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Synthesis of halogen bonding and crown ether-functionalised Ni(II)-salen receptors for cation, anion and ion-pair recognition†

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With the objective of utilising supramolecular host–guest chemistry as a potential method to stabilise Lewis basic intermediates in transition metal salen catalytic reactions, the synthesis of two families of Ni(II) salen complexes functionalised with appended supramolecular recognition motifs for the binding of charged guest species is reported. Detailed ^{1}H NMR anion binding studies in competitive DMSO-d_6/$CDCl_3$ mixed solvent media reveal the appendage of neutral halogen bonding donor groups facilitates the binding of Cl^-, Br^- and I^- halide anions in close proximity to the Ni(II) salen transition metal centre, with halide binding constants $>10^3$ M^{-1}. Furthermore, the incorporation of benzo-15-crown-5 (B15C5) alkali metal cation binding motifs enables the selective, near-quantitative, formation of an intramolecular bis-B15C5 sandwich potassium cation complex, which results in a binding cavity for a co-bound iodide anion, enabling binding of an ion-pair proximal to the Ni(II) salen complex centre.

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Introduction

Salen (*N*,*N*′-ethylenebis(salicylimine))-derived ligands (Fig. 1) are a class of tetradentate N_2O_2-coordinating bis-Schiff base ligands which form stable complexes with a wide range of metals. With their modular synthesis from functionalised salicylaldehyde and ethylenediamine derivatives, which allow facile tunability of the steric and electronic properties of the resultant metal complexes, salens have found a range of applications especially in transition metal catalysis.[1,2]

Derived from biorenewable monomers such as lactide or a range of epoxides,[3] polyesters and polycarbonates have been proposed as sustainable polymers, *via* efficient Lewis acid catalysis.[4] Notably, the facile synthesis of transition metal based salen complexes has made this class popular catalysts of choice for a range of ring-opening polymerisation (ROP) and ring-opening co-polymerisation (ROCOP) reactions.[5–9]

In addition to the Lewis acidic transition metal catalyst, ROCOP reactions with a monometallic catalyst typically proceed in conjunction with an exogenous co-catalyst, commonly a halide with a bulky, non-coordinating ammonium cation, such as bis(triphenylphosphine)iminium chloride (PPNCl).[10] However, as the presence of the co-catalyst may promote undesirable competing side reactions, such as the formation of thermodynamically-favoured cyclic carbonate species, low catalyst loadings are typically used. These low loadings, however, limit the effective concentration of the catalyst/co-catalyst pair, restricting their efficacy.[10]

Attempts to overcome this limitation have focused on the incorporation of co-catalyst-like pendant ammonium groups covalently tethered to the ligand framework, or integrated hydrogen bond donors capable of coordinating the halide counteranion in salen ROCOP catalysts.[11,12] Halogen bonding (XB) is a non-covalent 'sigma-hole' interaction which occurs between an electropositive region of a polarised halogen atom and a Lewis basic species, such as an anion.[13,14] Importantly, XB has been shown to exhibit a number of key advantages compared to hydrogen bonding (HB) including pH independence, stringent directionality and often exhibiting superior interaction strengths compared to HB donors, even in competitive aqueous media.[15–20]

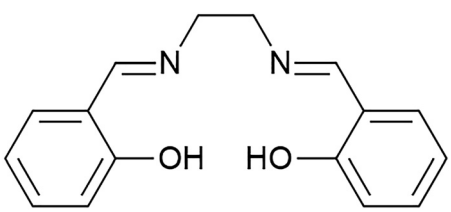

Fig. 1 *N*,*N*′-Ethylenebis(salicylimine), the simplest salen ligand.

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† Dedicated to Professor Giuseppe Resnati, celebrating a career in fluorine and non-covalent chemistry on the occasion of his 70th birthday.

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Within the field of ion-pair recognition, wherein receptors are capable of concerted cation and anion binding through distinct, but usually proximal, binding sites, XB-driven anion binding has proven to be a valuable tool in heteroditopic host design, modulating affinity and selectivity profiles.[21–27] Previous attempts to incorporate anion-binding sites into salen ligands have usually involved the use of charged pendants, however this generally compromises the selectivity of guest ion binding due to non-specific electrostatic interactions,[11,12] and very few examples of charge neutral systems exist.[28] We identified the introduction of neutral XB and HB groups into anion and ion-pair binding salen scaffolds to provide a promising supramolecular framework to target neutral transition metal catalyst salen complexes for the binding of co-catalytically relevant anions and ion-pairs.

