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Synthesis of Novel Copper(II) Complexes of Optically Active Schiff Bases

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Recently, there has been considerable interest displayed in the preparation of complexes of metals with optically active chelating Schiff base ligands derived from naturally occurring asymmetric amines [1–3]. Our interest in such complexes arises from reports that certain optically active copper(II) complexes catalyse the cycloaddition reactions of substituted olefins with diazoacetates to yield cyclopropane carboxylates enantioselectively [4–6]. These reports described copper(II) complexes of Schiff bases derived from salicylaldehyde, and closely related phenols, and optically active amines prepared by treatment of α-amino esters with Grignard reagents. In a search for more selective catalysts we have obtained a series of copper(II) complexes with Schiff bases derived from both aminoglycosides and α-amino acids as sources of chirality, in order to study the effect on catalytic properties of the size and nature of the chelating ring and of both nitrogen and oxygen as donor atoms, the Schiff base were prepared from aldehydes derived from phenol, pyrrole, pyridine and quinoline [11] nuclei.

Procedure

The amines described below were prepared by literature methods:
S-2-Amino-1,1-bis(2-methoxyphenyl)3-phenylpropan-1-ol (1) [7], methyl 4,6-*O*-benzylidene-2-amino-2-deoxy-α-*D*-altropyranoside (2) [8], methyl 4,6-*O*-benzylidene-2-amino-2-deoxy-α-*D*-glucopyranoside (3), methyl 2-amino-2-deoxy-β-*D*-glucopyranoside (4) [9] and methyl 4,6-*O*-benzylidine-2-amino-2-deoxy-α-*D*-allopyranoside (5) [10]. The following aldehydes were utilised: salicylaldehyde (A), 2-hydroxyl-1-naphthaldehyde (B), pyridine-2-carboxaldehyde (C), pyridine-2,6-dicarboxaldehyde (D), quinoline-8-carboxaldehyde (E) and pyrrole-2-carboxaldehyde (F).

Copper(II) complexes were prepared by the following four methods:

Method I

The amine was treated with one of the heterocyclic aldehydes (C), (D), (E) or (F) and the resulting Schiff base was used to form either the copper(II) chloride or tetrafluoroborate complex as described for simple 2-pyridinalalkylimine derivatives of iron(II) [12].

Method II

The amine was treated with copper(II) bis(salicylaldehyde) according to the literature method [13].

Method III

A solution of the Schiff base in warm methanol was added to a suspension of copper(II) bis(salicylaldehyde) in methanol. After stirring the mixture for several hours the complex was (i) isolated by filtration or (ii) isolated as a second crop of the complex after the removal of the bulk of the filtrate.

Method IV

Binuclear copper(II) complexes were prepared by a literature procedure [14].

Analytical and physical data for some of the complexes prepared by these methods are tabulated in Table I. Generally, the complexes were only slightly soluble in non-chlorinated organic solvents but both the chloride and tetrafluoroborate complexes of the Schiff bases derived from (C) and (4) were highly soluble in water.

Although the stoichiometries of the complexes have been deduced from analytical data, their stereochemistries have not been determined.

The extremes of planar and near-tetrahedral structures observed for copper(II) complexes with salicylaldimines [15] have been associated with the colours olive green and maroon, respectively [16]. The green colours of the salicylaldimine complexes recorded in the Table may be indicative of pseudo-planar structures.

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TABLE I. The Preparation and Characterisation of Optically Active Copper(II) Schiff Base Complexes.

Schiff Base		Method Preparation	Complex Formula	Analysis Found (%) (Calc)				Colour	Melting Point (°C)
Amine	Aldehyde			C	H	N	Cu		
(1)	(A)	III(i)	$C_{60}H_{56}N_2O_8Cu$	69.73 (72.30)	5.25 (5.66)	2.75 (2.81)	7.6 (6.4)	Blue-grey	217–220 (decomp)
(1)	(C)	I	$C_{58}N_{56}N_4O_6CuB_2F_8$	59.52 (60.98)	4.28 (4.94)	4.61 (4.91)	5.7 (5.6)	Brown	144–146 (decomp)
(1)	(D)	I	$C_{53}H_{51}N_3O_6CuCl_2$	64.21 (66.28)	4.54 (5.35)	3.62 (4.38)	7.2 (6.6)	Pale-green	164–166 (decomp)
(1)	(E)	I	$C_{66}H_{60}N_4O_6CuCl_2$	69.03 (69.56)	4.98 (5.31)	4.70 (4.91)	5.8 (5.6)	Pale green	177–180 (decomp)
(1)	(F)	I	$C_{56}H_{54}N_4O_6Cu$	70.68 (71.35)	5.46 (5.78)	5.17 (5.95)	6.3 (6.7)	Blue-grey	200–205 (decomp)
(2)	(A)	III(ii)	$C_{42}H_{44}N_2O_{12}Cu$	62.90 (60.60)	5.33 (5.33)	2.81 (3.37)		Green	190–205
(2)	(A)	IV	$C_{42}H_{42}N_2O_{12}Cu_2$	52.00 (56.43)	5.32 (4.74)	2.20 (3.13)		Green	188
(2)	(B)	III(i)	$C_{50}H_{48}N_2O_{12}Cu$	63.79 (64.40)	4.79 (5.19)	2.70 (3.00)		Green	218
(2)	(B)	IV	$C_{50}H_{46}N_2O_{12}Cu_2$	59.80 (60.41)	5.25 (4.67)	1.90 (2.82)		Green	>250 (decomp)
(3)	(A)	II	$C_{42}H_{44}N_2O_{12}Cu$	60.47 (60.60)	4.88 (5.69)	3.17 (3.37)	7.5 (7.6)	Green	121–124 (decomp)
(3)	(A)	IV	$C_{42}H_{42}N_2O_{12}Cu_2$	57.17 (56.43)	4.68 (4.74)	3.09 (3.13)	13.7 (14.2)	Green	280–290 (decomp)
(4)	(C)	I	$C_{26}H_{36}N_4O_{10}CuCl_2$	44.18 (44.67)	5.35 (5.15)	7.34 (8.02)		Brown	105
(4)	(C)	I	$C_{26}H_{36}N_4O_{10}CuB_2F_8$	38.79 (38.94)	4.60 (4.49)	5.52 (6.99)		Brown	191–193
(5)	(A)	II	$C_{42}H_{44}N_2O_{12}Cu$	61.77 (60.60)	5.40 (5.69)	2.91 (3.37)	7.4 (7.6)	Green	150–152
(5)	(A)	IV	$C_{42}H_{42}N_2O_{12}Cu_2$	56.15 (56.43)	5.05 (4.74)	2.63 (3.13)	13.6 (14.2)	Deep green	194–197

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