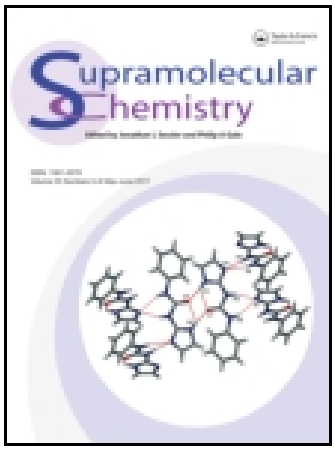

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Neutral Re(I) complexes for anion sensing

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Anion sensing properties toward F^-, OAc^- and $H_2PO_4^-$ were studied for new mononuclear and dinuclear Re(I) complexes based on a five-substituted phenanthroline moiety bearing a thiourea hydrogen-bonding receptor. Log($K_{1:1}$) values between 4 and 6 were obtained for the complexes by UV–vis titrations and between 3 and 5 by ^{1}H NMR titrations. The effect of hydrogen-bonding versus deprotonation of the thiourea receptor upon addition of the anions was also evaluated by UV–vis and NMR titration techniques. In addition, an X-ray structure of the Re(I) precursor complex is reported and the chirality of the mononuclear and dinuclear complexes is discussed.

Keywords: neutral Re(I) complexes; anion binding; thiourea receptors

Introduction

The field of anion recognition has been growing at an impressive rate since the start of the new millenium (*1*). One reason is that anions are ubiquitous throughout biological systems as they carry genetic information (DNA is a poly-anion) and the majority of enzyme substrates and co-factors are anionic (*2*, *3*). Thus, anion binding and recognition have attracted intense interest (*1–10*), and metal complexes have played an important role in anion receptor chemistry since its earliest examples (*11*, *12*). The presence of a metal ion can introduce a range of advantageous physicochemical properties to this class of receptor (*12*). Recently, Gale and co-workers (*13*) have shown that introduction of a transition metal into a purely organic system can enhance its anion binding capabilities dramatically. While both metal–ligand interaction (*11*, *14–16*) and van der Waals interactions (*8*, *9*, *17–19*) are employed to study anion binding phenomena, neutral metal complexes are challenging candidates for anion binding as the electrostatic component is not an available mode of interaction. With a few exceptions of metallocene complexes (*12*, *20*), neutral metal-based optical anion sensors are less well known. Neutral anion sensors with Re(I) as the metal centre are of particular interest, but their synthesis usually involves multiple steps (*21–24*). Recently, neutral alkynylrhenium(I) tricarbonyl diimine complexes with a triarylboron moiety, which can bind to F^- with a stability constant in the range of 10^5 was reported (*25*). This high binding constant is due to the interaction between the highly Lewis acidic and electron-accepting triarylboron moiety and the electron-rich guest F^-. Another report by Lin et al. (*26*) shows that a dinuclear neutral Re(I) complex with quinoxaline-bis(sulphonamide) functionalisation can be active as a good anion binder where both sulphonamide groups can orient themselves to a conducive position to form a cleft around the incoming anion. A similar approach reported earlier by Beer's group to surround the anion by amide functionalities attached to a Re(I) core lead to reasonably strong binding constants (*ca*. between 35 and 1790 depending on the anion and the receptor system) (*24*, *27*). Recently, the group of Lees circumvented this synthetic drawback by reporting the preparation of thioamide, urea and especially of readily accessible thiourea Re(I) bridged complexes, along with their use as luminescent anion receptor (*28*). Herein, we report the anion-binding properties of two neutral Re(I) complexes (**3** and **4**) also with a thiourea moiety as the anion receptor group, which can be synthesised very readily. A comparative anion sensing study by UV–vis and NMR titrations has been done in order to better understand the effect of hydrogen-bonding versus deprotonation of the thiourea receptor upon addition of monoanionic F^-, OAc^- and $H_2PO_4^-$ on the binding constants obtained.

Results and discussion

Our target ligand for combining both a bidentate binding site and a scaffold for the thiourea group was a 5-substituted phenanthroline. The reaction of 1,10-phenanthrolin-5-amine with $Re(CO)_5Br$ in refluxing toluene gave Re(I) complex **1** in 96% yield. Treatment of **1** with thiophosgene in the presence of Na_2CO_3 gave isothiocyanate functionalised