In an effort to integrate XB and HB anion recognition sites as well as alkali metal cation binding crown ether motifs into salen-based ligand design for anion and ion-pair binding investigations, herein, we report the synthesis of two families of Ni(II) salen complexes substituted with XB (iodotriazole) or HB (triazole) anion binding groups.

One host framework was specifically designed to target anion binding (Fig. 2a) and the second heteroditopic bis-benzo-15-crown-5 ether functionalised Ni(II) salen host (Fig. 2b) for alkali metal cation-halide ion-pair recognition.

Ni(II) was selected as the target metal for the complex as it is diamagnetic, non-aggregating, air-stable and forms salen complexes which are stable to column chromatography.[29] Furthermore, the d^8 electronic configuration of Ni(II) was expected to form square planar complexes with the tetradentate salen ligand, without an associated co-ligand. Preliminary cation, anion and ion-pair binding studies provide a proof-of-concept study for elucidating the potential influence of the Lewis acidic Ni(II) salen centre on the respective host's charged guest recognition properties.

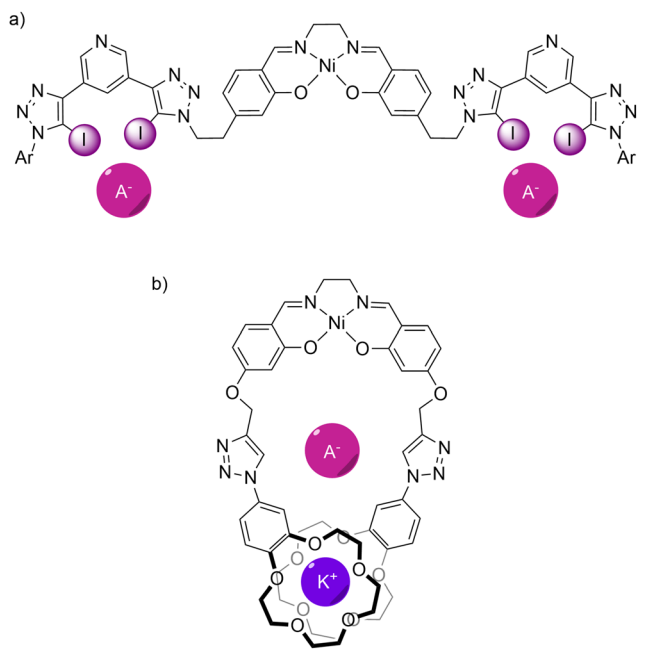

Fig. 2 Representative target (a) anion binding and (b) ion-pair binding Ni(II) salen complexes. A^- = halide anion.

Synthesis of an anion-binding salen

Synthesis of an azide-functionalised salicylaldehyde synthon

Earlier this year, Yang and co-workers reported a series of Ni(II) salen complexes substituted with thiourea groups.[28] However, they noted that the synthesis was challenging due to the tendency of the amine-substituted salicylaldehyde precursors to self-condense. Triazoles and iodotriazoles are promising supramolecular HB and XB donor groups respectively, which have become increasingly popular on account of their facile synthesis *via* a copper(I)-catalysed azide–alkyne Huisgen cycloaddition (CuAAC) reaction,[30] and the previously discussed stringent linearity and pH-independence of XB systems, when compared to HB analogues. Importantly, the azide and alkyne functionalities, and their precursor functional groups, are not nucleophilic, providing a facile route to incorporate binding sites for anionic co-catalysts into a salen framework.

Initial synthetic efforts targeted the incorporation of tethered anion-binding groups to the salen ligand. The use of halogen bonding motifs aimed to overcome the previously reported challenges of incorporating hydrogen bonding groups into the scaffold, wherein the hydrogen bonding motifs interact with the phenol functionality of the metal binding site necessitating the use of protecting groups.[28,31,32]

The introduction of halogen bonding sites was targeted *via* a copper(I)-catalysed alkyne–azide Huisgen cycloaddition, between a salen bis-azide and an iodoalkyne. We have previously demonstrated such CuAAC reactions to be a facile strategy for the incorporation of iodotriazole XB donor groups into anion receptors.[30,33]

The novel Ni(II) salen bis-azide complexes were prepared through the modified literature synthesis of azide-functionalised salicylaldehyde pro-ligand **1**,[34] followed by CuAAC reaction of **1** with the appendage alkyne. Subsequent Schiff base condensation of the resulting triazole-containing compound with 1,2-ethylenediamine, and subsequent metalation with Ni(II) acetate tetrahydrate formed the target functionalised Ni(II) salen complexes.

