Synthesis and characterisation of macrocyclic copper(II) complexes containing N_3O_4 donor sets

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Two new macrocyclic Schiff-base complexes of Cu(II) have been prepared by the template reaction of 2,6-bis(2-formylphenoxymethyl)pyridine with 1,2-bis(2'-aminophenoxy)benzene [L^1] or with 1,2-bis(2'-aminophenoxy)-4-*tert*-butylbenzene [L^2] in the presence of Cu(II) perchlorate. The amines used have low flexibility and therefore the formation of complexes was very difficult. The synthesised 23-membered, heptadentate N_3O_4 complexes were characterised by elemental analysis, IR, and FAB-mass spectroscopy.

Keywords: copper(II) complex, template synthesis, Schiff base, oxaazamacrocycle, heptadentate

Template Schiff base condensations between dicarbonyl compounds and diamines are among the simplest and most popular methods for macrocycle synthesis. The size and preferred coordination geometry of the metal ion control the structure of the condensation products.[1,2] The role of the metal ion is to control the supramolecular assembly of the components, presumably through their complexation and organisation.[3,4] However, the presumed ternary-complex intermediates have not normally been investigated. This effect is especially pronounced when rigid or less flexible building blocks are used, and relatively rigid or less flexible macrocycles are formed. In such cases conformational changes within the macrocyclic ligand are limited, and little adjustment of the coordination sphere geometry is possible.

The study of the complexation capability of Cu(II) towards oxaazamacrocyclic ligands derived from diketo- or diformyl-precursors and the appropriate aliphatic or aromatic diamine precursors, often by a template procedure, have been previously reported.[5-17] Previously, we have reported a number of copper(II) Schiff base polyazamacrocyclic complexes with and without pendant arms by a template procedure.[18-21] We report here the synthesis and characterisation of two new potentially heptadentate (N_3O_4) Schiff base macrocyclic copper(II) complexes, **1** and **2**, derived from cyclocondensation of 2,6-bis(2-formylphenoxymethyl)pyridine with 1,2-bis(2′-aminophenoxy)benzene (L^1) or 1,2-bis(2′-aminophenoxy)-4-*tert*-butylbenzene (L^2) (Fig. 1) by a template procedure.

Experimental

Physical measurements

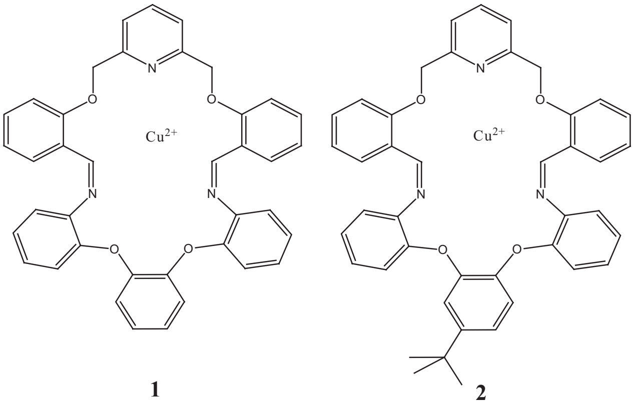
Elemental analyses were made on a Perkin-Elmer 240C elemental analyser. Infrared spectra were recorded as KBr discs using a Perkin-Elmer FT-IR spectrum GX spectrophotometer (4000–500 cm^{-1}). Mass spectra were recorded using a VG. Autospec FAB Magnetic sector spectrometer with 3-nitrobenzyl alcohol used as a matrix for FAB spectra.

Chemicals and starting materials

1,2-bis(2'-aminophenoxy)benzene, 1,2-bis(2'-aminophenoxy)-4-*tert*-butylbenzene and 2,6-bis(2-formylphenoxymethyl)pyridine were prepared according to previously published procedures.[22,23] All of the reagents and solvents used were of analytical grade and purchased commercially.

Preparation of complexes

Macrocyclic complexes were prepared by a modification of the procedure of Lodeiro *et al.*[17] A solution of the $Cu(ClO_4)_2.6H_2O$ (0.5 mmol) in hot absolute ethanol (10 ml) was added to a refluxing solution of 2,6-bis(2-formylphenoxymethyl)pyridine (0.5 mmol) in the same solvent (20 ml) and the resulting solution was heated at reflux for 1 h. Then, to this stirred and heated solution, 1,2-bis(2'-aminophenoxy)benzene or 1,2-bis(2'-aminophenoxy)-4-*tert*-butylbenzene (0.5 mmol) in absolute ethanol (20 ml) was slowly added. After refluxing for 12 h the solution was then concentrated in a rotary evaporator to *ca* 5–10 ml. A small volume of diethyl ether was slowly added into the solution producing powdery precipitates. The products were filtered off, washed with cold diethyl ether and dried under vacuum.



