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A Pair of Coordination Donor–Acceptor Ensembles for the Detection of Tartrate in Aqueous Media

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A chemosensing approach utilizing a pair of heterodimetallic chemodosimetric ensembles of different analyte selectivity for the specific detection of targeted analytes in aqueous media was developed. Two new trinuclear, heterodimetallic donor–acceptor complexes, $\{Ru(t\text{Bubpy})(CN)_4[Cu(cyclen)]_2\}(ClO_4)_2$ ([Ru-Cu]) and $\{Ru(t\text{Bubpy})(CN)_4[Ni(cyclen)]_2\}(ClO_4)_2$ ([Ru-Ni]), where *t*Bubpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine and cyclen = 1,4,7,10-tetraazacyclododecane, have been synthesized and characterized. Their formation constants from $K_2[Ru(t\text{Bubpy})(CN)_4]$ and $[Cu(cyclen)](ClO_4)_2$ and $[Ni(cyclen)](ClO_4)_2$ were measured to be 5.54×10^6 ([Ru-Cu]) and 1.24×10^7 M^{-2} ([Ru-Ni]), respectively, at 298 K. Luminescent chemodosimetric responses of these two ensembles towards various anionic analytes in neat aqueous buffer at pH 7.0 were evaluated. While each of these two ensembles showed relatively low analyte specificity, they can be used together to manifest a chemosensing XOR logic output for the specific detection of tartrate.

Introduction

Chemosensing of physiologically and environmentally significant chemical and biochemical analytes has long been an important and challenging goal in the field of molecular recognition.[1] There are already numerous successful synthetic organic receptors developed for the detection of different zwitterionic and anionic substrates such as amino acids (e.g. glutamate, cysteine and homocysteine),[2] simple halides,[1d,3] phosphates (e.g. AMP, ADP and ATP)[4] and carboxylic acids (e.g. citrate and tartrate).[5] Yet chemosensing of anions in neat aqueous media remains to be a difficult task. This is because of problems associated with the poor solubility of many synthetic receptors, the severe competition for receptor interaction by water and the demand for multiple receptor–analyte interactions that are needed to compensate for the energy expenditure for the removal of solvation water molecules from the solvated analyte before incorporation into the receptors.[6] In this context, the use of Lewis acid metal centres for the coordination of anions or anionic moieties of analytes has offered an alternative strategy in the design of chemosensors.[7] Such coordination interactions are much less susceptible to interference by water and are generally energetic enough to redeem the energy penalty for analyte dehydration. Moreover, anion coordination may perturb the spectroscopic properties of the metal-based receptors and bring about physically measurable optical/spectroscopic responses.

Our group has previously demonstrated the use of cyanido-bridged heterodimetallic coordination donor–acceptor complexes in the construction of chemodosimetric ensembles[8] for the detection of various analytes by the competitive displacement approach.[9] With different donor–acceptor couples like Ru–C≡N–Pt and Ru–C≡N–Cu, we were able to fine-tune the selectivity of these ensembles for sulfhydryl-containing amino acids and the cyanide anion, respectively. Such a chemodosimetric ensemble system offers several attractive features such as simple synthetic procedures for preparation, high sensitivity and good performance in both aqueous and organic solvents.

Instead of relying on analyte-specific receptors as in conventional chemosensors, analyte selectivity of this type of coordination donor–acceptor ensembles is controlled by the stability of the donor–acceptor complex relative to that of adducts formed between the acceptor metal centre and the analytes. Thus, a single donor–acceptor ensemble may respond to a series of substrates, which all bind in a thermodynamically more favourable manner with the acceptor metal centre than the donor. One approach to achieve analyte-specific detection with this type of coordination donor–acceptor ensemble systems, especially for those analytes with only moderate coordination strength, is the employment of a pair of such ensembles with different acceptor metal centres and the implementation of XOR logic for chemosensing[10] (Scheme 1).