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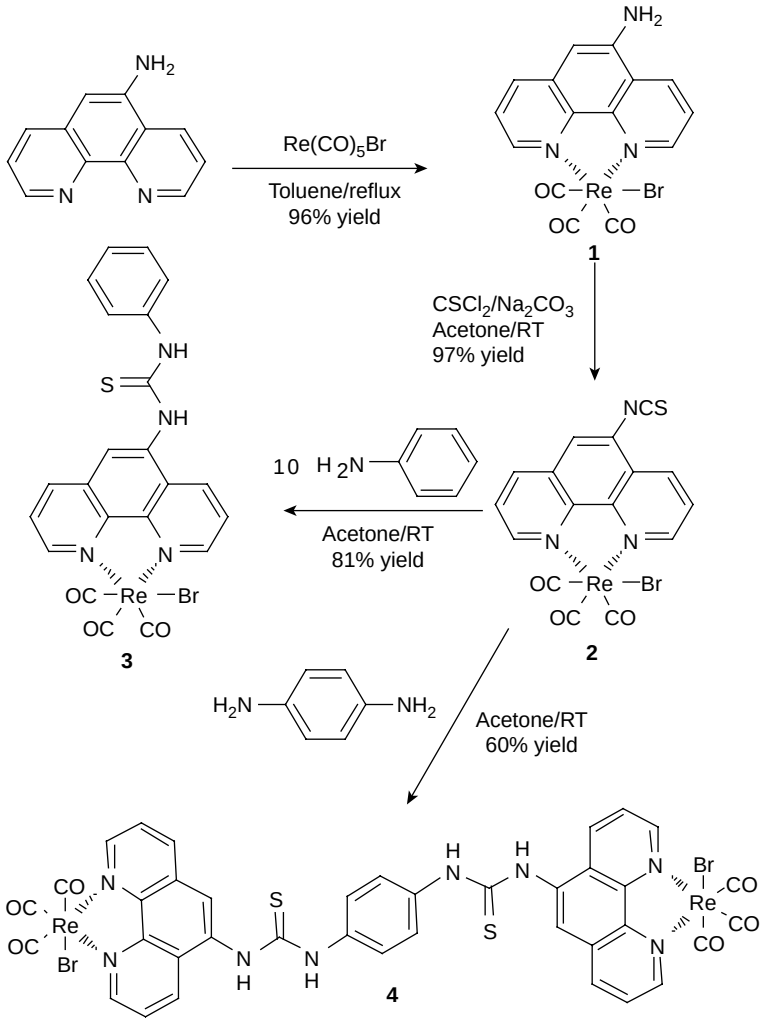
Re(I) complex **2** in nearly quantitative yield. Complex **2** proved to be a good precursor for the synthesis of thiourea [(—$NH)_2$C═S] containing rhenium(I) complexes. Reaction of **2** with 10 equiv. of aniline in acetone at ambient temperature and under inert atmosphere afforded the neutral Re(I) complex **3** containing thiourea receptor group in 81% yield (Scheme 1). Under similar conditions, reaction of **2** with p-phenylenediamine in a 2:1 ratio afforded the dinuclear neutral Re(I) complex **4** with two thiourea receptor units in 60% yield. All of the complexes were characterised by NMR spectroscopy, high-resolution mass spectrometry (HR-MS) and elemental analysis.

The isothiocyanate precursor **2** was further structurally characterised by X-ray crystallography (Figure 1). Complex **2** crystallises in triclinic $P\bar{1}$ space group with an acetone molecule as solvate. Complex **2** presents an octahedral ligand arrangement with a facial tricarbonyl moiety. A bidentate diimine ligand and a bromide fill its octahedral coordination sphere. The two equatorial carbonyl ligands, the rhenium centre and aromatic rings of the phenanthroline ligand are in a nearly ideal planar arrangement. The plane containing atoms C16, N3 and S deviates from the plane formed by N1, N2, Re, C2, C3 by only 4.5(0.4)°. Bond lengths and angles around the metal centre are comparable to those in closely related compounds (see ESI) (*29*, *30*). The C—Re bond lengths (1.921(4) and 1.919(3) Å) *trans* to phenanthroline are shorter than the C—Re bond *trans* to the anionic Br ligand (1.984(4) Å) due to increased backbonding from Re(I) with the π-donating Br ligand. The C—O bond distances, as a consequence, show the reverse trend. Whereas the equatorial C—O bonds are 1.147(4) and 1.149(4) Å, the one *trans* to the bromide is 1.034(5) Å, displaying considerably less backbonding from the Re(I) centre. The Re—Br bond is 2.6167(7) Å whereas the two Re—N bonds are almost identical at 2.180(3) Å. The isothiocyanate group is almost linear with a N—C—S angle of 175.19(0.35)°. The molecule is chiral on Re-atom, but the



Scheme 1. Synthesis of the neutral Re(I) complexes: precursors **1** and **2** and thiourea receptors **3** and **4**.

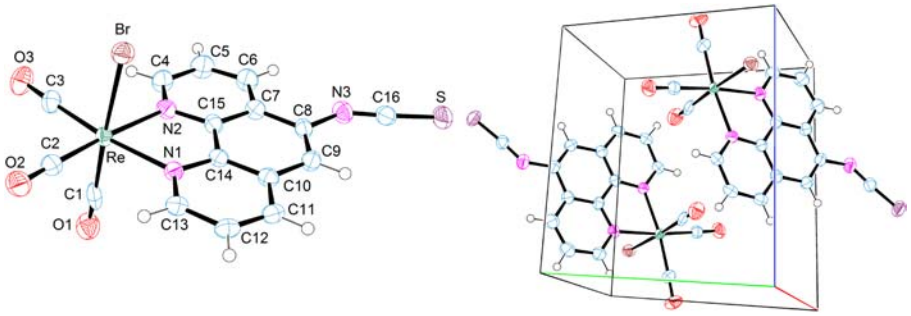


Figure 1. (Left) Ortep representation of **2** drawn at 50% probability level, showing a view of the molecule from above of the molecule. (Right) Ball and stick model of two different enantiomeric views of the chiral molecule. H atoms and the solvated acetone molecule have been omitted for clarity.

effect of this chirality is faded to affect the hydrogen bonding property of the thiocyanato group due to the long distance between the chiral Re-centre and the thiocyanate group.

The electrochemical behaviour of complexes **3** and **4** has been examined by cyclic voltammetry at a glassy carbon electrode in purified *N*,*N*′-dimethylformamide (DMF) under a dry argon atmosphere. At positive potentials, complex **3** shows an irreversible oxidation at 0.85 V versus saturated calomel electrode (SCE), attributable to the oxidation of the thiourea group, similar to that reported for the oxidation of a thiourea group of a cationic Re(I) polypyridyl complexes with thiourea receptors (*29*). As the Re(I/II) oxidation couples for similar rhenium complexes are reported to appear beyond 1.8 V versus SCE, we did not observe any such couples within the solvent potential window of DMF. At negative potentials, the quasi-reversible diimine-based reduction is observed at − 1.38 V versus SCE. Similar values were also reported earlier for reduction of the diimine ligand in Re(I) carbonyl complexes (*31*, *32*). For complex **4**, the irreversible oxidation and reduction are observed at 0.90 V versus SCE and − 1.36 V versus SCE, respectively.

