data for $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n\cdot 2.5H_2O$, $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n\cdot 0.25MeOH\cdot H_2O$, $[Cu(1,4\text{-bcc})H]ClO_4$ and $[Cr(1,4\text{-bcc})H_{0.5}](ClO_4)_{1.5}\cdot EtOH$

	$\{[Co(1,4\text{-bcc})]ZnCl_2\}_n\cdot 2.5H_2O$	$\{[Cu(1,4\text{-bcc})]CuCl_2\}_n\cdot 0.25MeOH\cdot H_2O$	$[Cu(1,4\text{-bcc})H]ClO_4$	$[Cr(1,4\text{-bcc})H_{0.5}](ClO_4)_{1.5}\cdot EtOH$
Formula	$C_{14}H_{31}Cl_2CoN_4O_{6.5}Zn$	$C_{14.25}H_{29}Cl_2Cu_2N_4O_{5.25}$	$C_{14}H_{27}ClCuN_4O_8$	$C_{16}H_{32.5}Cl_{1.5}CrN_4O_{11}$
M	554.63	538.39	478.39	562.14
T/K	203(2)	203(2)	203(2)	203(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	8.2370(16)	8.2431(1)	10.6771(2)	11.7521(1)
b/Å	16.152(3)	9.3178(1)	13.7835(2)	11.9632(1)
c/Å	17.347(4)	14.9549(1)	13.7784(1)	16.8661(1)
α/°	90	78.162(1)	90	90
β/°	90.30(3)	80.574(1)	101.718(1)	104.373(1)
γ/°	90	73.851(1)	90	90
V/Å^3	2307.9(8)	1072.235(19)	1985.48(5)	2297.03(2)
Z	4	2	4	4
μ/mm^{-1}	2.029	2.266	1.284	0.728
Reflections collected	12546	10063	11814	13843
Independent reflections, R_{int}	6773, 0.0748	4298, 0.0199	4344, 0.0198	5121, 0.0348
Final R indices [$I > 2\sigma(I)$] $R1$, $wR2$	0.0941, 0.2207	0.0299, 0.0843	0.0388, 0.0932	0.0545, 0.1538
R indices (all data) $R1$, $wR2$	0.1164, 0.2371	0.0368, 0.0889	0.0502, 0.1014	0.0639, 0.1622

Table 2 Important bond lengths (Å) and angles (°) for $[Co(1,4\text{-bcc})]ClO_4$,[1] $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$, $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$, $[Cu(1,4\text{-bcc})H]ClO_4$ and $[Cr(1,4\text{-bcc})H_{0.5}](ClO_4)_{1.5}$

	$[Co(1,4\text{-bcc})]ClO_4$	$\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$		$\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$	$[Cu(1,4\text{-bcc})H]ClO_4$	$[Cr(1,4\text{-bcc})H_{0.5}](ClO_4)_{1.5}$
M–N1	1.974(4)	2.142(13)	2.129(12)	2.069(3)	2.063(2)	2.107(2)
M–N2	1.980(3)	2.160(13)	2.153(12)	2.115(2)	2.070(2)	2.096(2)
M–N3	1.926(4)	2.063(12)	2.072(12)	2.022(3)	2.005(3)	2.091(2)
M–N4	1.960(4)	2.081(12)	2.064(12)	2.035(3)	2.018(2)	2.085(3)
M–N (av.)	1.960	2.112	2.099	2.060	2.039	2.095
M–O1	1.892(3)	2.065(10)	2.120(10)	2.294(2)	2.329(2)	1.968(2)
M–O3	1.887(3)	2.119(10)	2.097(10)	2.351(2)	2.429(2)	1.965(2)
M–O (av.)	1.890	2.092	2.109	2.323	2.379	1.967
N1–M–N2	88.30(14)	86.0(5)	85.7(5)	86.95(11)	88.66(10)	86.71(10)
N2–M–N3	92.95(15)	95.1(5)	94.9(5)	95.32(11)	93.67(11)	94.97(10)
N3–M–N4	86.50(15)	85.3(5)	85.3(5)	85.71(11)	86.10(12)	81.01(11)
N4–M–N1	92.48(15)	94.2(5)	94.7(5)	92.52(11)	92.47(12)	91.87(10)
O1–M–N1	87.18(13)	81.4(4)	81.6(4)	80.97(8)	79.58(7)	81.13(8)[a]
O3–M–N2	87.11(13)	80.3(4)	81.6(4)	77.75(8)	78.09(7)	80.27(9)[b]
O1–M–O3	178.04(12)	170.8(5)	172.2(4)	168.32(7)	162.59(6)	87.85(8)

[a] Angle given is O3–M–N1. [b] Angle given is O1–M–N2.