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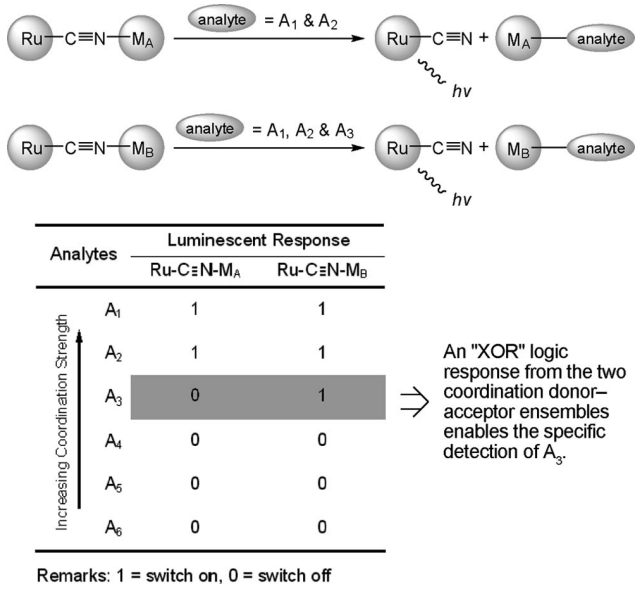


Scheme 1. The XOR logic in the chemosensing of a targeted analyte by a pair of coordination donor–acceptor ensembles with different acceptor metal centres.

In order to demonstrate this concept, we have designed, synthesized and characterized two cyanido-bridged trinuclear, heterodimetallic donor–acceptor complexes, $\{Ru(t\text{Bubpy})(CN)_4[Cu(cyclen)]_2\}(ClO_4)_2$ ([Ru-Cu]) and $\{Ru(t\text{Bubpy})(CN)_4[Ni(cyclen)]_2\}(ClO_4)_2$ ([Ru-Ni]) (*t*Bubpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; cyclen = 1,4,7,10-tetraazacyclododecane) for use as coordination donor–acceptor chemodosimetric ensembles (Scheme 2). $\{Ru(t\text{Bubpy})(CN)_4[Cu(cyclen)]_2\}(ClO_4)_2$ was further characterized by X-ray crystallography. The difference in visual responses of these two ensembles to common anionic and neutral substrates (Cl^-, F^-, SO_4^{2-}, $H_2PO_4^-$, NO_3^-, HCO_3^-, CN^-, pyruvate, acetate, citrate, tartrate and urea) was studied. Adopting the XOR logic, these two chemodosimetric ensembles, with relatively low analyte specificity on their own, were able to manifest the specific detection of tartrate in aqueous media.

Results and Discussion

Syntheses and Characterization

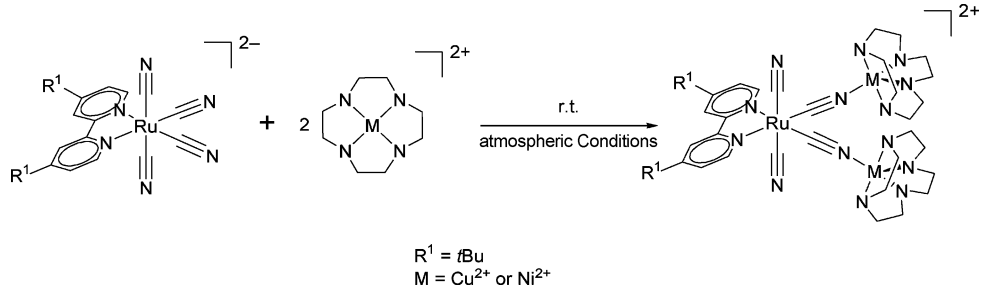
The chromotropic donor complex $K_2[Ru(t\text{Bubpy})(CN)_4]$ as well as the acceptor complexes $[Cu(cyclen)](ClO_4)_2$ and $[Ni(cyclen)](ClO_4)_2$ were synthesized according to literature methods.[11,12] All these complexes were well characterized by infrared spectroscopy, elementary analysis, electrospray mass spectrometry and ^1H NMR spectroscopy. All of these techniques gave satisfactory results relative to those in the literature.