1 **2**

Fig. 1 The proposed structures of complexes **1** and **2**.

$[CuL^1](ClO_4)_2.2EtOH$ (**1**): (178 mg, 38%). (Found: C, 54.0; H, 4.2; N, 4.8%. Calcd for $C_{43}H_{41}Cl_2CuN_3O_{13}$: C, 53.9; H, 4.3; N, 4.4%); ν_{max}/cm^{-1} (KBr disc): 3398 $(O–H)_{EtOH}$, 1635 $(C=N)_{imi}$, 1599, 1453 $(C=N)_{py}$, 1098, 622 (ClO_4); FAB MS *m/z* (%) 765 $[CuL^1(ClO_4)]^+$ (9), 666 $[CuL^1]^+$ (100), 604 $[L^1 + H]^+$ (97).

$[CuL^2](ClO_4)_2.7H_2O$ (**2**): (565 mg, 54%). (Found: C, 49.3; N, 4.4; H, 4.7%, Calcd for $C_{43}H_{51}Cl_2CuN_3O_{19}$: C, 49.3; N, 4.0; H, 4.9%; ν_{max}/cm^{-1} (KBr disc): 3380–3520 (H_2O), 1644 $(C=N)_{imi}$, 1604, 1458 $(C=N)_{py}$, 1143, 1108, 1088, 636, 622 (ClO_4); FAB MS *m/z* (%) 857 $[CuL^1(ClO_4)(H_2O)_2]^+$ (25), 821 $[CuL^1(ClO_4)]^+$ (35), 722 $[CuL^1]^+$ (100).

Results and discussion

The syntheses of complexes **1** and **2** were carried out *via* template [1 + 1] condensation of 2,6-bis(2-formylphenoxymethyl)pyridine with 1,2-bis(2'-aminophenoxy)benzene or 1,2-bis(2'-aminophenoxy)-4-*tert*-butylbenzene in the presence of copper(II) perchlorate in ethanol. The Schiff base macrocyclic complexes have been characterised by elemental analyses, IR and FAB mass spectroscopy. These complexes are air stable solids and have elemental analyses consistent with the formulations given in the Experimental section.

The IR spectra of the complexes are assigned and provide some information regarding the bonding in the complexes. The data show intense absorption bands at 1635 (**1**) and 1644 cm^{-1} (**2**), corresponding to an imine bond, and no peaks assignable to unreacted amine or carbonyl groups. Both the spectra exhibit medium-to-strong bands at 1599 and 1453 cm^{-1} (**1**), 1604 and 1458 cm^{-1} (**2**) as expected for the two highest energy ring vibrations of the coordinated pyridine.[24] The absorption bands occurring in the IR spectra of the complexes at 1088 and 626 cm^{-1} or 1098 and 622 cm^{-1} are assignable to the asymmetric Cl–O stretching mode and the asymmetric Cl–O bending mode, respectively, of the perchlorate group.[25-27] Both show considerable splitting due to a reduced symmetry of the coordinated

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species, suggesting some interaction of at least one of the ClO_4^- anions with the metal.[28] For complex **1**, the band is actually three maxima at ~1143, 1108 and 1088 cm^{-1}, the lower energy band also shows splitting with two maxima at ~636 and 626 cm^{-1}. This also indicates the presence of coordinated perchlorate groups.

The FAB mass spectral results serve an important role in confirming the [1 + 1] cyclic nature of two ligands in their complexes; two spectra feature peaks attributable to the macrocyclic ligand, confirming the stability of the two macrocycles in their metal complexes. The spectrum for **1** contain peaks due to different fragmentation species, including 765 $[CuL^1(ClO_4)]^+$, 666 $[CuL^1]^+$ and 604 $[L^1 + H]^+$. The spectrum of **2** contains peaks attributable to the species 857 $[CuL^1(ClO_4)(H_2O)_2]^+$, 821 $[CuL^1(ClO_4)]^+$ and 722 $[CuL^1]^+$. However, in the absence of crystal structure determinations our information is insufficient to allow the assignment of definitive molecular geometries.

Conclusion

The Cu(II) ion is effective as a template for the Schiff base condensation of 2,6-bis(2-formylphenoxymethyl)pyridine and two less flexible diamine ligands resulting in the formation of oxaazamacrocyclic complexes based on the 23-membered N_3O_4 rings. This process leads to the formation of two less flexible macrocyclic ligands. The FAB mass and elemental analysis of the Cu(II) complexes indicate that both the complexes have been synthesised mononuclearly.

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