Reaction of (4-hydroxyphenyl)ethanol with thionyl chloride in toluene formed 4-(2-chloroethyl)phenol in 62% yield, which after a near-quantitative S_N2 reaction with sodium azide formed 4-(2-azidoethyl)phenol.[34] Subsequent magnesium-mediated *ortho*-formylation formed the target pro-ligand **1** in good overall yield (Scheme 1).

Two halogen bonding iodoalkyne synthons were prepared, one with an iodotriazole appended with a benzyl group, $\mathbf{2^{Bn}}$, and a further with an electron withdrawing per-fluorophenyl group, $\mathbf{2^{ArF}}$. It was predicted that introducing the inductively withdrawing per-fluorophenyl substituents would further polarise the iodotriazole iodine XB donor atom, increasing the anion binding potency of the motif. 3,5-Di(iodoethynyl)pyridine was prepared *via* a modified literature procedure,[35] with

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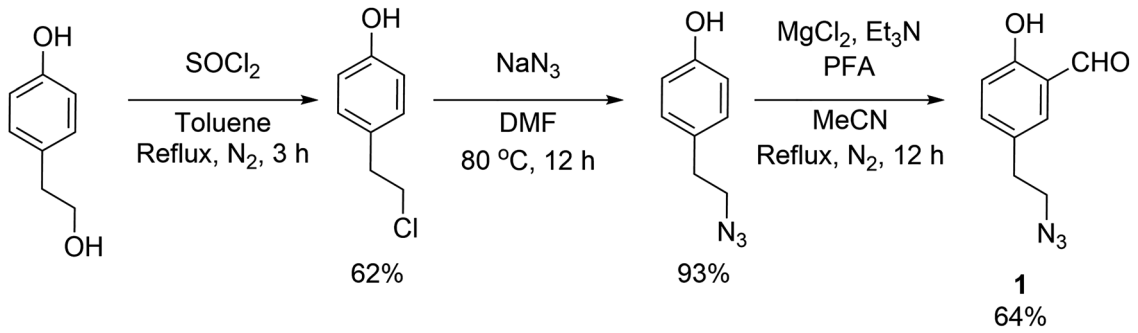
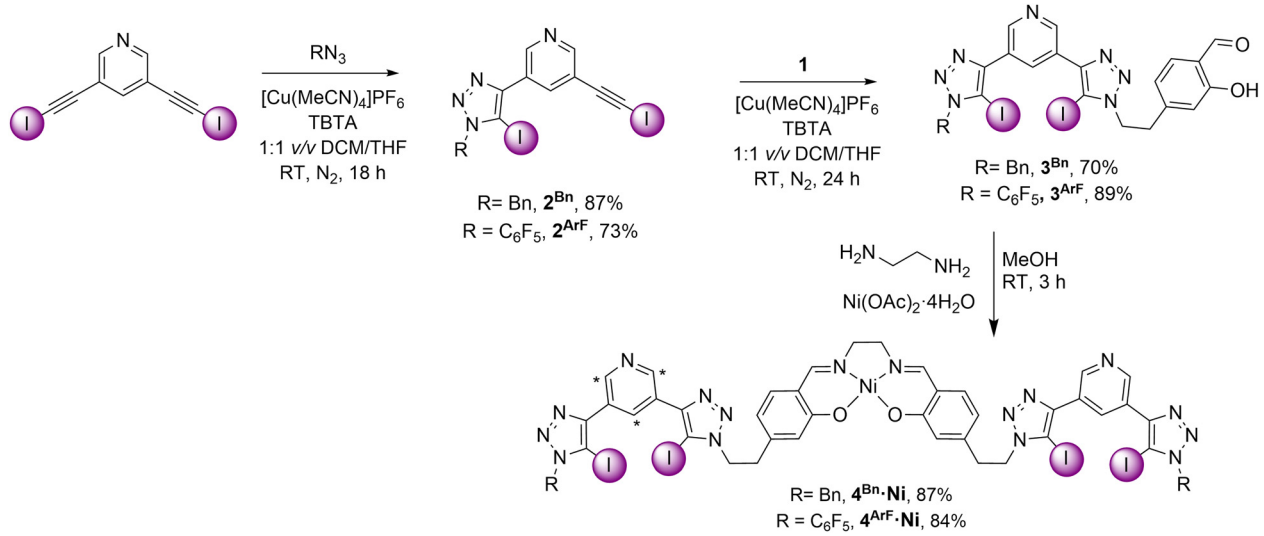


Scheme 1 Synthesis of azide-functionalised pro-ligand **1**.