In all three copper(II) complexes (two containing 1,4-bcc and one containing 1,8-bcc) the Cu–O bond lengths are significantly longer than the Cu–N bonds. This contrasts with the cobalt(III) and chromium(III) 1,4-bcc complexes in which the M–O bonds are markedly shorter than the M–N bonds, and is evidence for tetragonal elongation in the copper complexes resulting from Jahn–Teller distortions arising from the d^9 configuration.[6] The Cu–O bonds to the square-planar bridging copper atoms Cu(2) and Cu(3) in $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$ are significantly shorter than the Cu(1)–O bonds, indicative of both the lower coordination number and the square planar geometry which is not susceptible to Jahn–Teller distortion.

The *cis*(O) configuration observed for the $[Cr(1,4\text{-bcc})]ClO_4$ cation results in a folded cyclam macrocycle, which displays *R*,*S*,*R*,*R* (or enantiomeric) chirality at the nitrogen atoms in the racemic crystal. Although *trans*(O)-$[Co(1,4\text{-bcc})]^+$ and *cis*(O)-$[Cr(1,4\text{-bcc})]^+$ exhibit different geometries, the pattern of bond lengths is not markedly different (tertiary M–N longer than secondary M–N, M–O shorter than M–N) taking into account the smaller radius of the Co^{3+} compared to the Cr^{3+} ion.

Experimental

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM 400 spectrometer using D_2O as solvent and referenced to internal d_4-TSP (0.0 ppm). UV-visible spectra were recorded in water using a Shimadzu UV-2101 PC instrument. IR spectra were recorded as Nujol mulls between NaCl plates using a Perkin Elmer FT-IR Spectrum 1000 spectrometer. High resolution mass spectra (FAB$^+$) were recorded from a 3-nitrobenzyl alcohol matrix on a VG 70-SE mass spectrometer using argon gas. Elemental analyses were carried out by the Microanalytical Laboratory, University of Otago. $[Co(1,4\text{-bcc})]ClO_4$ was prepared as described in the literature.[1]

Syntheses

H_2(1,4-bcc)·4HCl. [Co(1,4-bcc)]ClO_4 (1.00 g, 2.12 mmol) and $CoCl_2\cdot6H_2O$ (0.50 g, 2.10 mmol) were dissolved in water (25 mL) in a round bottomed flask and the resulting red solution was deoxygenated by flushing with nitrogen and pumping under reduced pressure several times. The flask was fitted with a reflux condenser. Potassium cyanide (3.50 g, 53.75 mmol) was added to the mixture and the colour of the solution changed over a period of *ca.* 5 min from red to golden yellow. The solution was refluxed under nitrogen for 20 h, during which time the solution became colourless. After cooling the reaction mixture to room temperature the flask was opened to air. Concentrated HCl was carefully added dropwise to the reaction mixture in a well-ventilated fume hood (CAUTION: production of toxic HCN gas) until the mixture was acidic to litmus. The acidified mixture was diluted to 500 mL with H_2O and purified by ion-exchange chromatography on Dowex 50W-X2 resin (3 cm × 15 cm) in the fume hood. The desired product was observed as a narrow, pale-coloured band on the top of the ion-exchange column. The column was washed with water to remove anionic and neutral species, including $[Co(CN)_6]^{3-}$. Any remaining [Co(1,4-bcc)]$^+$ was eluted using 1.0 mol L^{-1} HCl, followed by 2.0 mol L^{-1} HCl to remove any remaining $[Co(H_2O)_6]^{2+}$. Finally, 6.0 mol L^{-1} HCl was used to remove the desired product, H_2(1,4-bcc)·4HCl. The solution was concentrated to *ca.* 10 mL at which point white solid began to precipitate. Ethanol (20 mL) was added to the concentrated solution which was refrigerated overnight. The product was collected by filtration, washed with ethanol and diethyl ether and dried in air (0.638 g, 63%). Found: C, 35.32; H, 7.10; N, 11.88. $C_{14}H_{28}N_4O_4\cdot4HCl\cdot H_2O$ requires: C, 35.01; H, 7.14; N, 11.67%; δ_H (D_2O) 3.56 (4 H, s, $\mathrm{C}H_2\mathrm{CO}_2$), 3.38 (4 H, s, $\mathrm{RNC}H_2\mathrm{C}H_2\mathrm{NR}$) 3.32 (4 H, t, $\mathrm{RNC}H_2\mathrm{CH_2CH_2NH}$), 2.92 (4 H, t, $\mathrm{RNCH_2CH_2C}H_2\mathrm{NH}$), 2.85 (4 H, s, $\mathrm{HNC}H_2\mathrm{C}H_2\mathrm{NH}$), 1.97 (4 H, q, $\mathrm{RNCH_2C}H_2\mathrm{CH_2NH}$); δ_C (D_2O) 177.96 (CO), 59.63 ($C\mathrm{H_2CO_2}$), 58.98, 57.28 ($C\mathrm{H_2NR}C\mathrm{H_2}$), 51.14, 47.01 ($C\mathrm{H_2NH}C\mathrm{H_2}$), 24.93 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$).

