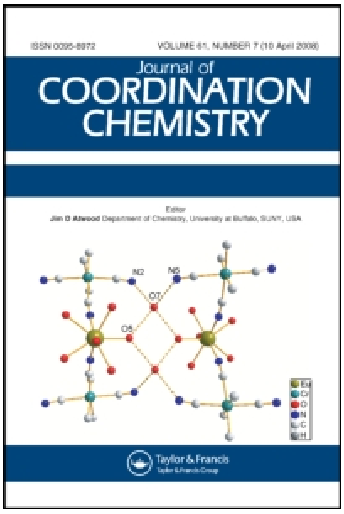

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Ligand assembly and metal ion complexation: syntheses and X-ray structures of Ni(II) and Cu(II) benzoate and 4-*tert*-butylbenzoate complexes of cyclam

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LIGAND ASSEMBLY AND METAL ION COMPLEXATION: SYNTHESES AND X-RAY STRUCTURES OF Ni(II) AND Cu(II) BENZOATE AND 4-*TERT*-BUTYLBENZOATE COMPLEXES OF CYCLAM

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The syntheses and X-ray structures of *trans*-[Ni(*O*-benzoato)$_2$(cyclam)], *trans*-[Cu(H$_2$O)$_2$(cyclam)]-(benzoate)$_2\cdot 2H_2O$ and *trans*-[Cu(H$_2$O)$_2$(cyclam)](4-*t*-butyl-benzoate)$_2$ (where cyclam is 1,4,8,11-tetra-azacyclotetradecane) are described. The nickel complex has a tetragonally distorted octahedral coordination geometry with cyclam occupying the equatorial plane in a stable *trans*-III arrangement, with benzoate ligands filling the axial positions. The structure closely resembles the arrangement in the previously described hydrogen-bonded (metal-free) ligand assembly [(cyclamH$_2$)$\cdot$(4-*t*-butyl benzoate)$_2$]$\cdot$2(benzoic acid) if the latter benzoic acid moieties, which do not interact directly with the cyclam moiety, are ignored. The 2 : 1 fragment thus may be viewed as a ligand assembly "preorganized" for nickel ion complexation. In contrast to the nickel structure, the two *trans*-axial sites in both copper structures are occupied by aqua rather than *O*-carboxylate ligands. Although they do not form part of the inner coordination sphere in either complex, the two carboxylate anions remain hydrogen bound to the (coordinated) cyclam ligand, with the mode of packing being generally similar in each complex.

Keywords: Nickel(II); Copper(II); Cyclam; X-ray; Ligand assembly

INTRODUCTION

In one of our laboratories we have been interested in investigating the influence of ligand assembly on metal-ion complexation in solution and have identified behaviour that we have termed the "assembly effect" [1,2]. Such an effect is postulated to occur when individual ligand components of a coordination sphere self-assemble in a host–guest manner in solution such that the resultant assembly forms the main species

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present in equilibrium with its corresponding metal complex. We have documented the formation of assemblies of this type for a range of aliphatic amines and aromatic carboxylic acids in (non-aqueous) solution as well as in the solid state [1–5].

One interest in these studies was to define, for a given carboxylic acid, the factors influencing the observed stoichiometries of the resulting assemblies. It was also of interest to determine whether the amine : acid ratio found for particular host–guest assemblies in solution is maintained in the solid state as well as to observe whether the composition of the assembly formed corresponded to that of a potential metal–ligand coordination sphere. A number of such assemblies have now been isolated and their X-ray structures [1,3,5] (and neutron diffraction structures in two cases) [1,3] have been determined.

In one investigation [1] the host–guest interaction between 1,4,8,11-tetraazacyclotetradecane (cyclam) and 4-*t*-butylbenzoic acid was investigated by NMR titration, calorimetry, X-ray diffraction, neutron diffraction and semi-empirical MO calculations. When the changes in the chemical shifts in the ^{1}H and ^{13}C NMR spectra were monitored during the incremental addition of 4-*t*-butylbenzoic acid to cyclam in $CDCl_3$, sharp end points were observed corresponding to 2 : 1 (carboxylic acid : cyclam) complex formation in each case. A similar result was obtained using titration calorimetry in chloroform. Slow crystallization from methanol containing cyclam and 4-*t*-butylbenzoic acid in a 1 : 2 ratio yielded a crystalline 1 : 4 (cyclam : 4-*t*-butylbenzoic acid) complex; however, the structure determination showed that only two 4-*t*-butylbenzoate ions interact directly with cyclam (the carboxylic protons having been transferred to individual amine groups on cyclam so that "intermolecular zwitterions" are formed). The two additional 4-*t*-butylbenzoic acid moieties present are not directly associated with the cyclam ring – each is hydrogen bonded to an oxygen atom on different 4-*t*-butylbenzoate guests. The guest carboxylate anions interact with the (doubly protonated) cyclam via a network of hydrogen bonds (three per guest) such that all six amine hydrogens associated with the macrocyclic dication are involved. The carboxylate anions are orientated axially above and below the N_4-plane of the macrocycle; the product was proposed to be a system pre-assembled for (octahedral) metal-ion complexation [1].