The heterodimetallic complex [Ru-Cu] was prepared by simply stirring 2 equiv. $[Cu(cyclen)](ClO_4)_2$ with 1 equiv. $K_2[Ru(t\text{Bubpy})(CN)_4]$ in a solvent mixture of water/methanol/ethanol with a ratio of 1:2:2 (v/v) in air at room temperature. It was isolated as green needle-shaped crystals in good yield. Formation of the cyanido-bridged bimetallic complex was confirmed by IR spectroscopic studies where the $\nu_{C\equiv N}$ bands of $[Ru(t\text{Bubpy})(CN)_4]^{2-}$ at 2042, 2057, 2073 and 2096 cm^{-1} were shifted to 2072 cm^{-1} in [Ru-Cu].

The heterodimetallic complex [Ru-Ni] was prepared in a similar way by stirring 2 equiv. $[Ni(cyclen)](ClO_4)_2$ with 1 equiv. $K_2[Ru(t\text{Bubpy})(CN)_4]$ in a solvent mixture of water/methanol with a ratio of 1:9 (v/v) in air at room temperature. It was isolated as yellow needle-shaped crystals in good yield. Formation of the cyanido-bridged bimetallic complex was checked by IR spectroscopic studies where the $\nu_{C\equiv N}$ bands of $K_2[Ru(t\text{Bubpy})(CN)_4]$ were shifted to 2030, 2049, 2057 and 2094 cm^{-1}.

X-ray Crystal Structure Determination

Single crystals of $[Ru\text{-}Cu]\cdot 5H_2O$ (green needles) were grown by slow evaporation of a concentrated complex solution in a 1:2:2 (v/v) water/methanol/ethanol mixture in air. A perspective view of the crystal structure, with atom labelling, is shown in Figure 1. The three metal centres adopt a V-shaped configuration in which two $[Cu(cyclen)]^{2+}$ moieties are bridged to a Ru^{II} metal centre through cyanido bridges. Each Cu^{II} centre has a distorted square-pyramidal coordination geometry by coordination with a tetradentate cyclen ligand and a cyanido bridge. The average bond length between Ru and the bridging C atom of the cyanido ligand is ca. 1.972 Å and that between Cu and the bridging N atom of the cyanido ligand is ca. 2.095 Å. The mean bond length between Cu and the N atom of cyclen is ca. 2.017 Å. The two Ru–C≡N–Cu bridges are slightly bent with a mean bond angle of 176.2° for Ru–C≡N and 133.0° for C≡N–Cu. The X-ray crystallographic details are summarized in Table 1, while selected bond lengths and angles are summarized in Table 2.



Scheme 2. A pair of heterodimetallic coordination donor–acceptor ensembles, [Ru-Cu] and [Ru-Ni], used in this work.

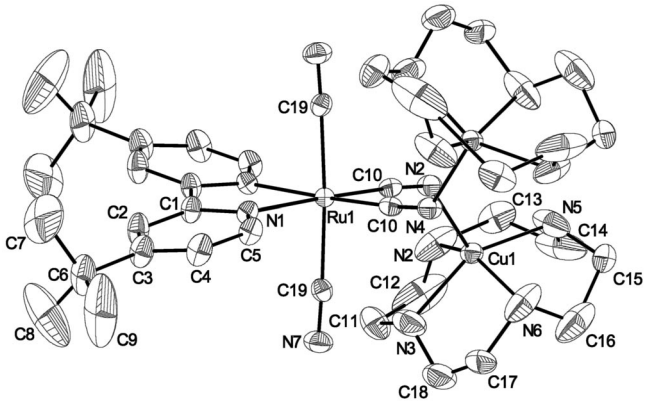


Figure 1. Perspective view of a crystallographically independent unit of the $\{Ru(t\text{Bubpy})(CN)_4[Cu(cyclen)]_2\}^{2+}$ cation. Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms have been omitted for clarity.

Table 1. Crystallographic data for $\{Ru(t\text{Bubpy})(CN)_4[Cu(cyclen)]_2\}(ClO_4)_2\cdot 5H_2O$ ([Ru-Cu]·$5H_2O$).