Scheme 2 Synthesis of anion binding Ni(II) salen complexes $\mathbf{4^{Bn}}$·**Ni** and $\mathbf{4^{ArF}}$·**Ni**. * denotes pyridyl protons discussed in main text.

Sonogashira coupling of 3,5-dibromopyridine and trimethylsilylacetylene, followed by iodination with *N*-iodosuccinimide. A controlled CuAAC reaction of the resulting iodoalkynes with the corresponding azide formed the mono-iodoalkyne, mono-iodotriazole substituted pyridine derivatives $\mathbf{2^{Bn}}$ and $\mathbf{2^{ArF}}$. A further CuAAC reaction with **1**, followed by condensation with 1,2-ethylenediamine in the presence of $Ni(OAc)_2{\cdot}4H_2O$ formed the target complexes in very good (>80%) yield (Scheme 2). $\mathbf{4^{Bn}}$·**Ni** and $\mathbf{4^{ArF}}$·**Ni** were fully characterised by ^{1}H, ^{13}C and ^{19}F ($\mathbf{4^{ArF}}$·**Ni** only) NMR spectroscopy and ESI-MS (see SI).

Anion binding studies

In order to probe the anion binding abilities of $\mathbf{4^{Bn}}$·**Ni** and $\mathbf{4^{ArF}}$·**Ni**, ^{1}H NMR anion binding studies were performed with the halide salts of the non-coordinating tetra-*n*-butylammonium (TBA) cation, TBAX (X = Cl, Br, I).‡ On account of the very limited solubility of $\mathbf{4^{Bn}}$·**Ni** and $\mathbf{4^{ArF}}$·**Ni** in common organic solvents, a competitive solvent medium of 20% v/v DMSO-d_6 in $CDCl_3$ was employed.

Upon successive addition of the halide salt solution, a marked upfield shift was observed in the pyridyl proton resonances consistent with the anion binding at the XB bis-iodotriazole binding site (see SI, Fig. S31).§

Fitting of the binding isotherms *via* Bindfit,[36] allowed for calculation of the host–guest association constants (Table 1). Following the principles laid out by Hibbert and Thordarson,[37] a host : guest binding stoichiometry of 1 : 2 was established, and the suitability of a statistical binding model established. This is consistent with the structures of $\mathbf{4^{Bn}}$·**Ni** and $\mathbf{4^{ArF}}$·**Ni**, in which a rigid Ni(II) salen linker maintains separation between the two bis-iodotriazole XB binding motifs, such that each binds an anion with no significant cooperativity occurring between the two, distanced, binding sites.

‡ Fluoride host–guest binding studies were not attempted, as the highly basic fluoride anion is known to attack electron deficient aryl-iodide groups, such as iodotriazoles,[45] leading to receptor decomposition.

§ Host–guest UV-vis spectroscopic binding studies on the Ni(II) salen receptor complexes were attempted, however no significant perturbations in the Ni(II) salen electronic spectra were observed.

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Table 1 Anion binding constants of $\mathbf{4^{Bn}}$·**Ni** and $\mathbf{4^{ArF}}$·**Ni** with halide anions in 20% DMSO-d_6 v/v in $CDCl_3$. Errors < 10%. Anions added as their TBA salts. Binding model assumes $K_{11} = 4\ K_{12}$

	$\mathbf{4^{Bn}}$·**Ni**		$\mathbf{4^{ArF}}$·**Ni**	
	K_{11}/M^{-1}	K_{12}/M^{-1}	K_{11}/M^{-1}	K_{12}/M^{-1}
Cl^-	610	155	1060	270
Br^-	780	195	2780	690
I^-	1650	410	3120	780