EXPERIMENTAL

All chemicals and solvents employed in the study were of analytical grade where available. Microanalyses were performed using a CHNS Carlo Erba EA 1108 Elemental Analyser.

Syntheses

Trans-[bis(benzoato)(1,4,8,11-tetraazacyclotetradecane)nickel(II)]

To a solution of benzoic acid (15.15 g, 124 mmol) in hot methanol (174 cm^3) was added solid $NiCO_3 \cong 2Ni(OH)_2 \cong 4H_2O$ (12.25 g, 35 mmol). The mixture was stirred and heated for 24 h, during which the volume was reduced to 80 cm^3. The solution was filtered and set aside at 3°C. The yellow-green *bis*(*benzoato*)*nickel*(*II*) solid that formed was removed by filtration, washed with methanol and dried over silica gel. Anal. Calcd. for $C_{14}H_{10}NiO_4$(%): C, 55.9; H, 3.4. Found: C, 54.2; H, 3.6. A stoichiometric amount of this intermediate product and 1,4,8,11-tetraazacyclotetradecane were dissolved in hot methanol. The hot solution was then reduced in volume and filtered. Purple crystals of the product formed on cooling. Yield, 40%. Anal. Calcd. for $C_{24}H_{34}NiN_4O_4$(%): C, 57.5; H, 6.8; N, 11.2. Found: C, 57.6; H, 6.7; N, 11.5.

Trans-[diaqua(1,4,8,11-tetraazacyclotetradecane)copper(II)] benzoate dihydrate and trans-[diaqua(1,4,8,11-tetraazacyclotetradecane)copper(II)] 4-t-butylbenzoate dihydrate

The bis(benzoato)copper(II) intermediate was synthesized from $CuCO_3 \cong Cu(OH)_2 \cong H_2O$ and benzoic acid by using a procedure similar to the nickel(II) analogue described above. Anal. Calcd. for $C_{14}H_{10}CuO_4$(%): C, 55.0; H, 3.3. Found: C, 55.1; H, 3.3. Reaction of stoichiometric amounts of this solid and 1,4,8,11-tetraazacyclotetradecane in hot methanol resulted in bluish-purple crystals of the desired product in 40% yield. These were used directly for the X-ray analysis. *trans*-[Diaqua(1,4,8,11-tetraazacyclotetradecane)copper(II)] *t*-butylbenzoate was prepared [from bis(*t*-butylbenzoate)copper(II)] by an identical procedure to that described above and used directly for the X-ray structure analysis.

Structure Determinations

Unique room-temperature (*ca.* 295 K) single-counter diffractometer data sets were measured ($2\theta_{max}$ as specified; monochromatic Mo Kα radiation, $\lambda = 0.7107$ Å) yielding N unique reflections, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinements after Gaussian absorption corrections. Anisotropic displacement parameter forms were refined for both structures, together with $(x, y, z, U_{iso})_H$ for the nickel complex; for the copper complex the latter were constrained at estimates. Conventional residuals R, R_w on $|F|$ are cited at convergence. Computation used the Xtal 3.2 program system [6], employing neutral atom complex scattering factors. Pertinent results are given below and in Tables I and II and Figs. 1 and 2, the latter showing 20% displacement amplitude ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å; *cif* depositions have been lodged with the Cambridge Crystallographic Data Centre, CCDC 188536–188538.

Crystal/Refinement Data

Ni(*benzoate*)$_2 \cong$ *cyclam* $\equiv$ *trans*-[Ni(*O*-benzoato)$_2$(cyclam)] $\equiv C_{24}H_{34}N_4NiO_4, M = 501.3$. Orthorhombic, space group *Pbca* (D_{2h}^{15}, No. 61), $a = 18.034(10)$, $b = 12.981(2)$, $c = 10.318(3)$ Å, $V = 2415$ Å^3. D_c $(Z = 4) = 1.37_8$ g cm^{-3}. $\mu_{Mo} = 8.4$ cm^{-1}; specimen: $0.92 \times 0.34 \times 0.90$ mm; $A^*_{min, max} = 1.29$, 1.53. $2\theta_{max} = 65°$; $N = 4286$, $N_o = 2480$; $R = 0.035$, $R_w = 0.039$. $|\Delta\rho_{max}| = 0.3_4$ e Å^{-3}.

Cu(*benzoate*)$_2 \cong$ *cyclam* $\cong 4H_2O \equiv$ *trans*-[Cu(H$_2$O)$_2$(cyclam)](benzoate)$_2 \cdot 2H_2O \equiv C_{24}H_{42}CuN_4O_8$, $M = 578.2$. Triclinic, space group $P\bar{1}$ (C_i^1, No.2), $a = 10.951(2)$, $b = 9.142(2)$, $c = 7.136(2)$ Å, $\alpha = 96.14(2)$, $\beta = 96.58(2)$, $\gamma = 90.69(1)°$, $V = 705._4$ Å^3. D_c $(Z = 1) = 1.36_1$ g cm^{-3}. $\mu_{Mo} = 8.3$ cm^{-1}; specimen: $0.11 \times 0.25 \times 0.28$; $A^*_{min, max} = 1.09$, 1.17. $2\theta_{max} = 50°$; $N = 2229$, $N_o = 1759$; $R = 0.071$, R_w 0.078. $|\Delta\rho_{max}| = 0.5_6$ e Å^{-3}.