Empirical formula	$C_{38}H_{56}Cl_2Cu_2N_{14}O_8Ru\cdot 5H_2O$
Formula weight	1226.10
Temperature [K]	273 (2)
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
a, *b*, *c* [Å]	29.1436(15), 15.2575(8), 14.3704(7)
α, *β*, *γ* [°]	90, 113.5440(10), 90
Volume [Å^3]	5858.0 (5)
Z	4
D_c [Mg m^{-3}]	1.390
Absorption coefficient [mm^{-1}]	1.129
F (000)	2528
Crystal dimensions [mm]	0.22 × 0.10 × 0.08
θ Range for data collection [°]	2.39 to 25.00
Limiting indices *h*, *k*, *l*	–34 to 34, –15 to 18, –14 to 17
Reflections collected	14336
Unique reflections	5136
R_{int}	0.0342
Observed reflections [$I > 2\sigma(I)$]	3949
Completeness to θ = 25.00%	99.6
Max./min. transmissions	1.0000/0.9144
Data/restraints/parameters	5136/0/317
Goodness-of-fit on F^2	1.050
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0530, wR_2 = 0.1352
R indices (all data)	R_1 = 0.0731, wR_2 = 0.1494
Largest different peak/hole [e Å^{-3}]	1.099/–0.786

Table 2. Selected bond lengths [Å] and angles [°] of $\{Ru(t\text{Bubpy})(CN)_4[Cu(cyclen)]_2\}(ClO_4)_2\cdot 5H_2O$ ([Ru-Cu]·$5H_2O$).

Bond length			
Ru1–C10	1.972(5)	Cu1–N2	2.095(4)
Ru1–C19	2.041(5)	Cu1–N3	2.031(6)
Ru1–N1	2.119(4)	Cu1–N4	2.023(6)
C10–N2	1.158(6)	Cu1–N5	2.000(6)
C19–N7	1.150(6)	Cu1–N6	2.015(6)
Bond angle			
C10–Ru1–C10#1	87.4(3)	N7–C19–Ru1	176.7(5)
C10–Ru1–C19	89.57(19)	N2–C10–Ru1	176.2(4)
C10–Ru1–C19#1	93.10(19)	C10–N2–Cu1	133.0(4)
C10#1–Ru1–C19	176.2(3)	N5–Cu1–N6	87.8(4)
C10#1–Ru1–N1	173.55(17)	N6–Cu1–N4	148.5(3)
C10–Ru1–N1#1	173.56(17)	N6–Cu1–N3	84.8(3)
C10#1–Ru1–N1#1	98.10(17)	N5–Cu1–N2	112.5(2)
C19–Ru1–C19#1	90.31(18)	N4–Cu1–N2	107.0(2)

Spectroscopic Properties

$K_2[Ru(t\text{Bubpy})(CN)_4]$ is well known for its rich photophysical properties – a low-energy absorption band at ca. 375–500 nm and an emission band at ca. 550–750 nm dominates its UV/Vis absorption and emission spectra, respectively.[13] With reference to previous studies, the low-energy absorption band is attributable to the Ru(dπ) → *t*Bubpy(π*) metal-to-ligand charge transfer (MLCT) transition while the low-energy emission band is assigned to the *t*Bubpy(π*) → Ru(dπ) ^{3}MLCT emission. Figure 2 and Figure 3 show the spectrofluorimetric titration traces of $K_2[Ru(t\text{Bubpy})(CN)_4]$ with $[Cu(cyclen)](ClO_4)_2$ and $[Ni(cyclen)](ClO_4)_2$ in HEPES buffer at pH 7.0 and 298 K, respectively. Upon coordination with the $[M(cyclen)]^{2+}$ (M = Cu or Ni) acceptors, the ^{3}MLCT emission of the Ru^{II}–diimine chromophore undergoes a minor blue shift with a drastic reduction in the luminescent intensity. The blue shift in the ^{3}MLCT emission can be rationalized in terms of the electron-withdrawing effect of the $[M(cyclen)]^{2+}$ acceptors, which stabilize the d orbitals of the Ru^{II}–diimine chromophore and enlarge the Ru(dπ) → *t*Bubpy(π*) MLCT bandgap. Indeed, this effect is consistent with a number of related solvatochromic systems in which protons,[14] boron halides[15] or other transition-metal ions[16] were used as Lewis acids. The reduction in the ^{3}MLCT emission intensity is a consequence of the coordination of the diamagnetic Cu^{II} and Ni^{II} complexes to the Ru^{II}–diimine chromophore.[17]

