The Solution and Solid State Analysis of Xylylic Di-copper Complexes as Receptors for Encapsulating Anions

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Abstract

The investigation into neutral aryl-linked oxime dicopper helicates encapsulating a number of anions was carried out. Two dicopper aryl-linked salicyloxime derived complexes were synthesized and studied which contained either *p*-xylylic (**1**) or *m*-xylylic (**2**) incorporated spacer groups. UV-visible spectroscopy was used to determine the binding stability constants of the anion complexes. Complex binding, encapsulation of anions and the conformational flexibility of **1** and **2** was supported and ascertained by the crystal structural data obtained. Receptor **1** expressed an exceptional binding strength for sulfate in THF where a log *K* value of 5.5 ± 0.3 was acquired. Receptor **2** could form both helical and non-helical structures. This was able to bind bromide selectively in a 2:1 stoichiometry of anion:receptor with a log K_2 value of 9.2 ± 0.1 and showed an unexpectedly high association constant for the perchlorate anion in a 1:1 stoichiometry with a log *K* value of 4.6 ± 0.2 (presumably in a helical structure).

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Abbreviations

⊂	Indicates encapsulation of a guest molecule within a host molecule/complex.
1	Anion-free complex formed between Cu(II) acetate and ligand **L[1]**. It is used within this report to represent the unprotonated complex $[Cu_2(L^1\text{-}2H)_2]$.
1a	N, N'-dimethyl-p-xylylenediamine.
1b	3, 3'-(1, 4-phenylenebis(methylene))bis(methylazanediyl)bis (methylene)bis(5-*tert*-butyl-2-hydroxybenzaldehyde).
2	Anion-free complex formed between Cu(II) acetate and ligand **L[2]**, representing the unprotonated form $[Cu_2(L^2\text{-}2H)_2]$.
2a	N, N'-dimethyl-m-xylylenediamine.
2b	3, 3'-(1, 3-phenylenebis(methylene))bis(methylazanediyl)bis (methylene)bis(5-*tert*-butyl-2-hydroxybenzaldehyde).
3	$[ClO_4{\subset}(Cu_2L^1{}_2)](ClO_4)_3$; the zwitterionic form with a captured perchlorate anion.
4	$[BF_4{\subset}(Cu_2L^1{}_2)](BF_4)_3$; the zwitterionic form with a captured tetrafluoroborate anion.
5	$[NO_3{\subset}(Cu_2L^2{}_2)](NO_3)_3$; the zwitterionic form with a captured nitrate anion.
6	$[2Br{\subset}(Cu_2L^2{}_2)](Br)_2$; the zwitterionic form with two captured bromide anions and two counter bromide anions.
7	$[2Br{\subset}(Cu_2L^2{}_2)](BF_4)_2$; the zwitterionic form with two captured bromide anions and two counter tetrafluoroborate anions.
CCDC	Cambridge Crystallographic Data Centre.
$CHCl_3$	Chloroform.
DCE	1,2-dichloroethane.
DMSO-d_6	Deuterated dimethyl sulfoxide.

ESMS	Electrospray Ionization Mass Spectrometry.
IPA	Isopropanol.
IR	Infrared spectroscopy.
K	Formation constant. The equilibrium constant for the formation of a complex in solution. Also referred to as the binding, stability or association constant throughout the text.
L^1	(1*E*, 1'*E*)-5-*tert*-butyl-3-(((4-(((5-*tert*-butyl-2-hydroxy-3-((*E*)-(hydroxyimino)methyl)benzyl)(methyl)amino)methyl)benzyl)(methyl)amino)methyl)-2-hydroxybenzaldehyde oxime.
L^2	(1*E*, 1'*E*)-5-*tert*-butyl-3-(((3-(((5-*tert*-butyl-2-hydroxy-3-((*E*)-(hydroxyimino)methyl)benzyl)(methyl)amino)methyl)benzyl)(methyl)amino)methyl)-2-hydroxybenzaldehyde oxime.
MeOH	Methanol.
MeCN	Acetonitrile.
NMR	Nuclear magnetic resonance.
THF	Tetrahydrofuran.
TBABr	Tetra-*n*-butylammonium bromide.
t-Bu	tertiary butyl group or 1,1-dimethylethyl group ($(CH_3)_3C$–).
UV-vis	Ultraviolet-visible spectroscopy.