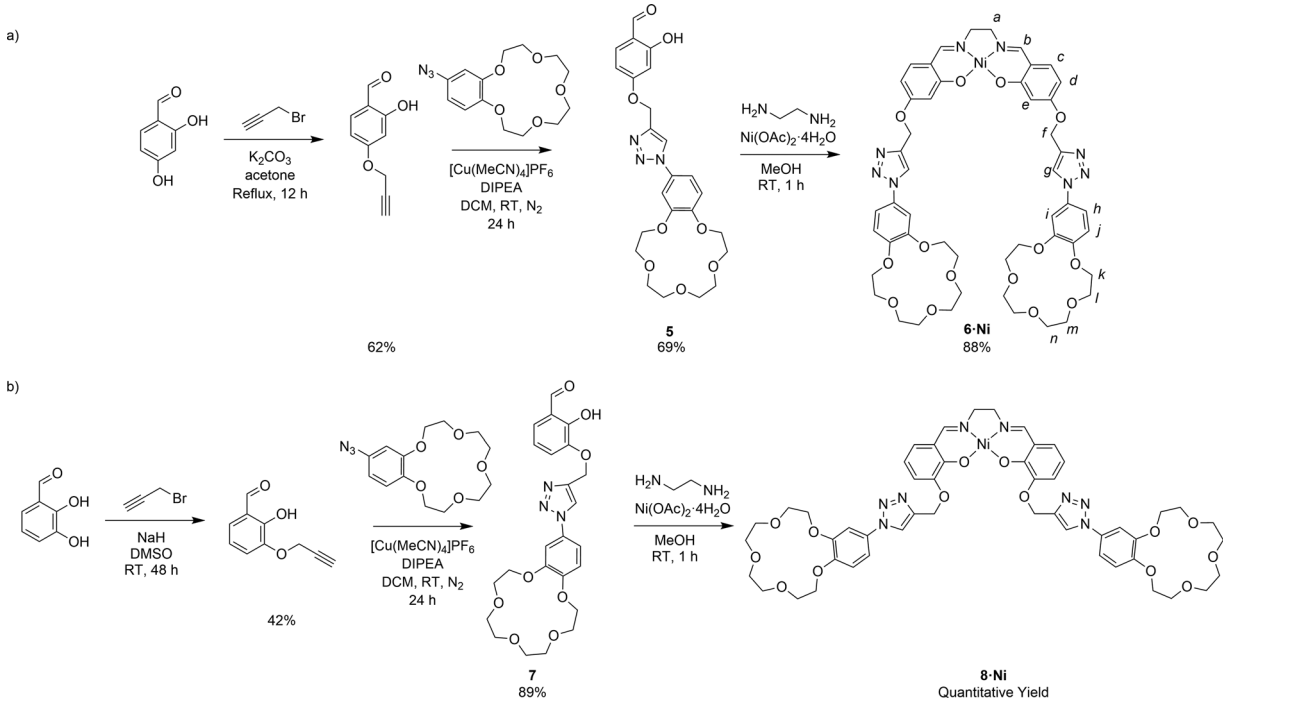
For both neutral receptors, which bound all the halide species strongly, selectivity for iodide binding was observed over the more charge dense chloride and bromide anions. Such selectivity may arise on account of the increased polarisability of the more diffuse iodide anion, allowing for increased covalency in binding, and on account of the poorer solvation of iodide by the coordinating DMSO-d_6 solvent. Importantly, a marked increase in binding constants was observed for $\mathbf{4^{ArF}}$·**Ni** over $\mathbf{4^{Bn}}$·**Ni**. Such an increase is consistent with the inductively-induced polarisation of the C–I bond in the case of $\mathbf{4^{ArF}}$·**Ni** due to the electron-withdrawing nature of the per-fluorophenyl triazole substituent.[38] While the poor solubility of these systems precluded catalytic testing, the appendage of halogen bonding groups to the salen scaffold is shown to be a potent strategy for the incorporation of anion-binding groups into neutral salen species with high synthetic yields, utilising the facile synthesis of halogen bonding motifs to give rise to a promising future direction for the synthesis of transition metal catalysts with anion co-catalyst binding appendages.

Synthesis of an ion-pair binding salen

Having demonstrated the potential for supramolecular XB interactions to append anion-binding groups to Ni(II) salen complexes, attention turned to the synthesis of a salen system capable of the selective binding of an alkali metal cation in proximity to the Ni(II) centre. The formation of transition metal/alkali metal bimetallic systems has previously been demonstrated to increase the activity of catalysts for ring-opening co-polymerisation reactions.[8]

Benzo-15-crown-5 (B15C5) is known to selectively form 2:1 host : guest stoichiometric complexes with K^+ over other alkali metals such as Na^+.[22,39–41] Therefore, a salen with two appended B15C5 appendices attached with a flexible linker, would provide a proximal Ni(II)/M(I) bimetallic arrangement which could be selectively formed by K^+ binding, potentially acting as a supramolecular mechanism for achieving on/off switchable catalysis,[42] and furthermore could act as an ion-pair receptor by binding an anion in the resulting cleft between the salen and the bis-crown ether K^+ sandwich complex.

