Results and Discussion

In the $^1$H NMR spectra of $L^2$ and $ML^2$, there are two well resolved signals, one due to the 2 equivalent sets of CH$_2$ protons and 1 due to the remaining CH$_2$ protons (see Figure S1) and both are affected by added anions in a similar manner. The change in chemical shifts of the methylene protons was used to determine the association constants ($K_a$) in the presence of anions such as fluoride and succinate (as a tetrabutyl ammonium salt) at various concentrations but constant temperature (25 °C) (see Figures S2 and S3). In a typical titration, a total of 1 mL of the solution of (fluoride or succinate) anion was titrated in 0.05 mL aliquots into 1 mL of a 0.01 M receptor solution ($L^2$ or $ML^2$) resulting in an anion concentration range from 0.0038 to 0.04 M. Acetone-d$_6$ was used in the case of $L^2$, whereas CD$_3$CN was used in the case of $ML^2$ (M= Zn or Cd). On each addition the mixture was allowed to equilibrate and the NMR spectrum was recorded. Significant changes in the chemical shift of the methylene protons are found in the NMR titration of receptor ($L^2$) with fluoride and succinate anions (Fig. S4 and S6). In all titrations, the concentration of the receptor was kept constant.
The titration curves for fluoride and succinate with L^2 are different and suggests a stronger binding for succinate (Fig. S2 and S3). This stronger binding has been confirmed when calculating the binding constant using an in-house written multiple independent (binding) sites (MIS) model in the Origin programme. Both the succinate and fluoride data sets have been analysed globally, i.e. both the titration curves (corresponding to the two sets of CH2 protons) in each graph were used during the data analysis. The MIS model used assumes the presence of N identical binding sites on each ligand (complex) and the same binding affinity of the anion for each of these identical binding sites. The best-fit binding parameters are (K_a = 4,265 M^-1 and N = 2.8) for fluoride and slightly stronger binding for succinate (K_a = 16,190 M^-1 and N = 1.7). The binding stoichiometry N of 1.7 for succinate binding together with the availability of two hydrogen-bond donating sites in L^2 suggests a 2:1 binding mode. The apparent binding stoichiometry N of 2.8 for fluoride is significantly higher than 2, which would be difficult to reconcile with the structure of L^2. We note, however, that standard NMR tubes were used in these experiments and that this may have led to some loss of fluoride
anion. The stoichiometry of 2.8 is therefore an upper estimate and the underlying binding event likely involves a 2:1 stoichiometry, as was the case for succinate.

Finally, the MIS model is a relatively simple binding model (vide supra) and the observation of a 2:1 binding mode may suggest the use of more elaborate models. For example, one could propose a model in which an initial 1:1 complex involving cooperative hydrogen bonding (as illustrated in Figure S1) eventually accepts a second anion. Although such a model would be reasonable, in principle, our data is reproduced very well by the MIS model and does not appear to warrant analysis in terms of extended binding models.

![Figure S2: Fluoride titration into L².](image)

![Figure S3: Succinate titration into L².](image)
Figure S4: The changes in chemical shift of the 2CH₂ and 1CH₂ peaks in the ¹H NMR titration of receptor L² with the fluoride anion in (CD₃)₂CO solution at (25 °C). various equivalents of the F⁻ illustrated on the graph.

Figure S5: ¹H NMR titration curves of the receptor L² (0.01 mM) and the guest F⁻ (0.04 mM) (as tetrabutylammonium salts) in (CD₃)₂CO at (25 °C). Small aliquots of anion solutions of (0.05 mL) were added to the NMR tube without changing the overall concentration of the receptor.
Figure S6: The changes in chemical shift of the 2CH$_2$ and 1CH$_2$ peaks in the $^1$H NMR titration of receptor L$^2$ with the succinate anion in (CD$_3$)$_2$CO solution at (25 °C). various equivalents of the succinate$^{2-}$ illustrated on the graph.

Figure S7: $^1$H NMR titration curves of the receptor L$^2$ (0.01 mM) and the guest succinate$^{2-}$ (0.04 mM) (as tetrabutylammonium salts) in (CD$_3$)$_2$CO at (25 °C). Small aliquots of anion solutions of (0.05 mL) were added to the NMR tube without changing the overall concentration of the receptor.
Titration of [ML₂]²⁺ with F⁻ or succinate

Interestingly, for Zn and Cd L² complexes, different behaviour is observed in the ¹H NMR spectra as more than 2 sets of peaks are observed for the two methylene groups, suggesting a more complex situation (Figures S8-S15). It seems likely we are observing slow exchange strongly suggesting strong binding between anion and the metal-based receptor. Perhaps this may be indicating a co-ordination of the anion to the metal centre leading to lower symmetry and perhaps multiple species in solution. Clearly this data cannot be interpreted using our MIS model, as the products are not in fast exchange and it appears that there are complex equilibria being observed.

