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**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 $[Cu_2(L^1-2H)_2]$.
- 1a** N, N'-dimethyl-p-xylylenediamine.
- 1b** 3, 3'-(1, 4-phenylenebis(methylene))bis(methylazanediy)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 $[Cu_2(L^2-2H)_2]$.
- 2a** N, N'-dimethyl-m-xylylenediamine.
- 2b** 3, 3'-(1, 3-phenylenebis(methylene))bis(methylazanediy)bis(methylene)bis(5-*tert*-butyl-2-hydroxybenzaldehyde).
- 3** $[ClO_4⊂(Cu_2L^1_2)](ClO_4)_3$; the zwitterionic form with a captured perchlorate anion.
- 4** $[BF_4⊂(Cu_2L^1_2)](BF_4)_3$; the zwitterionic form with a captured tetrafluoroborate anion.
- 5** $[NO_3⊂(Cu_2L^2_2)](NO_3)_3$; the zwitterionic form with a captured nitrate anion.
- 6** $[2Br⊂(Cu_2L^2_2)](Br)_2$; the zwitterionic form with two captured bromide anions and two counter bromide anions.
- 7** $[2Br⊂(Cu_2L^2_2)](BF_4)_2$; the zwitterionic form with two captured bromide anions and two counter tetrafluoroborate anions.
- CCDC Cambridge Crystallographic Data Centre.
- CHCl₃ Chloroform.
- DCE 1,2-dichloroethane.
- DMSO-*d*₆ Deuterated dimethyl sulfoxide.

ESMS	Electrospray Ionization Mass Spectrometry.
IPA	Isopropanol.
IR	Infrared spectroscopy.
<i>K</i>	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.
L¹	(1 <i>E</i> , 1' <i>E</i>)-5- <i>tert</i> -butyl-3-(((4-(((5- <i>tert</i> -butyl-2-hydroxy-3-((<i>E</i>)-(hydroxyimino)methyl)benzyl)(methyl)amino)methyl)benzyl)(methyl)amino)methyl)-2-hydroxybenzaldehyde oxime.
L²	(1 <i>E</i> , 1' <i>E</i>)-5- <i>tert</i> -butyl-3-(((3-(((5- <i>tert</i> -butyl-2-hydroxy-3-((<i>E</i>)-(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- <i>n</i> -butylammonium bromide.
<i>t</i> -Bu	tertiary butyl group or 1,1-dimethylethyl group ((CH ₃) ₃ C-).
UV-vis	Ultraviolet-visible spectroscopy.