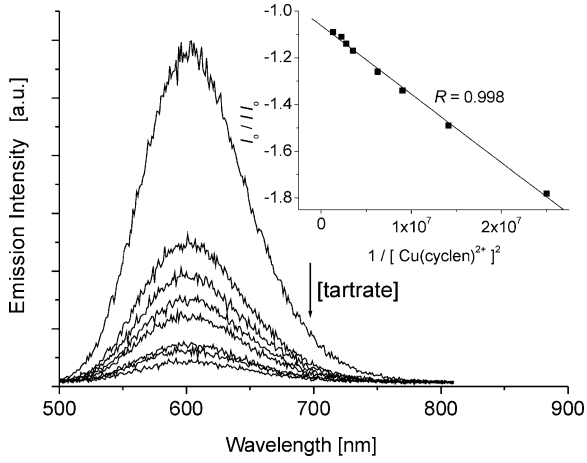


Figure 2. Spectrofluorimetric titration traces of $K_2[Ru(t\text{Bubpy})(CN)_4]$ (2.0×10^{-4} M) with $[Cu(cyclen)](ClO_4)_2$ in HEPES buffer (pH = 7.0) at 298 K (excitation at 398 nm). The inset shows the best fit for $I_0/(I - I_0)$ versus $1/[Cu(cyclen)(ClO_4)_2]^2$.

For both acceptors, spectrofluorimetric responses of their titration with the $K_2[Ru(t\text{Bubpy})(CN)_4]$ donor in aqueous buffer conformed to the formation of 1:2 donor–acceptor adducts. Such a formation of donor–acceptor adducts was further confirmed by electrospray mass spectrom-

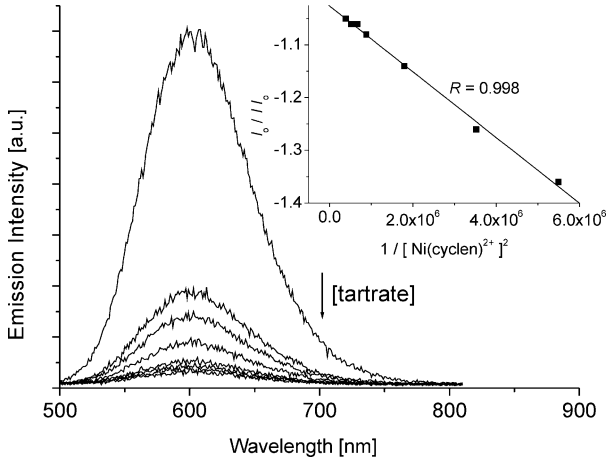


Figure 3. Spectrofluorimetric titration traces of $K_2[Ru(t\text{Bubpy})(CN)_4]$ (2.0×10^{-4} M) with $[Ni(cyclen)](ClO_4)_2$ in HEPES buffer (pH = 7.0) at 298 K (excitation at 398 nm). The inset shows the best fit for $I_0/(I - I_0)$ versus $1/[Ni(cyclen)(ClO_4)_2]^2$.

etry – in situ prepared donor–acceptor adducts from $K_2[Ru(t\text{Bubpy})(CN)_4]$ and $[M(cyclen)](ClO_4)_2$ (M = Cu and Ni) in a mole ratio of 1:10 in aqueous HEPES buffer solution at pH 7.0 revealed the presence of parent ions of $\{Ru(t\text{Bubpy})(CN)_4[Cu(cyclen)]_2\}(ClO_4)]^+$ at m/z = 1045 and $\{Ru(t\text{Bubpy})(CN)_4[Ni(cyclen)]_2\}(ClO_4)]^+$ at m/z = 1035. This indicates that the heterodimetallic donor–acceptor ensembles [Ru-Cu] and [Ru-Ni] can also be formed and stay intact in aqueous media. Although no X-ray quality crystal of $\{Ru(t\text{Bubpy})(CN)_4[Ni(cyclen)]_2\}(ClO_4)_2$ ([Ru-Ni]) was obtained, it is believed that its molecular configuration is similar to that of [Ru-Cu]. From the spectrofluorimetric titrations, the formation constant of [Ru-Cu] and [Ru-Ni] are 5.54×10^6 and 1.24×10^7 M^{-2} at 298 K, respectively.