A further investigation should be carried out for these systems. At higher temperature we may observe fast exchange behaviour in the ¹H NMR spectra, allowing us to determine binding constants. Alternatively, we might try an approach utilising dye displacement allowing us to determine binding constants by UV-Vis spectroscopy.

Figure S8: The changes in chemical shift of the 2 CH₂ and 1 CH₂ peaks in the ¹H NMR titration of receptor ZnL²⁺ with the fluoride anion in CD₃CN solution at (25 °C). various equivalents of the F⁻ illustrated on the graph.
Figure S9: $^1$H NMR titration curves of the receptor ZnL$^2$ (0.01 mM) and the guest F$^-$ (0.04 mM) (as tetrabutylammonium salts) in CD$_3$CN at (25 °C). Small aliquots of anion solutions of (0.05 mL) were added to the NMR tube without changing the overall concentration of the receptor.

Figure S10: The changes in chemical shift of the 2CH$_2$ and 1CH$_2$ peaks in the $^1$H NMR titration of receptor ZnL$^2$ with the succinate anion in CD$_3$CN solution at (25 °C). various equivalents of the succinate$^-$ illustrated on the graph.
Figure S11: $^1$H NMR titration curves of the receptor $\text{ZnL}_2$ (0.01 mM) and the guest succinate$^2$ (0.04 mM) (as tetrabutylammonium salts) in CD$_3$CN at (25 °C). Small aliquots of anion solutions of (0.05 mL) were added to the NMR tube without changing the overall concentration of the receptor.

Figure S12: The changes in chemical shift of the 2 CH$_2$ and 1 CH$_2$ peaks in the $^1$H NMR titration of receptor CdL$^2$ with the fluoride anion in CD$_3$CN solution at (25 °C). various equivalents of the F$^-$ illustrated on the graph.
Figure S13: \(^1\)H NMR titration curves of the receptor CdL\(^2\) (0.01 mM) and the guest F\(^-\) (0.04 mM) (as tetrabutylammonium salts) in CD\(_3\)CN at (25 °C). Small aliquots of anion solutions of (0.05 mL) were added to the NMR tube without changing the overall concentration of the receptor.

Figure S14: The changes in chemical shift of the 2 CH\(_2\) and 1 CH\(_2\) peaks in the \(^1\)H NMR titration of receptor CdL\(^2\) with the succinate anion in CD\(_3\)CN solution at (25 °C). various equivalents of the succinate\(^2\) illustrated on the graph.
Figure S15: $^1$H NMR titration curves of the receptor CdL$_2$ (0.01 mM) and the guest succinate$^{2-}$ (0.04 mM) (as tetrabutylammonium salts) in CD$_3$CN at (25 °C). Small aliquots of anion solutions of (0.05 mL) were added to the NMR tube without changing the overall concentration of the receptor.
# Experimental

$^1$H NMR spectra were measured on a Bruker AC-250 Plus FT-NMR spectrometer. All the titration experiments were recorded using deuterated solvents (CD$_3$)$_2$CO for (L$^2$-G) and CD$_3$CN for ( ML$^2$-G) at room temperature (G = Fluoride or Succinate; M = Zn$^{II}$ or Cd$^{II}$).

1- In an NMR tube was added 1 mL of (CD$_3$)$_2$CO or CD$_3$CN containing 0.01 mmol of host.

2- A stock solution was made of 1 mL of (CD$_3$)$_2$CO or CD$_3$CN containing 0.01 mmol of the host together with 0.08 mmol of Bu$_4$N$^+$F$^-$ or (Bu$_4$N$^+$)$_2$ succinate$^{2-}$.

3- 0.05 mL aliquots of guest solution were added and the $^1$H NMR spectrum was recorded after every addition. Each addition of 0.05 mL by micropipette contains 0.004 mmol of guest. Overall, after 20 additions the final ratio of host to guest was 1:8. Note that the concentration of host remains constant at all times.

4- The variation of the chemical shift of the protons on the methylene groups was plotted as a function of the concentration of added anionic guest.