To this end, the initial synthetic target was formed by preparing a propargyl substituted salen pro-ligand, to undergo a CuAAC reaction with azide-substituted B15C5, synthesised by a literature procedure (Scheme 3).[43] The propargyl-substituted salicylaldehyde derivative was prepared by reaction of 2,4-dihydroxybenzaldehyde with propargyl bromide, using K_2CO_3 as the base. Pro-ligand **5** was then prepared by CuAAC reaction of this alkyne with B15C5-N_3. Subsequent condensation of **5** with ethylenediamine and metalation with $Ni(OAc)_2{\cdot}4H_2O$, formed the target Ni(II) complex, **6**·**Ni**, in 88% yield (Scheme 3a).



Scheme 3 Synthesis of ion-pair binding Ni(II) salen complexes (a) **6**·**Ni** and (b) **8**·**Ni**.

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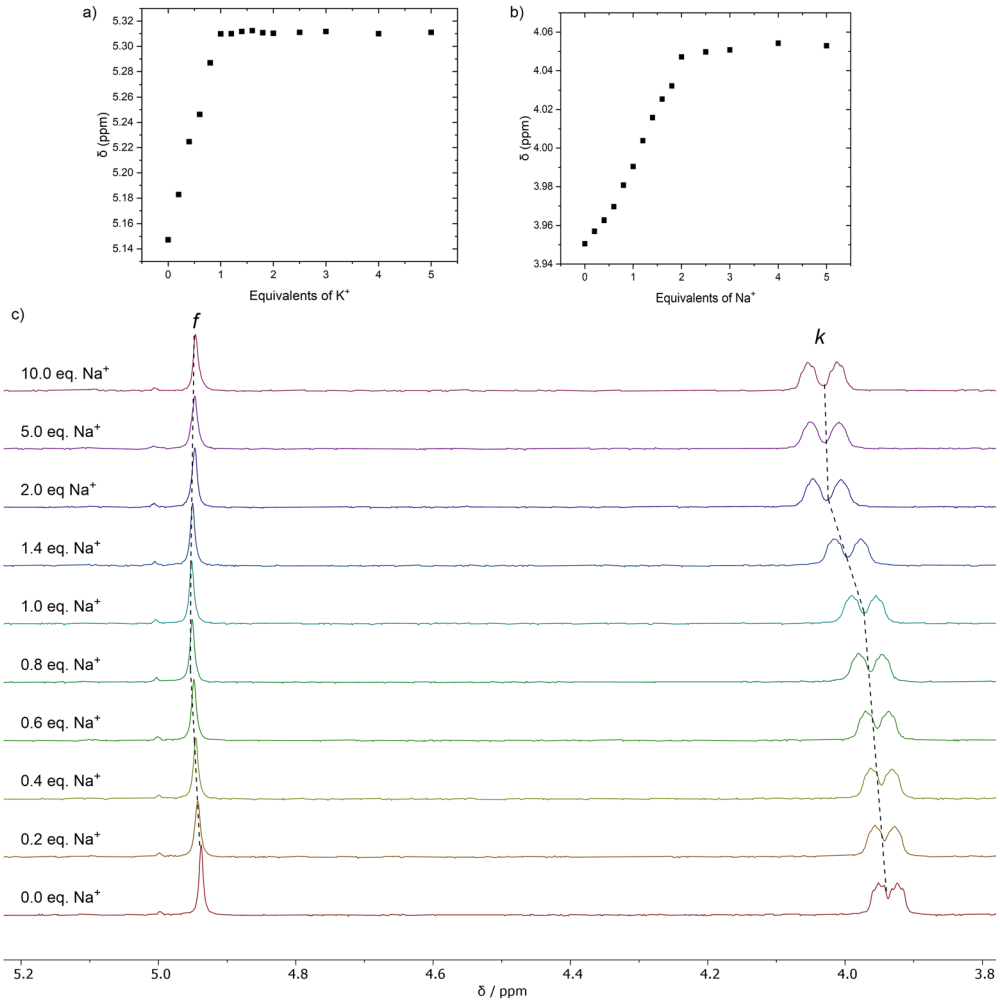