The monoanionic ions F^-, OAc^- and $H_2PO_4^-$ are well known to bind to thiourea (*31–36*) and, therefore, we studied their binding to the Re(I) thiourea complexes (Figures 2 and 3; ESI). However, as thiourea receptors are subject to a deprotonation of relatively acid NH's when a strong conjugated anionic base like OAc^- is added (*37*), efficiency of the anion sensing properties of our organometallic systems needed to be establish. In facts, Yatsimirsky et al. showed that deprotonation is favoured in highly diluted solutions due to a ratio of H-bonded and deprotonated forms of thiourea linkage being proportional to the total receptor concentration. Similar results of acid–base reaction were also observed by Gale and co-workers (*38*) for 3,4-dichloro-2,5-diamidopyrroles. Consequently, we were curious to establish to which extent apparent binding constant (K_{app}) values resulting from such multi-equilibrium systems would be affected by varying the

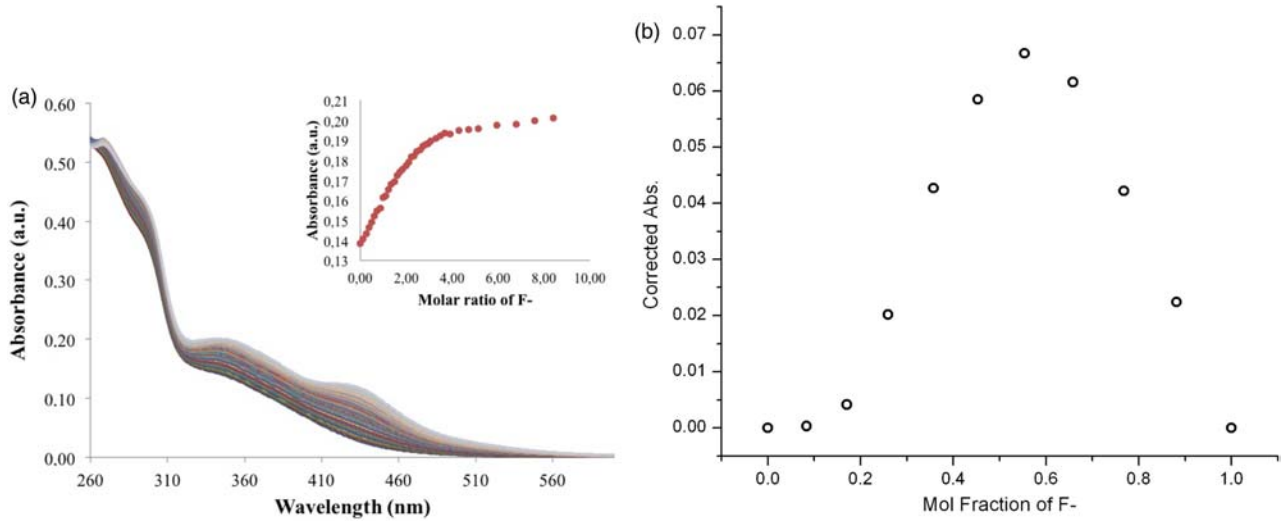


Figure 2. (a) UV–vis titrations of receptor **3** (1.5×10^{-5} M) with F^- in DMSO–0.5% water. Inset: Corresponding titration profile at 347 nm. (b) Job plot of receptor **3** with F^- in DMSO–0.5% water at 440 nm, showing 1:1 binding.

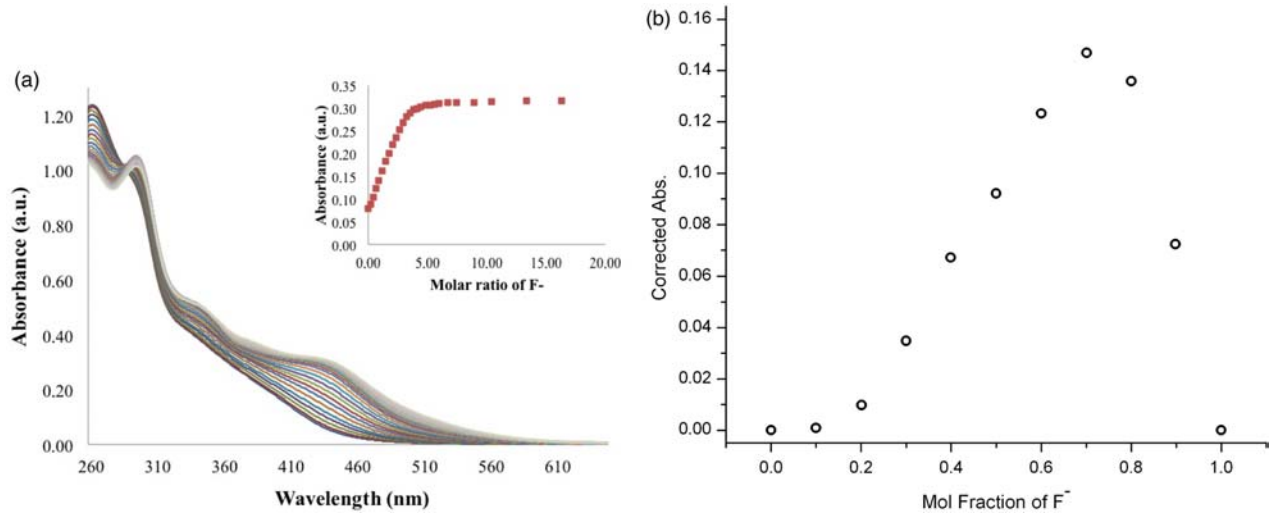


Figure 3. (a) (Left) UV–vis titrations of receptor **4** (1.5×10^{-5} M) with F^- in DMSO–0.5% water. Inset: Corresponding titration profile at 430 nm. (b) (Right) Job plot of receptor **4** with F^- in DMSO–0.5% water at 450 nm, showing 1:2 receptor to anion binding.