Comment The latter determination is less than ideal in at least two major ways: (a) Crystals are fibrous; the faces of individual specimens are not smooth but ridged,

TABLE I Selected inter-atomic distances (Å) and bond angles (°) for [Ni(O-benzoato)$_2$(cyclam)]

Ni–N(1)	2.074(2)
Ni–N(5)	2.052(2)
Ni–O(11)	2.126(2)
C(111)–O(11)	1.251(2)
C(111)–O(12)	1.234(3)
O(12) $\cdots$ N(1)	2.917(3)
O(12) $\cdots$ H(1)	2.07(2)
O(11)–Ni–N(1)	93.71(6)
O(11)–Ni–N(5)	89.49(7)
N(1)–Ni–N(5)	94.70(7)
Ni–O(11)–C(111)	131.5(1)
O(11)–C(111)–C(11)	116.2(2)
O(12)–C(111)–C(11)	118.1(2)
O(11)–C(111)–O(12)	125.7(2)

The interplanar dihedral between the C_6 aromatic plane and the CCO_2 carboxylate plane is 20.44(9)°, these two planes having dihedral angles of 72.48(7) and 81.02(7)° to the N_4 plane. Torsion angles around the ligand, commencing with the N(1)–C(2) bond are −179.6(2), −71.5(3), 69.8(3), −178.2(2), 170.4(2), −55.4(3) and −168.3(2)°.

TABLE II Selected inter-atomic distances (Å) and bond angle (°) for *trans*-[Cu(H$_2$O)$_2$(cyclam)]$^{2+}$[a]

Cu–N(1)	1.997(6), 2.016(2)
Cu–N(5)	2.009(5), 2.006(2)
Cu–O(1)	2.471(4), 2.551(3)
O(1)–Cu–N(1)	90.2(2), 91.6(1)
O(1)–Cu–N(5)	90.9(2), 89.4(1)
N(1)–Cu–N(5)	94.3(2), 94.2(1)

[a] The two values in each entry are for benzoate and 4-*t*-butyl-benzoate counterparts respectively.

Torsion angles around the ligand, commencing at the N(1)–C(2) bond are 177.8(7), −65(1), 68.3(9), 179.2(6), 167.6(6), −53.3(7), 170.9(7)° (benzoate); 178.5(4), −68.0(4), 71.3(4), 176.8(3), 168.6(3), −53.5(3) and 171.2(3)° (4-*t*-butyl-benzoate). CCO_2/C_6 interplanar dihedral angles are 15.2(4) and 5.9(2)° respectively.

in keeping with "fibrous" cleavage, and achievement of usefully diffracting specimens was attained only with some difficulty. (b) We believe the true unit cell is a superlattice achieved by a doubling of a; this was evident in the room-temperature data, but the additional reflections were very weak and made no useful contribution to meaningful refinement of the structure. Prior to submission for publication, with the advent of a low-temperature CCD facility, a new data set was obtained at *ca.* 150 K using the doubled cell. At this temperature the rather large displacement envelopes (most notably evident on the aromatic ring) were resolved into numerous components, again with uncongenial refinement behaviour. Despite its deficiencies, the original determination using sub-cell data is recorded, hydrogen atoms being located and the salient features of the structure described; derivative geometries should be treated circumspectly.

Cu(4-t-butyl-benzoate)$_2$ $\cong$ cyclam $\cong$ 2H$_2$O $\equiv$ *trans*-[Cu(H$_2$O)$_2$(cyclam)](4-*t*-butyl-benzoate)$_2$ $\cong$ 2H$_2$O $\equiv$ $C_{32}H_{54}CuN_4O_6$, $M = 654.4$. Triclinic, space group $P\bar{1}$, $a = 13.750(8)$, $b = 9.114(4)$, $c = 7.143(5)$ Å, $\alpha = 87.06(5)$, $\beta = 79.14(5)$, $\gamma = 86.04(8)°$, $V = 876._3$ Å^3. $D_c(Z = 1) = 1.24_0$ g cm^{-3}. $\mu_{Mo} = 6.7$ cm^{-1}; specimen: $0.05 \times 0.30 \times 0.60$ mm;