Binding Properties of [Ru-Cu] and [Ru-Ni] with Common Neutral and Anionic Analytes

Figure 4 summarizes the spectrofluorimetric titrations of in situ prepared [Ru-Cu] and [Ru-Ni] with common anions (Cl^-, F^-, SO_4^{2-}, $H_2PO_4^-$, NO_3^-, HCO_3^-, CN^-, pyruvate, acetate, citrate, tartrate and urea) in aqueous media at pH 7.0. For [Ru-Cu], the titrations with only cyanide and citrate are able to restore the characteristic ^{3}MLCT emission of $[Ru(t\text{Bubpy})(CN)_4]^{2-}$. At equal substrate concentration, the response for cyanide is significantly stronger than that for citrate. For [Ru-Ni], the titrations with cyanide, citrate and tartrate were able to restore the luminescence of $[Ru(t\text{Bubpy})(CN)_4]^{2-}$. In this case, the response for citrate is significantly stronger, at equal substrate concentration, than those for cyanide and tartrate. Besides cyanide, citrate and tartrate, all the other common anions are not able to induce any luminescent response from the ensembles.

The mechanism for the luminescent responses of [Ru-Cu] and [Ru-Ni] towards the selected anions is believed to be very similar to that proposed for the previously reported Ru–C≡N–Pt system for the detection of sulfhydryl-containing amino acids or peptides. Scheme 3 shows such a heterodimetallic M_A–C≡N–M_B displacement mechanism for the "switch on" luminescent response. The ^{3}MLCT emission of

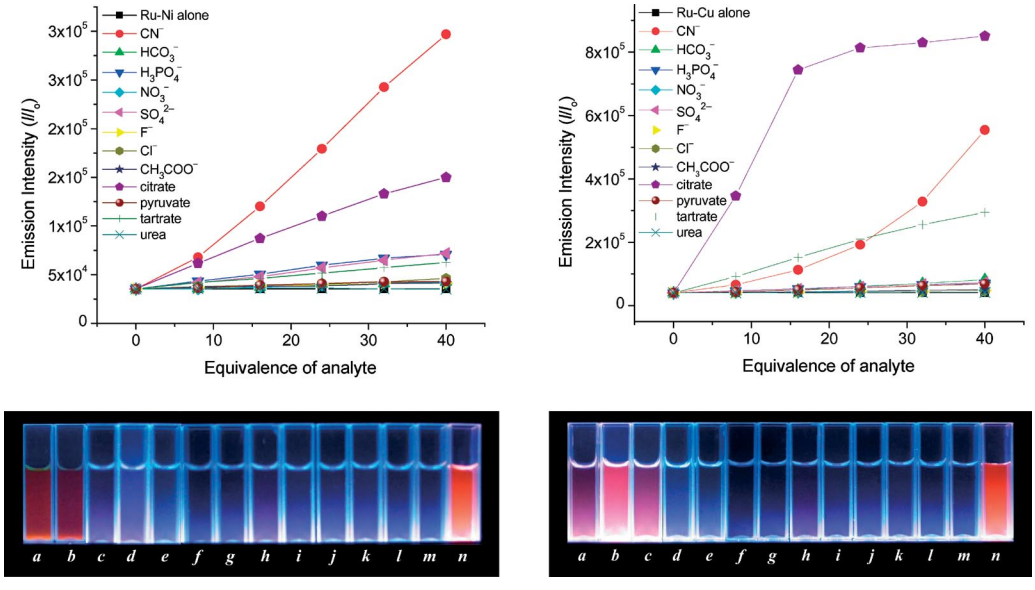
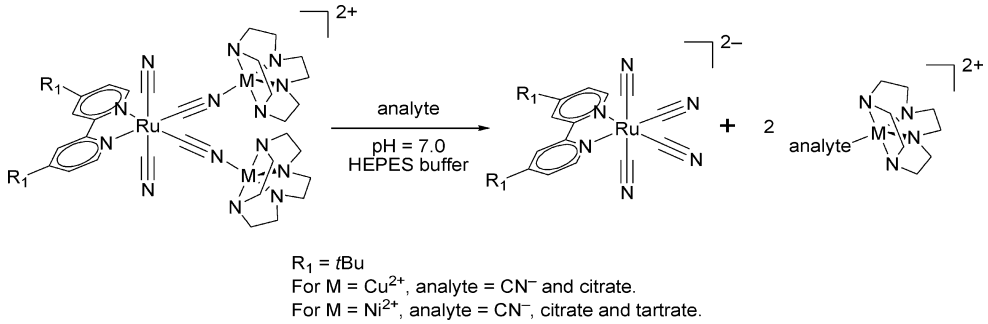