Table 1. Apparent binding constants (K_{app}) determine by UV–vis and NMR titrations.

		UV–vis[a]		NMR[b]		
Compound	Anion[c]	Log($K_{1:1}$) (±0.1)	Log($K_{2:1}$) (±0.1)	Log($K_{1:1}$) (±0.2)	Log($K_{2:1}$) (±0.2)	Log($K_{3:1}$) (±0.2)
3	F^-	4.4	NA	3.7	NA	NA
	OAc^-	5.8	NA	3.9	8.9	NA
	$H_2PO_4^-$	4.7	NA	2.8	6.2	NA
4	F^-	3.9	10.3	3.6	5.8	3.0
	OAc^-	5.4	11.2	4.8	9.0	6.1
	$H_2PO_4^-$	5.7	9.8	2.9	5.5	4.0

[a] Acquisitions at 298 K. In DMSO–0.5% H_2O (v/v). Data fitted with the HypSpec software.
[b] Acquisitions at 298 K. In DMSO-d_6–0.5% H_2O (v/v). Data fitted with the HypNMR2008 software.
[c] All anions were added as their TBA salts.

concentration from a 1.5×10^{-5} M of complexes by UV–vis to a 200-fold concentration of 3×10^{-3} M by NMR (Table 1).

The UV–vis anion-binding studies were performed in a DMSO–0.5% water medium (Figure 2 and ESI). Absorption spectra of both complexes show intense intra-ligand ($\pi \rightarrow \pi*$) absorption bands in the range of 260–300 nm. The less intense absorption shoulder between 350 and 400 nm is assigned to a spin-allowed metal-to-ligand charge-transfer (^{1}MLCT) ($d\pi(Re) \rightarrow \pi*(phen)$) transition. On addition of the F^-, OAc^- and $H_2PO_4^-$ ions as their tetrabutyl ammonium (TBA) salts during titration of **3** and **4**, gradual rises in the absorption at *ca*. 350 and 440 nm were observed.

The use of Job plots by UV–vis allowed a preliminary fitting of the data to a 1:1 complex:anion model for **3** (ESI) and to 1:2 for **4** (Figure 3 and ESI). While some of the results tend to be slightly offset from the ideal fittings, e.g. **3** with F^- and $H_2PO_4^-$, it appears that a deprotonation equilibra exist in the system. Moreover, it has already been established by Jurczak and co-workers (*39*) that the deprotonation process on bishydrazide derivatives of isoindoline induced the appearance of a new band between 390 and −445 nm, a behaviour very similar to what is observe in our case around 440 nm.

UV–vis titration curves allowed for the determination of K_{app}. Values obtained in log(K_{app}) for a 1:1 anion to complex **3** are 4.4 (F^-), 5.8 (OAc^-) and 4.7 ($H_2PO_4^-$). It is noteworthy that $K(OAc^-)/K(H_2PO_4^-)$ is ∼12.6 and $K(OAc^-)/K(F^-)$ is ∼25, which demonstrates a preference for the acetate anion. The K values obtained for **3** are considerably higher than those previously reported for neutral Re(I) complexes with cleft-type amide receptors (*22*) and of a similar magnitude for positively charged Re(I) polypyridyl complexes with thiourea receptors (*31*, *40*). Strong binding with neutral receptors is remarkable as favourable electrostatic interactions are usually one of the stongest contributors to anion-binding (*4–6*). The Re(I) centre is an excellent electron-withdrawing (EWG) group that acidifies the NH group and the extended π-conjugation of the phenanthroline stabilises the deprotonated form of the receptor by delocalisation of the charge.

This combination of structural elements could be offering an increased tendancy for deprotonation over H-bonding behaviour and, therefore, the apparent binding constant should be driven by basicity of the anion used. Following this idea, a quick look at the pK_a table for acetic acid (4.76), hydrofluoric acid (3.17) and phosphoric acid (2.12) gives an insight that acetate anion is the strongest conjugate base of the three. Between $H_2PO_4^-$ and F^-, the latter should be stronger, but the higher solvation of unbound F^- in presence of water molecules should hinder its ability to deprotonate the thiourea group. All together, this rationalisation seems to support the K_{app} obtained empirically for the mono-receptor complex **3**.

Complex **4** also shows high apparent stability constants for the three anions. Having two identical receptor sites, **4** is expected to furnish two K_{app} values, $K_{1:1}$ and $K_{2:1}$, respectively, where the latest should be lower due to disfavourable electrostatic arguments. The log(K_{app}) values obtained for **4** are 3.9 and 10.3 (F^-), 5.4 and 11.2 (OAc^-); 5.7 and 9.8 ($H_2PO_4^-$). Those values are greater than the ones found for other bis-thiourea receptors (*37*), although the contribution of deprotonation must also be considered. Interestingly enough, the results obtained clearly exhibit a $K_{2:1}$ between *ca*. 4 and 6 orders of magnitude higher than the $K_{1:1}$, which at first look might seem counterintuitive. However, a precedent in literature is known from Jurczak and co-workers (*39*) where the interaction of $H_2PO_4^-$ with a mono-receptor led to a $K_{2:1}$ of three orders of magnitude higher than $K_{1:1}$ (i.e. $\log(K_{2:1}) = 7.2$ vs $\log(K_{1:1}) = 4.3$). While no formal explanation for the presence of a second binding constant was reported there, it seems plausible that the presence of two hydrogens on hydrophosphate anions can play a role, that is, multiple H-bonding with the receptor's heteroatoms of their hydrazide linkages might add their effect to the classical NH bond interaction. In our case, as observation of the second binding constants for F^-, OAc^- or $H_2PO_4^-$ all displayed a higher value than the first one in a system where no multiple H-bonding of the anion with receptors was possible, it seems that the presence of deprotonated receptors do interfer with a good fitting of data. To further prove that idea and evaluate its impact, NMR titrations were also performed (*41*).