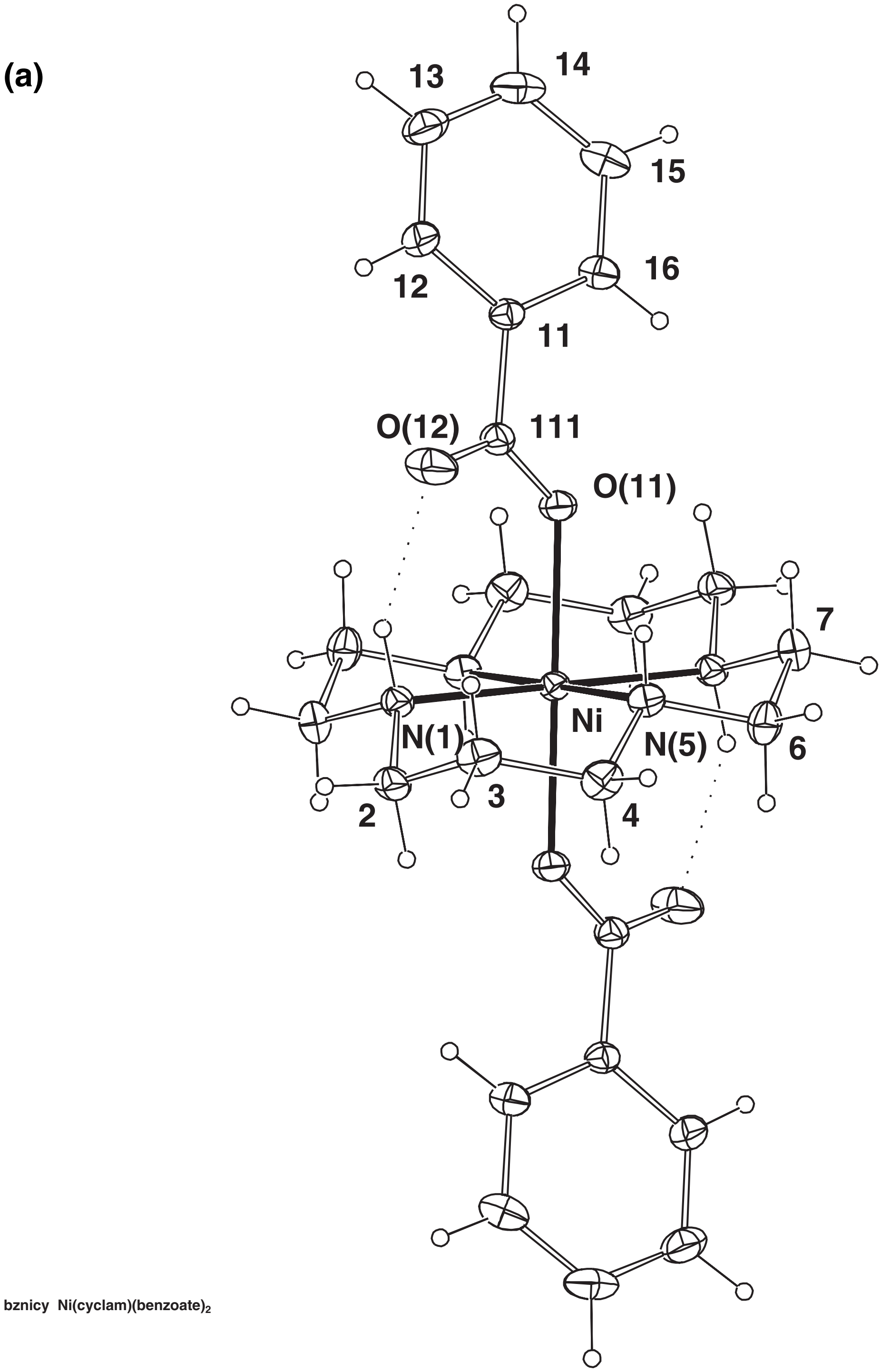

FIGURE 1 (a) Projection of the centrosymmetric molecule of *trans*-[Ni(*O*-benzoato)$_2$(cyclam)]; (b) A similar projection of the 1 : 2 host–guest adduct [(cyclamH$_2$) · (4-*t*-butyl-benzoate)$_2$] [3] (see text). (*continued overleaf*)