Fig. 3 (a) Binding isotherm showing ^{1}H NMR (500 MHz, 298 K, 1 : 1 v/v $CDCl_3$: CD_3CN) resonance of proton H_f of **6·Ni** upon sequential addition of $KBAr^F{}_4$ solution. (b) Binding isotherm showing ^{1}H NMR (500 MHz, 298 K, 1 : 1 v/v $CDCl_3$: CD_3CN) resonance of proton H_k of **6·Ni** upon sequential addition of $NaBAr^F{}_4$ solution. (c) Stacked partial ^{1}H NMR (500 MHz, 298 K, 1 : 1 v/v $CDCl_3$: CD_3CN) spectra of **6·Ni** upon sequential addition of $NaBAr^F{}_4$ solution.

Furthermore, to investigate the impact of the size of the anion binding pocket in the receptor·K^+ sandwich complex, the regioisomeric congener **8·Ni**, with the crown-ether appendage *meta*, rather than *para*, to the imine substituents of the salen phenyl rings was also prepared using a modified synthesis of **6·Ni**, using 2,3-dihydroxybenzaldehyde and sodium hydride in the first step of the synthesis in place of 2,4-dihydroxybenzaldehyde and K_2CO_3,[8] forming **8·Ni** in 38% overall yield (Scheme 3b).¶

Alkali metal cation binding studies

^{1}H NMR binding titrations were performed, using sodium and potassium alkali metal tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate ($BAr^F{}_4{}^-$) salts, on account of the non-coordinating nature of the sterically bulky $BAr^F{}_4{}^-$ anion. Upon successive additions of the alkali metal salts to 1 : 1 v/v $CDCl_3$: CD_3CN solutions of **6·Ni**, as expected marked downfield shifts in the crown ether proton resonances, $H_{k–r}$, were observed, consistent with binding of the respective alkali metal cation by the B15C5 moiety (see SI, Fig. S34 and S35).

Importantly, these binding studies revealed significant differences in the binding mode depending on the identity of the alkali metal cation. While in both cases binding was near-quantitative ($K_a > 10^5$ M^{-1}), the ^{1}H NMR shift magnitudes in the B15C5 protons plateaued after addition of one equivalent of K^+ (Fig. 3a), but continued until two equivalents of Na^+ were added (Fig. 3b), strongly indicating 1 : 1 and 1 : 2 host : guest binding stoichiometries respectively.[37] Upon addition of K^+, a significant ($\Delta\delta \approx 0.2$ ppm) downfield shift in the methylene proton resonance H_f was also observed, while no such shift ($\Delta\delta < 0.01$ ppm) was observed upon Na^+ binding (Fig. 3c). Such a difference in behaviour is attributed to a change in conformation of the B15C5 binding pendants, which fold inwards to enable the formation of an intramolecular 2 : 1 B15C5 : K^+ sandwich complex. The lack of any such shift upon sodium cation binding, coupled with B15C5 shifts indicating 1 : 2 host : guest binding stoichiometry confirms that the smaller Na^+ cation is bound in each B15C5 moiety. Analogous perturbations

¶ Attempts at preparing the iodotriazole halogen-bonding analogues of **6·Ni** and **8·Ni**, *via* a range of synthetic methodologies, were unfortunately unsuccessful.

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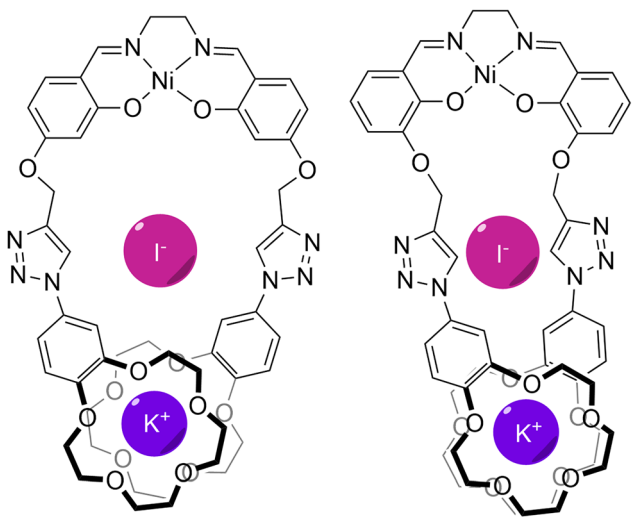
were observed for alkali metal cation binding studies conducted with **8·Ni**, indicating this regioisomeric receptor displays the same distinct stoichiometric binding modes for Na^+ and K^+.