$\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$. [Co(1,4-bcc)]$ClO_4$ (0.200 g, 0.42 mmol) was dissolved in 1.0 mol L^{-1} HCl (2.0 mL) in a vial. A piece of amalgamated zinc was added to the solution and the vial was sealed. After standing at RT for 48 h the desired product was observed as yellow crystals on the surface of the zinc amalgam. The crystals were removed, washed under nitrogen with ethanol followed by diethyl ether, and dried under N_2. Found: C, 28.70; H, 5.40; N, 9.52. $C_{14}H_{26}CoN_4O_4\cdot ZnCl_2\cdot4H_2O$ requires: C, 28.91; H, 5.89; N, 9.63%.

$\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$. H_2(1,4-bcc)·4HCl (0.100 g, 0.22 mmol) was dissolved in water (10 mL) and $CuCl_2\cdot2H_2O$ (0.034 g, 0.20 mmol) was added, immediately giving rise to a dark blue solution. The solution was adjusted to pH 5 by addition of sufficient 1.0 mol L^{-1} KOH, and left to stand overnight. After removal of the solvent under reduced pressure the residue was dissolved in methanol, giving a blue solution, filtered to remove KCl, and further purified by gel-filtration on Sephadex LH-20 resin. The blue band collected from the gel-filtration column was evaporated to dryness, and the product washed with acetone, producing a microcrystalline blue solid which was washed with diethyl ether and air-dried (0.045 g, 44%). *m/z* (FAB^+) 378.13298 (M + H^+). $C_{14}H_{27}CuN_4O_4$ requires 378.13283.

Cu(1,4-bcc). H_2(1,4-bcc)·4HCl (0.100 g, 0.22 mmol) was dissolved in water (10 mL) and $Cu_2(OAc)_4(H_2O)_2$ (0.044 g, 0.11 mmol) was added, immediately giving rise to a dark blue solution. The solution was adjusted to pH 5 by addition of 1.0 mol L^{-1} KOH, and left to stand overnight. The product was isolated and purified as described for $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$ to give a microcrystalline purple solid. *m/z* (FAB^+) 378.13221 (M + H^+). $C_{14}H_{27}CuN_4O_4$ requires 378.13283.

Ni(1,4-bcc). H_2(1,4-bcc)·4HCl (0.100 g, 0.22 mmol) was dissolved in water (10 mL) and $Ni(OAc)_2\cdot4H_2O$ (0.050 g, 0.20 mmol) was added. The initial slurry of aqua-coloured solid was adjusted to pH 5 by addition of 1.0 mol L^{-1} KOH, causing the nickel salt to dissolve giving a lavender solution which was left to stand overnight at RT. After removal of the solvent under reduced pressure the residue was dissolved in methanol, and filtered to remove KCl. This process was repeated, and the solution then further purified by gel-filtration on Sephadex LH-20 resin. The solvent was removed from the lavender band collected from the gel-filtration column, and the product washed with acetone, producing a lavender coloured powder which was washed with diethyl ether and air-dried (0.043 g, 53%). Found: C, 41.31; H, 7.61; N, 13.70. $C_{14}H_{26}N_4NiO_4\cdot2H_2O$ requires: C, 41.10; H, 7.39; N, 13.69%.