Figure 4. Top left: summary of the spectrofluorimetric titrations of in situ prepared [Ru-Cu] (1.33×10^{-4} M) with the selected analytes (0 to 5.33×10^{-3} M) monitored as a function of emission intensity I/I_0 at 606 nm. Bottom left: photograph of the fluorimetric responses of [Ru-Cu] towards various analytes in aqueous HEPES buffer at pH 7.0, 298 K. Top right: summary of the spectrofluorimetric titrations of in situ prepared [Ru-Ni] (1.33×10^{-4} M) with the selected analytes (0 to 5.33×10^{-3} M) monitored as a function of emission intensity I/I_0 at 606 nm. Bottom right: photograph of the fluorimetric responses of [Ru-Ni] towards various analytes in aqueous HEPES buffer at pH 7.0, 298 K. All titrations were carried out in aqueous HEPES buffer at pH 7.0, 298 K with an excitation wavelength of 398 nm. (*a*: ensemble + cyanide; *b*: ensemble + citrate; *c*: ensemble + tartrate; *d*–*l*: ensemble + dihydrogen phosphate, pyruvate, acetate, hydrogen carbonate, sulfate, nitrate, chloride, fluoride and urea; *m*: ensemble alone; *n*: $K_2[Ru(t\text{Bubpy})(CN)_4]$ alone).



Scheme 3. Chemosensing of selected anionic substrates in aqueous media by the competitive displacement of $[Ru(t\text{Bubpy})(CN)_4]^{2-}$ from the [Ru-Cu] and [Ru-Ni] ensembles.

$[Ru(t\text{Bubpy})(CN)_4]^{2-}$ is quenched upon coordination to the electron accepting $[Cu(cyclen)]^{2+}$ and $[Ni(cyclen)]^{2+}$ moieties. Preferential coordination of the Cu^{2+} centre with cyanide and citrate (cyanide, citrate and tartrate for Ni^{2+}) in aqueous HEPES buffer at pH 7.0 causes the cleavage of the cyanido bridges of the donor–acceptor ensemble and the return of $[Ru(t\text{Bubpy})(CN)_4]^{2-}$ to the solution, which restores its ^{3}MLCT emission. Additional evidence from electrospray mass spectrometry shows that specific analytes (e.g. the tartrate anion) indeed can bind with the receptor, e.g. $[Ni(cyclen)]^{2+}$, to form adducts (see Figure S5 in the Supporting Information). It has to be pointed out that while the binding of the acceptor metal centres to the $[Ru(t\text{Bubpy})(CN)_4]^{2-}$ donor and to the anion substrates are reversible processes, the overall displacement reaction depicted in Scheme 3 is irreversible. Thus, both [Ru-Cu] and [Ru-Ni] are essentially chemodosimeters that produce irreversible chemodosimetric responses to the presence of their targeted substrates.

Constraint on Analyte Specificity of the Coordination Donor–Acceptor Chemodosimetric Ensembles

Unlike most molecular sensors and chemosensing ensembles where specific molecular receptor units with a complementary molecular configuration as that of their targeted substrates are employed, analyte selectivity of our heterodimetallic coordination donor–acceptor ensembles relies on the thermodynamic properties of the acceptor metal complexes. In order to effect competitive displacement of the chromotropic donors from the acceptor metal centres, the free energy of formation of the resultant acceptor–analyte adducts must be greater than that of the donor–acceptor ensembles. While such an analyte-selection mechanism simplifies the design and synthesis of the chemosensing ensembles, it put serious constraints on the analyte specificity of the sensing process. Very stable coordination donor–acceptor ensembles are more specific to substrates that are strong electron donors to the accepting metal centres. Weaker donor–acceptor ensembles are much less substrate-specific and may respond to a range of analytes of various degrees of electron donor properties. In either case, this type of coordination donor–acceptor ensembles cannot produce specific responses to medium/weak donors.

