

Metal Ion Activated Anion Sensors

A Thesis Presented for the Degree of

Doctor of Philosophy

By

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at

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October 2007



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Abstract

A series of new, octadentate, fluorescent, macrocyclic ligands have been prepared with a view to using them to study aromatic anion sequestration. The eight-coordinate Cd(II) complexes of the ligands have been shown capable of acting as receptors for a range of aromatic oxoanions. This has been demonstrated by perturbation of both ^1H NMR chemical shift values and the anthracene derived fluorescence emission intensity as the potential guest anion and the host are combined. Non-linear least squares regression analysis of the resulting titration curves leads to the determination of binding constants in 20% aqueous 1,4-dioxane which lie in the range $10^{2.3} \text{ M}^{-1}$ (benzoate) to $10^{7.5} \text{ M}^{-1}$ (2,6-dihydroxybenzoate). By reference to the X-ray determined structures of related, but non-fluorescent inclusion complexes, the primary anion retention force is known to arise from hydrogen bonding between the anion and four convergent hydroxy groups that exist at the base of a cavity that develops in the complexes as their aromatic groups juxtapose upon coordination. This work reveals significant stability enhancement when hydroxy groups are positioned on the anion at points where O-H... π hydrogen bonding to the aromatic rings that constitute the walls of the cavity becomes geometrically possible.

Declaration

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.



A. J. Bradbury

2007

Acknowledgements

Firstly, I would like to thank my supervisor, Professor Kevin P. Wainwright for all the help and support he has given me throughout these studies, and most of all for his patience. I would also like to thank Professor S. F. Lincoln of the University of Adelaide for many of the same reasons. I would also like to thank Dr Martin Johnson for his help and also his wealth of information regarding the NMR. I would also like to thank Professor Sadegh Salehzadeh for his modeling work. My thanks also go out to everyone who I ever shared room 337 with, for all the discussions that we held about our work, and the help and support everyone has provided, so many thanks go out to Rebecca Campbell, Akhmad Damsyik, Professor Hassan Keypour, Hamid Khanmohammadi, Melissa Latter, Tim Robinson, Jozef Hodyl, Yakub, Professor Xu Xingyou, La Ode Kadidae and Rachel King. My family and friends I would like to thank for putting up with me these past few years, for both the times when I was there, and those times when I wasn't. Finally my love and thanks go out to my wife Barbara, without whom I would not have been able to survive this PhD, who has been so very patient and encouraging throughout the years.

Thank you.

Abbreviations

AcOH	acetic acid
Å	Ångstrom (10^{-10} m)
antac-12	<i>N</i> -(2-(-9-anthracenylmethyl)aminoethyl) -1,4,7,10-tetraazacyclododecane
bp	boiling point
Bn	benzyl
Bu	butyl
CBn	benzyloxycarbonyl
cyclen	1,4,7,10-tetraazacyclododecane
δ	chemical shift
d	doublet
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulphoxide
eT	Electron transfer
ET	Energy transfer
EtOH	ethanol
ϵ	molar extinction coefficient or molar absorptivity
ϵ'	molar fluorescence
<i>I</i>	ionic strength
IR	infra red
<i>J</i>	coupling constant
<i>K</i>	apparent stability constant
L	unspecified ligand
ν_{\max}	maximum infrared absorbance (cm^{-1})
λ_{ex}	fluorescence excitation wavelength (nm)
λ_{\max}	maximum wavelength
m	multiplet
M^{2+}	unspecified divalent metal ion
Me	methyl
MeCN	acetonitrile
MHz	megahertz (10^6 s^{-1})
mp	melting point
NMR	Nuclear magnetic resonance (spectroscopy)

PeT	Photoinduced electron transfer
pK_a	$-\log_{10}[K_a]$
q	quartet
RT	room temperature
s	singlet
SD	standard deviation
t	triplet
<i>tert-</i>	tertiary
TLC	Thin layer chromatography
UV-vis	Ultraviolet-visible (spectroscopy)