Zn(1,4-bcc). H_2(1,4-bcc)·4HCl (0.100 g, 0.22 mmol) was dissolved in water (10 mL) and $Zn(OAc)_2\cdot2H_2O$ (0.051 g, 0.22 mmol) was added. The resulting solution was heated at 70–80 °C for 4 h. The solution was then concentrated to give a colourless residue which was triturated under acetone to give an extremely hygroscopic white solid. *m/z* (FAB^+) 379.13133 (M + H^+). $C_{14}H_{27}N_4O_4Zn$ requires 379.13238; δ_H (D_2O) 3.69, 2.98 (4 H, ABq, ^2J = 18.3 Hz, $\mathrm{C}H_2\mathrm{CO}_2$) 3.11 (4 H, m, $\mathrm{RNC}H_2\mathrm{C}H_2\mathrm{NR}$), 3.01 (2 H, dd, $\mathrm{RNCH_2CH_2C}H_2\mathrm{NH}$), 2.90 (2 H, dd, $\mathrm{RNCH_2CH_2C}H_2\mathrm{NH}$), 2.81 (2 H, ddd, $\mathrm{HNC}H_2\mathrm{C}H_2\mathrm{NH}$), 2.70 (4 H, m, $\mathrm{RNC}H_2\mathrm{CH_2CH_2NH}$), 2.46 (2 H, m, $\mathrm{HNC}H_2\mathrm{C}H_2\mathrm{NH}$), 1.80 (4 H, m, $\mathrm{RNCH_2C}H_2\mathrm{CH_2NH}$); δ_C (D_2O) 181.88 (CO), 61.24 ($\mathrm{RN}C\mathrm{H_2}C\mathrm{H_2NR}$), 60.83 ($C\mathrm{H_2CO_2}$), 59.41 ($\mathrm{HN}C\mathrm{H_2}C\mathrm{H_2NH}$), 51.55 ($\mathrm{RNCH_2CH_2}C\mathrm{H_2NH}$), 50.86 ($\mathrm{RN}C\mathrm{H_2CH_2CH_2NH}$), 28.32 ($\mathrm{RNCH_2}C\mathrm{H_2CH_2NH}$).

[Cr(1,4-bcc)]ClO_4. H_2(1,4-bcc)·4HCl (0.100 g, 0.22 mmol) was dissolved in water (6 mL) and $Cr(ClO_4)_3\cdot6H_2O$ (0.200 g, 0.44 mmol) was added. The solution was adjusted to pH 4 using 1.0 mol L^{-1} NaOH and heated at reflux for 23 h. The reaction mixture was diluted to *ca.* 200 mL and loaded onto a Sephadex-SP C-25 ion-exchange column (2 cm × 15 cm). After washing the column with water (100 mL), elution with 0.1 mol L^{-1} $NaClO_4$ produced a pink band containing the desired product, while some blue material, $[Cr(H_2O)_6]^{3+}$, remained at the origin. The band containing the desired product was concentrated to a small volume and ethanol was added, resulting in precipitation of the product as a microcrystalline solid (0.043 g, 38%). *m/z* (FAB^+) 366.13631 (M^+). $C_{14}H_{26}CrN_4O_4$ requires 366.13595.

X-Ray crystallography

Data were collected at 203 K on a Bruker SMART diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS 97)[8] and refined on F^2 by full matrix least squares (SHELXL 97).[8] Hydrogen atoms attached to the heteroatoms O4, N3 and N4 were located *via* the difference map and refined using a riding model. All other hydrogen atoms except those on some solvent water molecules were placed in calculated positions and refined using a riding model. All non-hydrogen and non-solvent atoms were refined anisotropically. In one of the two independent molecules of $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$ one of the chlorine atoms attached to Zn appears to be present 0.25, with an H_2O ligand the remaining 0.75. This is balanced in the solvent spaces where there is a Cl^- (0.75) and a H_2O (0.25) to maintain the overall formulation. For $\{[Cu(1,4\text{-bcc})]CuCl_2\}_n$ diffuse solvent was modelled as one half of a methanol molecule and two water molecules per unit cell. The C–O bond for the partially occupied methanol molecule was restrained to be 1.5 Å in length. For $[Cu(1,4\text{-bcc})H]ClO_4$, the occupancy of the perchlorate anion was evenly disordered over two sites and the Cl–O bond lengths were constrained to be equal. The proton associated with the $HClO_4$ was located on O(4) in each of $[Cu(1,4\text{-bcc})H]ClO_4$ and $[Cr(1,4\text{-bcc})H_{0.5}](ClO_4)_{1.5}$. For $[Cr(1,4\text{-bcc})H_{0.5}](ClO_4)_{1.5}$ diffuse solvent equivalent to four ethanol molecules per unit cell was treated in the manner described by van der Sluis and Spek.[9] The final refinement statistics are presented in Table 1.

The molecular arrangement in $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$ approximates to that in an orthorhombic cell under space group $P2_12_12$, however the β angle of 90.30(3)° is significantly different from 90.0°, the R_{merge} intensity statistics were consistent with Laue group $2/m$ but not mmm, and there were no systematic absences along $h00$. Hence the original $P2_1$ space group has been retained.

CCDC reference numbers 283173–283176.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512798j

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