NMR titration experiments were conducted in a 99.5% DMSO-d_6/0.5% H_2O solvent mixture to match with the conditions used in UV–vis tritration. As mentioned previously, a 200-fold higher concentration of complexes **3** and **4** was used, i.e. 3×10^{-3} M, in order to evaluate the impact of concentration on the K_{app} observed at a suitable concentration for NMR. To keep the overall concentration of complex **3** constant throughout the titration, microlitre-scale additions of a solution containing ~30-fold higher concentration of the anion as its TBA salt (1×10^{-1} M) over the complex were done to 0.7 ml of starting solution containing the complex alone (Figure 4 and ESI). Initial increments of 0.2 equiv. were used until 2 equiv. of anion was reached, followed by 1 equiv. additions until the final 6 equiv. was reached. For complex **4**, which bears two thiourea receptor groups, the same starting concentration of complex was used, but initial increments of 0.25 equiv. were used until 6 equiv. of anion was reached, followed by 2 equiv. additions until the final 10 equiv. was reached (Figure 5 and ESI). Interestingly, both complexes exhibit broadening then quick disappearance of the two NHs signals (around 10.25 ppm) upon addition of the various anions, which has been noted previously during deprotonation (*39*). Based on stabilisation arguments, the NH proton next to the phenanthroline moiety is the more likely to be deprotonated.

For determination of K_{app}, the three peaks showing biggest variation in ppm were used in order to diminish the potential error on the binding constant obtained. *A priori*, one might think that the protons providing higher variations in shift upon addition of anions should be the nearest to the thiourea receptor. However, peaks presenting this behaviour are the ones allowing the stabilisation of an electronic charge by delocalisation. In this respect, positions 3-, 7- and 9- on the phenanthroline moiety are the more sensible to receive this charge. Therefore, they should exhibit the largest shift during the titration. In complex **3**, the ^{1}H NMR shifts of positions 7- and 9-, appearing at 8.94 and 9.41 ppm, respectively, were studied. The H *para* (7.18 ppm) to the thiourea in the phenyl group also exhibited a large shift by NMR. For complex **4**, the peak at position 3- on the phenanthroline (8.08 ppm) replaced the *para*- one of the phenyl for K_{app} determination due to a bigger shift observed in that case. Positions 7- and 9- presented similar NMR displacements as in complex **3**.

Fitting of the data for complex **3** led to K_{app} values in the same order of magnitude as to what was obtained by UV–vis titration ($\log(K_{1:1}) = 3.7 \pm 0.2$ by NMR vs 4.4 ± 0.1 for UV–vis) for F^- (Table 1). However, necessity for a $K_{2:1}$ appeared to better fit data in the cases of stronger conjugate bases $H_2PO_4^-$ and OAc^-. Values of $\log(K_{2:1})$ were higher than the one of one anion binding to one receptor for both OAc^- ($\log(K_{1:1}) = 3.9 \pm 0.2$; $\log(K_{2:1}) = 8.9 \pm 0.2$) and $H_2PO_4^-$ ($\log(K_{1:1}) = 2.8 \pm 0.2$; $\log(K_{2:1}) = 6.2 \pm 0.2$). Data for complex **4** (Table 1) are even more peculiar as they force to consider for a good fitting an association of three anions to one complex bearing two receptors ($K_{3:1}$). While we have no formal explanation for this unusual behaviour from a supramolecular point of view, it might only be artefacts arising from the interference of deprotonation equilibra compared to H-bonding at the concentrations required for NMR experiments. Another point to take in consideration is the appearance in the baseline of NMR spectrums of what seems to be a new species upon addition of anions; potentially due to a decomposition phenomena leading