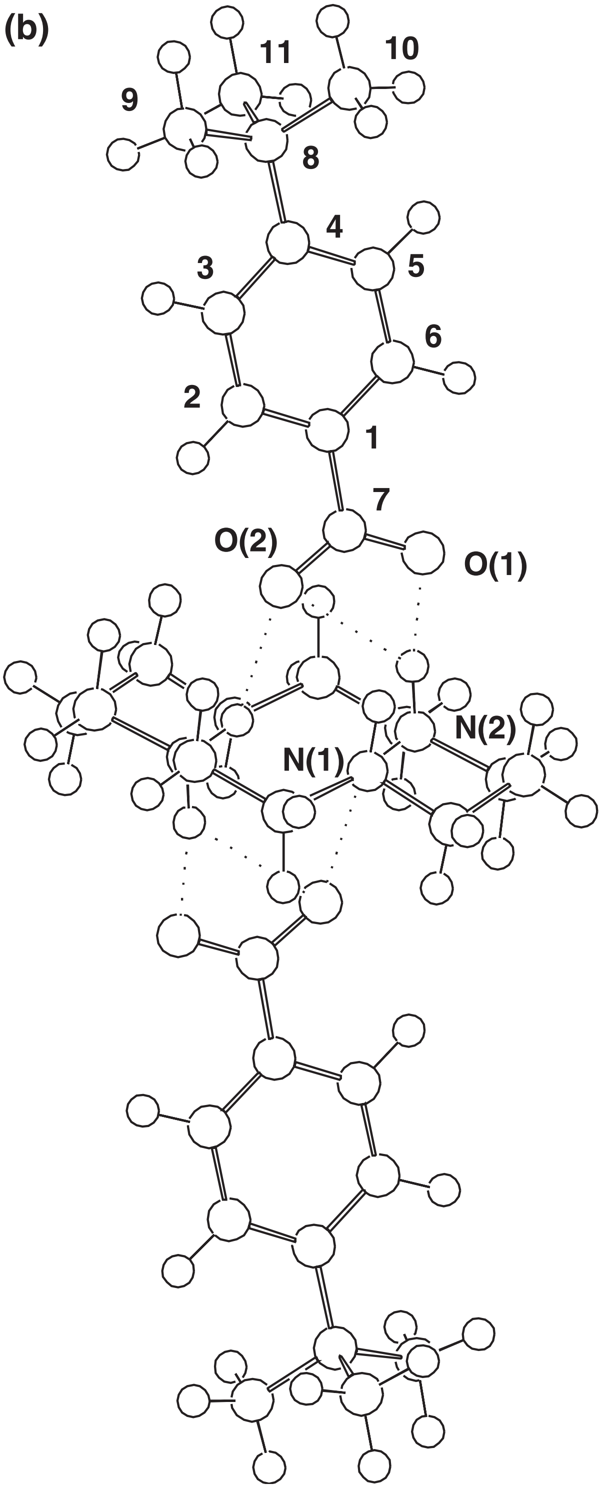

FIGURE 1 Continued.

$A^*_{\mathrm{min,max}} = 1.03$, 1.19. $2\theta_{\mathrm{max}} = 50°$; $N = 3085$, $N_{\mathrm{o}} = 2539$; $R = 0.039$, $R_{\mathrm{w}} = 0.040$; $|\Delta\rho_{\mathrm{max}}| = 0.26(3)\,\mathrm{e\,Å^{-3}}$.

Variata The *t*-butyl group was modelled as rotationally disordered over two sets of sites, occupancies refining to 0.56(2) and complement. $(x, y, z, U_{\mathrm{iso}})_{\mathrm{H}}$ were refined for all except the *t*-butyl hydrogen atoms.