Preliminary ion-pair binding studies

The inherent conformational preorganisation of **6·Ni**·K^+ and **8·Ni**·K^+ resulting from intramolecular bis-B15C5:K^+ sandwich complex formation was predicted to form a cavity in which an anion could be potentially bound through a combination of hydrogen bonding C—H···A^- interactions from the HB-donor triazole motifs and favourable proximal electrostatic effects between the anion and the co-bound K^+ cation.[44]

To this end, ^{1}H NMR halide anion and ion-pair host–guest binding studies were performed on **6·Ni** and **8·Ni**, in the absence and presence of one equivalent of KPF_6 in 1 : 1 v/v CD_3CN : $CDCl_3$. In the absence of K^+, no significant perturbations were observed in the ^{1}H NMR spectra of **6·Ni** or **8·Ni** upon sequential addition of a TBAX (X = Cl, Br, I) salt. In contrast, upon addition of TBAI to an equimolar solution of receptor and KPF_6, significant downfield perturbations in the triazole proton H_g were observed, strongly suggesting I^- was bound in the cavity between the bis-B15C5 complexed potassium cation and the triazole HB donor groups (Fig. 4). Analysis of the resulting binding isotherms, using Bindfit,[36] revealed a 1 : 1 host : guest binding stoichiometry and enabled the calculation of apparent anion binding constants (K_{app}) revealing a modest I^- association with **6·Ni**·K^+ K_{app} = 26 M^{-1}, and a notably stronger association of the large halide anion with **8·Ni**·K^+ K_{app} = 270 M^{-1}. The approximately ten-fold increase in K_{app} I^- for **8·Ni**·K^+ over **6·Ni**·K^+ may be attributed to enhanced triazole C–H···I^- interactions due to the relatively smaller anion binding cavity (Fig. 4).

Upon successive addition of TBACl or TBABr to equimolar solutions of **6·Ni** or **8·Ni** and one equivalent of KPF_6 in the same 1 : 1 v/v CD_3CN : $CDCl_3$ solvent medium, visible precipitation of the halide salt KX (X = Cl or Br) was observed, indicating the relatively weak halide anion binding was unable to overcome the higher lattice energy of these KX salts, resulting in salt recombination, and preventing the determination of K_{app}. Nevertheless, intramolecular bis-B15C5:K^+ sandwich complex formation with both Ni(II) salen complexed species clearly facilitates halide anion binding and may provide a selective mechanism for ON/OFF switchable co-catalyst binding for ROCOP reactions.



6·Ni·K^+I^- **8·Ni**·K^+I^-

Fig. 4 Proposed K^+/I^- ion-pair binding mode of **6·Ni** and **8·Ni**.

Conclusions

Ni(II) salen complexes, functionalised with anion and cation binding motifs were prepared using initial alkyne–azide CuAAC 'click' chemistry to produce triazole precursors and subsequent Schiff-base condensation and transition metal complexation. Such an approach represents a facile modular methodology for the synthesis of functionalised transition metal salen complexes, providing a potential future direction for the production of potent transition metal salen catalysts.

The incorporation of halogen bonding iodotriazole groups to the salen complexes $\mathbf{4^{Bn}}$**·Ni** and $\mathbf{4^{ArF}}$**·Ni**, enabled the strong binding of halides in the competitive 20% DMSO-d_6 v/v in $CDCl_3$ solvent medium, with binding affinities notably augmented by the polarisation of the iodotriazoles with electron-withdrawing per-fluorophenyl substituents.

Synthesis of Ni(II) salen complexes **6·Ni** and **8·Ni** with bis-appended B15C5 cation-binding sites revealed an alkali metal cation-dependent binding mode selectivity, with binding of K^+ selectively forming an intramolecular bis-B15C5 sandwich complex. Importantly, this results in an anion binding cavity wherein iodide was co-bound as evidenced from ^{1}H NMR titration experiments. These preliminary observations demonstrate the applicability of utilising a supramolecular chemistry approach to functionalise the salen ligand framework in order to provide a platform for stimuli-responsive transition metal catalytic complexes with potential application in ON/OFF switchable catalysis.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this manuscript are available in the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d5nj04351d.

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