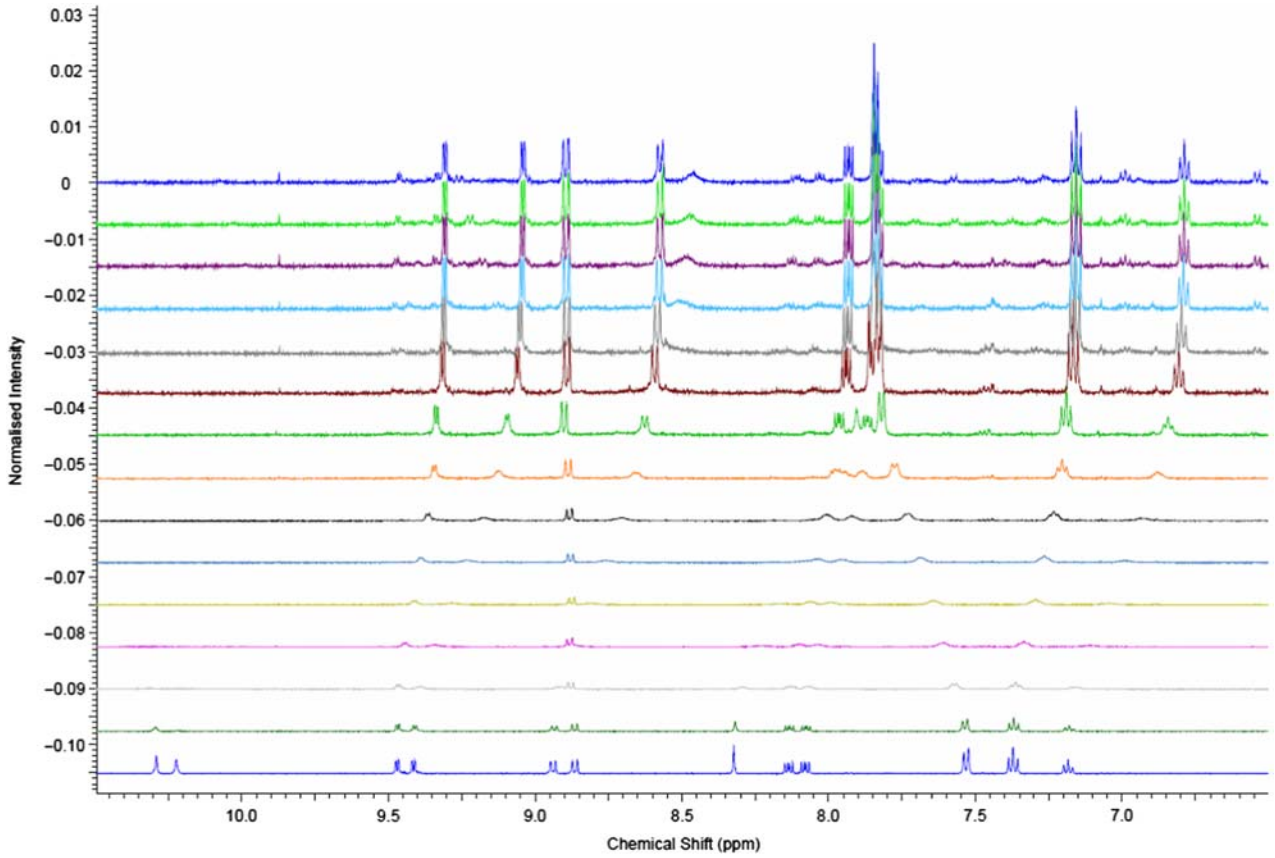


Figure 4. NMR titration of receptor **3** (3×10^{-3} M) from 0 to 6 equiv. of OAc^- added by increments in 99.5% DMSO-d_6/0.5% water. Only aromatic region is shown for clarity.

back to the 5-amino-1,10-diaminophenanthroline derivative in basic conditions. Overall, the titrations by NMR of complexes **3** and **4** allowed a better understanding of the possible deprotonation equilibra in competition with H-bonding, as this technique offers access to structural characterisation of anion interactions with the receptor at higher concentration compared to UV–vis.

Of note, titration attempts were also made using fluorescence emission quenching method; however, no useful results were obtained in order to determine K_{app}. In fact, the appearance of a second emission peak overlapping with the one under evaluation render the tracking of emission maxima impossible. This second peak might be the result of emission from the deprotonated receptor R^-. In any case, this behaviour is an additional point which suggests that a competitive system exists in which both H-bonding and deprotonation equilibria are at play. Decomposition phenomena may also be implied, as the NMR titration experiments showed, a situation that further can affect apparent binding constants.

From a supramolecular point of view, complexes **3** and **4** should be *a priori* integrable into higher order self-assembled structures when combine with suitable H-bonding linkers. Based on that concept, the dianionic terephtalate could potentially form a dimeric structure in the case of **3** and or even a molecular triangle by combining three complexes **4** with three bridging dianions. In order to quickly test if such assemblies were easily accessible, HR-MS studies by direct infusion of 2.8E–03 M solutions of both the complex and the dianion were done under the mildest ESI conditions possible. While self-assembled structures are not always stable in the HR-MS due to the weak nature of H-bonding, many examples were still observed and reported in the literature. Unfortunately, complex **3** exhibited mainly the deprotonated specie $[\mathbf{3} - H]^-$ at 678.9536 *m*/*z* along with a 1:1 assembly with the dianion still bearing one of the two TBA cations $[\mathbf{3} + \text{terephtalate} + TBA]^-$ at 1086.2502 *m*/*z*. For complex **4**, only the doubly deprotonated specie $[\mathbf{4} - 2H]^{2-}$ at 639.9224 *m*/*z* and the TBA-stabilised one $[\mathbf{4} + TBA - 2H]^-$ at 1522.1217 *m*/*z* were observed. Therefore, no indication of dimer or molecular triangle is reportable. However, the presence of deprotonated complexes in the HR-MS for both cases further support the hypothesis of a thiourea deprotonation phenomena.

In conclusion, we have demonstrated in this work a very simple and high-yielding synthetic protocol for mono and polynuclear Re(I) complexes based on a five-substituted