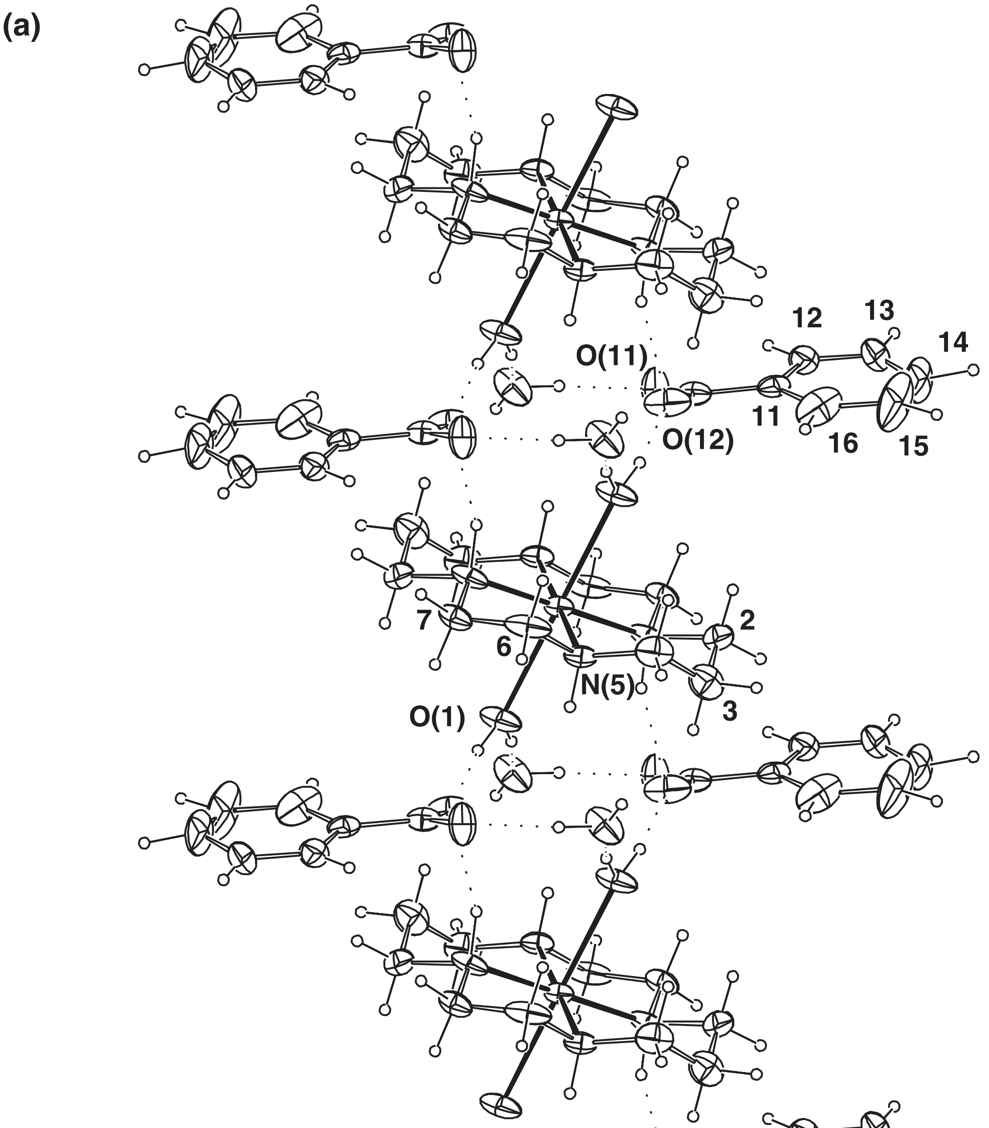

FIGURE 2 (a) A column of the hydrogen-bonded components of the 1 : 1 copper(II) benzoate : cyclam tetrahydrate, *trans*-$[\mathrm{Cu(H_2O)_2(cyclam)}](\mathrm{benzoate})_2 \cdot 2\mathrm{H_2O}$, crystallographic *c* lying vertically in the page; (b) *trans*-$[\mathrm{Cu(H_2O)_2(cyclam)}](4\text{-}t\text{-butyl-benzoate})_2$ projected similarly. (*continued overleaf*)

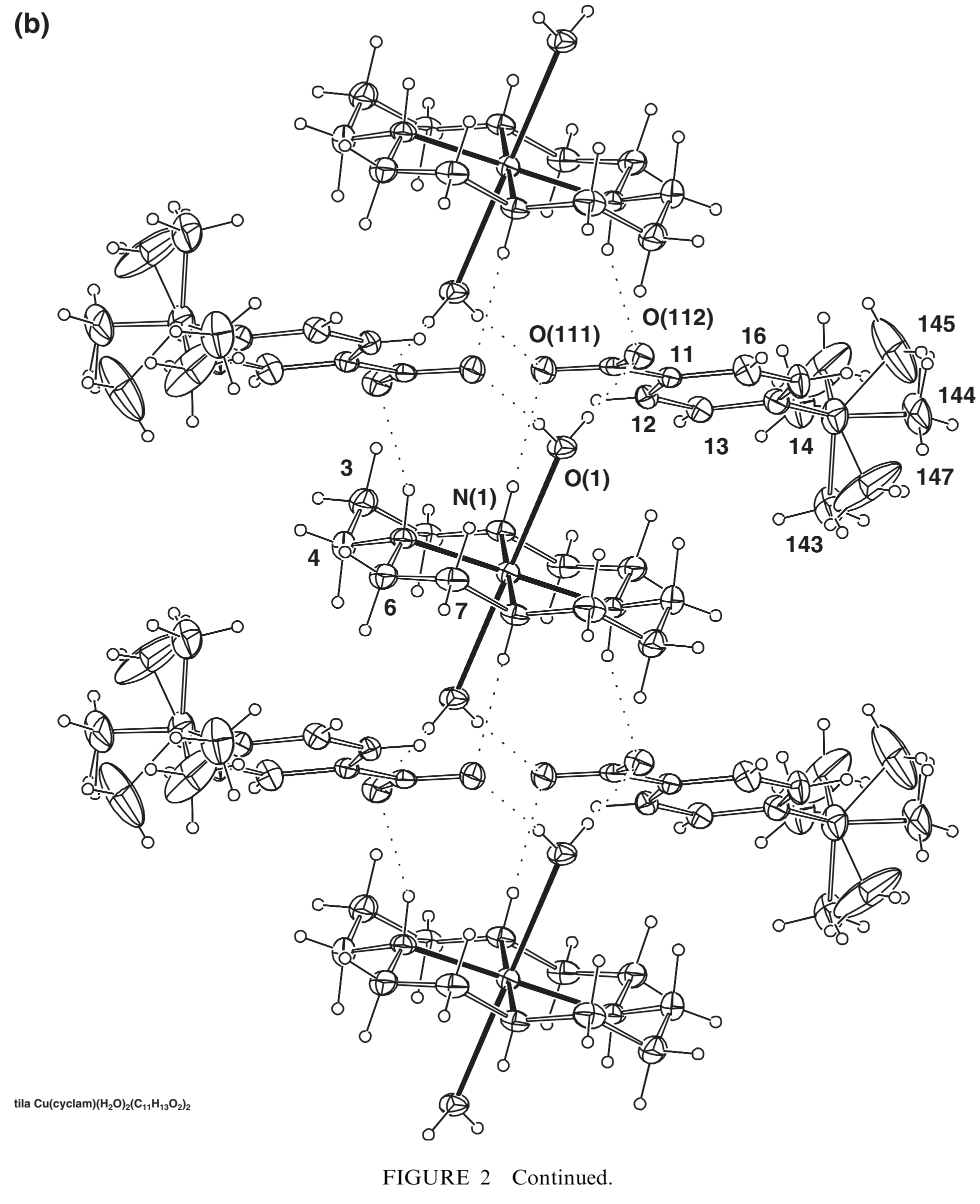

FIGURE 2 Continued.

RESULTS AND DISCUSSION

As mentioned in the Introduction, solution (NMR, calorimetric) studies showed that the assembly between 4-*t*-butylbenzoic acid and cyclam in chloroform [1] (and in 95% methanol) [2] has a 2 : 1 stoichiometry. In view of this result, it was of interest to determine whether such a ligand assembly could be employed as a metal coordination shell for metals capable of achieving six-coordination such as nickel(II) and copper(II). In this context nickel(II) and copper(II) complexes incorporating cyclam and benzoate or 4-*t*-butylbenzoate anions were successfully synthesized by reaction of the corresponding metal benzoate (or 4-*t*-benzoate) with cyclam in methanol. Each of the products had the expected 2 : 1 : 1 ratio of carboxylate anion to cyclam to metal ion. While the nickel complex was anhydrous, the copper complexes contained four and two water molecules, respectively (see below). The visible spectrum of the purple nickel complex in methanol yielded absorptions at 522, 635, 721, 873 and ~975(sh) nm in accordance with the coordination geometry being tetragonally distorted octahedral. Each of the copper complexes yielded a broad absorption in the visible region that was, however, of little use for structure assignment. In order to obtain detail of their solid-state coordination behaviour, each of the above complexes was subjected to single crystal X-ray analysis.

Crystal Structures

The structures of "cyclam" complexes of numerous nickel(II) and copper(II) salts have now been described. The disposition of the ligands about the divalent metal atom may entail the four nitrogen atoms coordinating in a planar array, sometimes with coincidence of the metal atom with a symmetry element. The coordination number of the metal atom may be lifted to six by the approach of one or two other ligands to the *trans*-unidentate sites to either side of the plane, resulting in electronic consequences within the metal configuration. On occasion, particularly in the presence of chelating systems, these may occupy a pair of *cis*-sites in the coordination sphere, entailing conformational adaptation by the cyclam; this form is also observed on occasion with unidentate ligands, most notably perhaps in *cis*-$[Ni(H_2O)_2(cyclam)]Cl_2 \cdot 2H_2O$ [7]. A critical dependence on the interplay between conformational, ligand field, hydration and lattice energies, as well as relative acid/base characteristics is evidenced in the record of a corresponding higher hydrate as *trans*-$[Ni(H_2O)_2(cyclam)]Cl_2 \cdot 4H_2O$ [8], while the anhydrous $[NiCl_2(cyclam)]$ [9] is also trans. In contrast, the iodide has been described as $[Ni(cyclam)]I_2$, containing (planar) four-coordinate nickel [10].

The present nickel complex is consistent in terms of stoichiometry with the formulation [Ni(*O*-benzoate)$_2$(cyclam)] (anhydrous), the stereochemistry being trans by virtue of the metal atom being disposed on a crystallographic centre of symmetry, in orthorhombic space group *Pbca*. Relevant geometries are presented in Table I, the present molecule being depicted in Fig. 1, with the uncoordinated carboxylate oxygen hydrogen bonded intramolecularly to one of the amine hydrogen atoms, Ni–N to the latter being perceptibly longer than its counterpart. The cyclam is present in its stable *trans*-III configuration [11].

Recent parallel studies have reported the structural characterization of a number of similar adducts of anions of which the present benzoate may be regarded as the parent [12]. In the majority of these, the nickel atom lies on an inversion centre, with *trans*-unidentate *O*-benzoate components bound to the metal and the uncoordinated oxygens hydrogen bonded to two of the cyclam amine hydrogens; in a number of cases, ring substituents give rise to more extended interactions between [Ni(*O*-benzoate)$_2$(cyclam)] components. The geometries about the metal atom in all such cases are similar to the present complex. In a more restricted number of cases here and elsewhere [13], water solvent molecules are competitive in a donor capacity with the carboxylate, the latter now excluded from the coordination sphere as counterions to $[Ni(H_2O)_2(cyclam)]^{2+}$ cations.