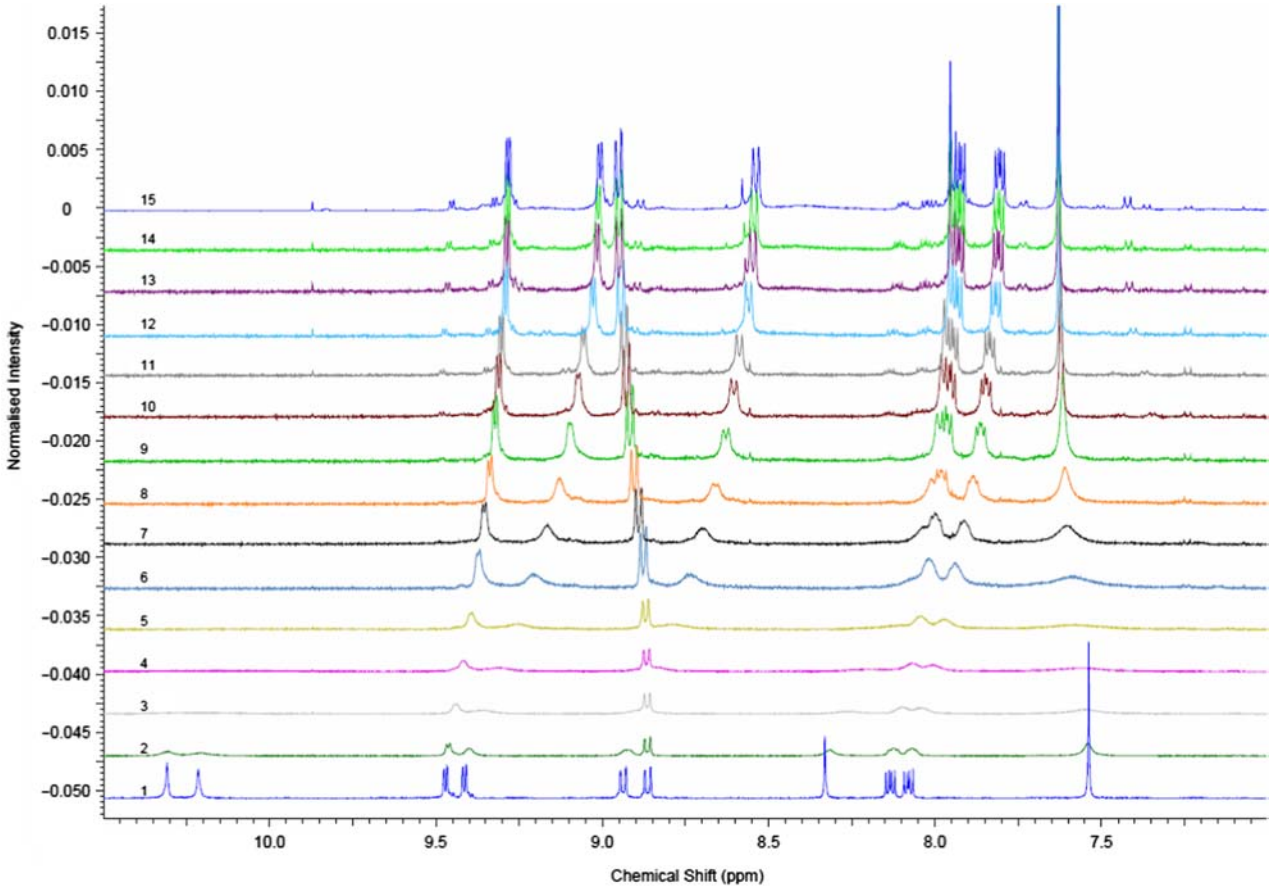


Figure 5. NMR titration of receptor **4** (3×10^{-3} M) from 0 to 12 equiv. of OAc^- added by increments in 99.5% DMSO-d_6/0.5% water. Only aromatic region is shown for clarity.

phenanthroline moiety with thiourea linkages. An X-ray molecular structure of the precursor **2** also confirmed that these systems are inherently chiral. To the best of our knowledge, complexes **3** and **4** in our present work represent the first example of neutral Re(I) complexes with thiourea receptor groups that can be used as anion binding agents. Moreover, we have studied the tendency of thiourea receptors toward deprotonation in presence of F^-, OAc^- and $H_2PO_4^-$ to conclude such an equilibrium might be present in our systems as Re(I) centre can be considered as an EWG, which greatly enhances the NH proton's acidity. In addition, delocalisation into the extended π-conjugation on the phenanthroline moiety may also stabilise the negative charge generated by deprotonation. Future work will be focus towards the incorporation of such high-energy absorbing Re(I) polynuclear complexes by the developed synthetic protocol into artificial molecular antenna for light-harvesting applications.

Experimental section

Experimental NMR spectra were recorded in DMSO-d_6 at room temperature (r.t.) on a Bruker AV400 spectrometer at 400 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR. Chemical shifts are reported in part per million (ppm) relative to residual solvent protons and the carbon resonance of the solvent (1.93 and 33.5 ppm, respectively, for DMSO-d_6). Absorption spectra for UV–vis titration and the Job plot method were measured in DMSO–0.5% water at r.t. on a Cary 500i UV–vis–NIR spectrophotometer. Experimental uncertainties are as follows: absorption maxima, ± 2 nm; molar absorption coefficient, 10%. Solvents were removed under reduced pressure using a rotary evaporator unless otherwise stated.

Re(CO)$_3$Br(5-NH$_2$-phen) (1)

To a suspension of $Re(CO)_5Br$ (406 mg, 1 mmol) in toluene (30 ml) was added the 1,10-phenanthroline-5-amine (200 mg, 1 mmol). The mixture was then stirred and refluxed for 1 h, during which time an orange compound precipitated. After cooling to ambient temperature, the orange precipitate was isolated by filtration and was washed with *n*-hexane and air dried. Yield = 525 mg (96%). ^{1}H NMR (DMSO-d_6, 400 MHz); 9.40 (dd, $J^d = 5.0$ Hz, $J^d = 1.0$ Hz, 1H, H), 9.11 (dd,

$J^d = 9.0$ Hz, $J^d = 1.0$ Hz, 1H), 8.95 (dd, $J^d = 5.0$ Hz, $J^d = 1.0$ Hz, 1H), 8.47 (dd, $J^d = 8.0$ Hz, $J^d = 1.0$ Hz, 1H), 8.05 (dd, $J^d = 8.0$ Hz, $J^d = 5.0$ Hz, 1H), 7.78 (dd, $J^d = 8.0$ Hz, $J^d = 5.0$ Hz, 1H), 7.07 (s, 1H, H_7), 6.90 (s, 2H, —NH_2). Elemental analysis: calcd for $C_{15}H_9BrN_3O_3Re$: C = 33.04%, H = 1.66%, N = 7.71%; found: C = 33.95%, H = 1.62%, N = 7.60%.