In the recorded complexes of copper(II) salts with cyclam, there appear to be no examples as yet of cis-octahedral systems, perhaps unsurprisingly, the types recorded varying between planar four-coordinate, five-coordinate and six-coordinate (with the bonds to the axial ligands in the latter being inevitably both longer and variable in length). Apart from a methoxycarbonate/perchlorate salt in which the two carboxyl oxygens catenate successive copper atoms through the trans-axial sites [14], there appear to be no other copper(II) carboxylate/cyclam adducts structurally characterized. The results of the present single crystal X-ray study, despite the deficiencies noted above, are consistent in terms of stoichiometry and connectivity with its clearcut formulation as a 1 : 1 copper(II) benzoate : cyclam adduct (as a tetrahydrate) of the form *trans*-$[Cu(H_2O)_2(cyclam)](benzoate)_2 \cong 2H_2O$. As in the nickel adduct, the six-coordinate copper atom is disposed on a crystallographic inversion centre, with one half of the formula unit comprising the asymmetric unit of the structure. Unlike the nickel parent structure, however, the two trans-axial sites are here occupied by aqua rather than *O*-carboxylate ligands, the latter together with a further pair of uncoordinated water molecules being disposed independently in the lattice. It is noted that a further example of the *trans*-$[Cu(H_2O)_2(cyclam)]^{2+}$ cation, also centrosymmetric, has been defined in the hydrated fluoride salt, $[Cu(H_2O)_2(cyclam)]F_2 \cdot 4H_2O$ [15].

The above fluoride-containing structure is of considerable interest. The *c*-axis of that structure [7.123(3) Å in monoclinic space group $C2/m$] is almost identical with the present situation, the cations similarly disposed about the origin, with the O–Cu–O axis quasi-parallel to the short axis. The anions and lattice water molecules lie between these columns, hydrogen bonding with them. In the case of the fluoride complex, the anion, in association with the water molecules, is postulated to form $[F(OH_2)_4]^-$ entities, these in turn linking and linked by the cations into a three-dimensional hydrogen-bonded web. In the present structure, the anions, being of lower symmetry and with one hydrophilic end, are more limited in the extent and dimensionality of their interactions. Despite the relative imprecision of the determination, hydrogen atoms may be located, their interactions between coordinated and uncoordinated water molecules and anions linking these moieties in one-dimensional columnar arrays along *c*, (the usual amine–hydrogen interactions also being found), Fig. 2(a), with centrosymmetrically related aromatic rings interweaving in a stack at the centre of the cell. Pertinent contacts are: N,H(1)$\cdots$O(12) 2.979(8), 2.1 (est.); O(1),H(1a0)$\cdots$O(12)(x, y, $1+z$) 2.692(7), 1.9 (est.); O(1),H(1b0)$\cdots$O(2)(x, $y-1$, $1+z$) 2.793(7), 1.9 (est.); O(2), H(2a0)$\cdots$O(11)($\bar{x}$, $1-y$, $1-z$) 2.736(8), 1.8 (est.); O(2),H(2b0)$\cdots$O(11) 2.814(8), 1.9 Å (est.). It is of interest to note that the Cu–O(H_2) distances in the two structures, despite the presumed sensitivity of this parameter to local ambience, are equivalent (as are their *c*-axis).

A similar situation is found in the 4-*t*-butylbenzoate analogue, which presents as $[Cu(H_2O)_2(cyclam)]$(4-*t*-butylbenzoate)$_2$, but is devoid of lattice hydration. The mode of packing is similar, reflected again in a similar *c* cell dimension, although the absence of lattice hydration simplifies the nature of the columnar array, Fig. 2(b). N,H(1)$\cdots$O(111) ($\bar{x}$, 1–y, $\bar{z}$) are 2.972(4, 2.19 (3); N,H(5)$\cdots$O(112) (x, $y-1$, $z-1$) are 2.872(4), 2.06(3); O(1),H(1a0)$\cdots$O(111) (x, $y-1$, $z-1$) 2.800(3), 2.03(3); O(1)H(1b0)$\cdots$O(112) ($\bar{x}$, $1-y$, $\bar{z}$) 2.782(3), 1.95(3) Å. Cu–O in this complex is rather longer than the values found in the benzoate and fluoride; all three values are considerably longer than in the nickel counterpart cations, as might be expected from the different electron configurations.

CONCLUSION

As illustrated by Fig. 1(a) and 1(b), the structure of [Ni(*O*-benzoato)$_2$(cyclam)] quite closely parallels that of [(4-*t*-butylbenzoato)$_2$(cyclamH$_2$)] $\cong$ 2(4-*t*-butylbenzoic acid) if the latter two 4-*t*-butylbenzoic acid moieties that are not directly associated with the cyclam ring are ignored. Indeed some of the hydrogen bonding between the axial benzoate groups and cyclam in the metal-free adduct remains intact in the nickel complex. In contrast, while the 2 : 1 (carboxylate : cyclam) package remains partially intact in the copper complexes in the sense that the two carboxylate anions remain hydrogen bound to the (coordinated) cyclam ligand, they do not form part of the metal's inner coordination sphere in either complex. Thus based on the solid-state evidence (which, of course, must be treated with caution when used to extrapolate to solution behaviour), the metal-free assembly appears much less "preorganized" for complexation to copper(II) than it is for nickel(II).

Acknowledgements

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