Re(CO)$_3$Br(5-NCS-phen) (2)

To a suspension of Re(CO)$_3$Br(5-NH$_2$-phen) (240 mg, 0.45 mmol) in acetone (90 ml) was added the Na_2CO_3 (180 mg, 1.7 mmol). To the mixture was added $CSCl_2$ (0.16 ml) and stirring was continued at ambient temperature for 6 h under N_2 atmosphere. The reaction mixture was then filtered and the filtrate was evaporated under reduced pressure. The resulting brownish yellow solid was dissolved in minimum volume of dichloromethane and was filtered again. Evaporation of the solvent under reduced pressure yielded the product **2** as a brownish yellow powder. Yield = 250 mg (97%). ^{1}H NMR (DMSO-d_6, 300 MHz); 9.55 (dd, $J^d = 5.0$ Hz, $J^d = 1.0$ Hz, 1H, H), 9.45 (dd, $J^d = 5.0$ Hz, $J^d = 1.0$ Hz, 1H), 8.98 (dd, $J^d = 8.0$ Hz, $J^d = 1.0$ Hz, 1H), 8.89 (dd, $J^d = 8.0$ Hz, $J^d = 1.0$ Hz, 1H), 8.60 (s, 1H, H_7), 8.21 (dd, $J^d = 8.0$ Hz, $J^d = 5.0$ Hz, 1H), 8.11 (dd, $J^d = 8.0$ Hz, $J^d = 5.0$ Hz, 1H). Elemental analysis: calcd for $C_{16}H_7BrN_3O_3ReS(CH_3)_2CO$: C = 35.35%, H = 2.03%, N = 6.51, S = 4.97%; found: C = 35.05%, H = 1.83%, N = 6.28, S = 5.07%.

Re(CO)$_3$Br(5-(NH—CS—NH—Ph)-phen) (3)

Re(CO)$_3$Br(5-NCS-phen) (60 mg, 0.1 mmol) was dissolved in acetone (15 ml) with stirring. To this was added aniline (20 µl, 0.1 mmol) under a N_2 atmosphere. The resulting mixture was stirred for 20 h under N_2, by which time a pale yellow precipitate formed, which was filtered, washed with *n*-hexane and air dried. Yield = 41 mg (63%). ^{1}H NMR (DMSO-d_6, 400 MHz); 10.31 (s, 1H, Phen-N*H*-CS-NH-Ph), 10.23 (s, 1H, Phen-NH-CS-N*H*-Ph), 9.47 (d, $J^d = 5.0$ Hz, 1H), 9.42 (d, $J^d = 5.0$ Hz, 1H), 8.94 (d, $J^d = 8.0$ Hz, 1H), 8.87 (d, $J^d = 8.0$ Hz, 1H), 8.32 (s, 1H, H_7), 8.14 (dd, $J^d = 8.0$ Hz, $J^d = 5.0$ Hz, 1H), 8.08 (dd, $J^d = 8.0$ Hz, $J^d = 5.0$ Hz, 1H), 7.53 (d, $J^d = 8.0$ Hz, 2H, Ph-*o*), 7.37 (t, $J^t = 8.0$ Hz, 2H, Ph-*m*), 7.18 (t, $J^t = 7.0$ Hz, 1H, Ph-*p*). Elemental analysis: calcd for $C_{22}H_{14}BrN_4O_3ReS$: C = 38.83%, H = 2.07%, N = 8.23, S = 4.71%; found: C = 38.79%, H = 1.54%, N = 8.05, S = 4.39%.

[Br(CO)$_3$Re(µ-phen-5-(NH—CS—NH)-5-phen) Re(CO)$_3$Br] (4)

Re(CO)$_3$Br(5-NCS-phen) (120 mg, 0.2 mmol) was dissolved in acetone (20 ml) with stirring. To this solution was added *p*-phenylenediamine (11 mg, 0.1 mmol) under a N_2 atmosphere. The resulting mixture was stirred for 24 h under N_2, by which time a brownish orange precipitate formed, which was filtered, washed with *n*-hexane and air dried. Yield = 61 mg (60%). ^{1}H NMR (DMSO-d_6, 400 MHz); 10.35 (s, 1H, Phen-N*H*-CS-NH-Ph), 10.25 (s, 1H, Phen-NH-CS-N*H*-Ph), 9.47 (d, $J^d = 5.0$ Hz, 1H), 9.41 (d, $J^d = 5.0$ Hz, 1H), 8.94 (d, $J^d = 8.0$ Hz, 1H), 8.87 (d, $J^d = 8.0$ Hz, 1H), 8.34 (s, 1H, H_7), 8.13 (dd, $J^d = 8.0$ Hz, $J^d = 5.0$ Hz, 1H), 8.08 (dd, $J^d = 8.0$ Hz, $J^d = 5.0$ Hz, 1H), 7.54 (s, 4H, Ph). Elemental analysis: calcd for $C_{36}H_{22}Br_2N_8O_6Re_2S_2$: C = 35.57%, H = 1.73%, N = 8.73, S = 5.00%; found: C = 36.06%, H = 1.75%, N = 8.60, S = 4.57%.

Supporting Information Available

UV–vis and NMR titrations, corresponding titration profile and Job plots of compounds **3** and **4**; table containing bond lengths of structurally similar compounds and CIF file for **2** (available online). The CCDC deposit number for the X-ray crystal structure of **2** is 796139.

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