The Use of XOR Logic for the Specific Detection of Tartrate by Both [Ru-Cu] and [Ru-Ni]

In order to overcome the intrinsic constraint on analyte specificity of this type of coordination donor–acceptor chemodosimetric ensembles, it is possible to make use of two ensemble assemblies of slightly different stability in a cooperative manner and apply XOR logic to interpret the chemosensing responses from the resultant array. The present two donor–acceptor ensembles, [Ru-Cu] and [Ru-Ni], are good examples to demonstrate such a concept. While both ensembles are sensitive to cyanide and citrate, only [Ru-Ni] is responsive towards tartrate (Figure 5). Thus, if these two ensembles were put into an array of sensors, tartrate can be singled out since only tartrate can trigger a luminescence response from [Ru-Ni] but not [Ru-Cu], while other analytes can either only "switch on" or "switch off" both [Ru-Ni] and [Ru-Cu] (Scheme 4).

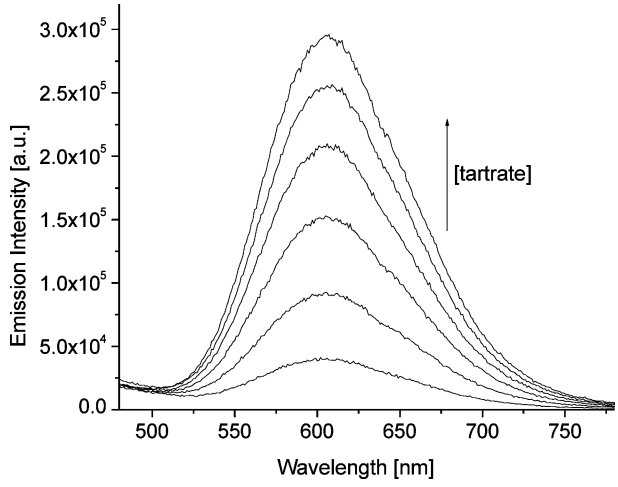
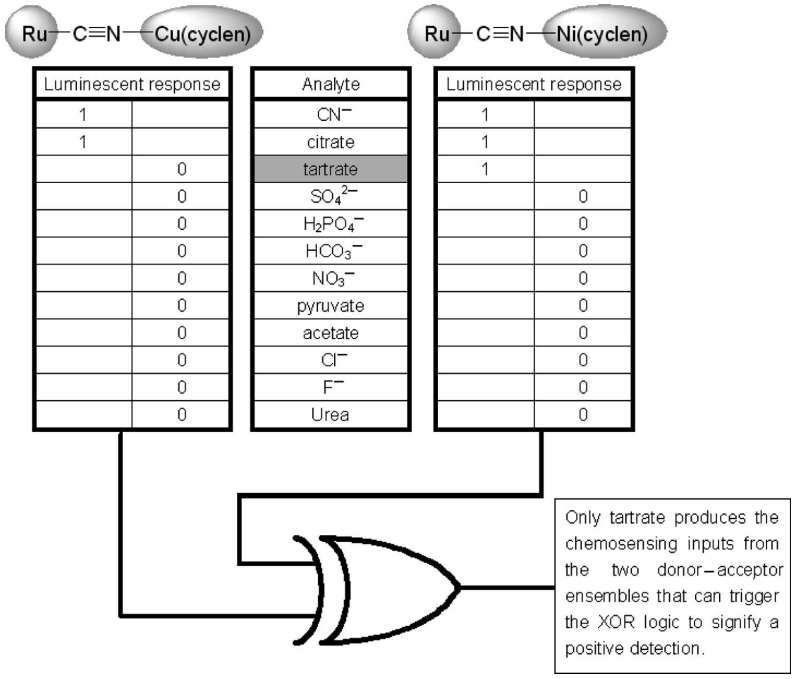


Figure 5. Spectrofluorimetric titrations of in situ prepared [Ru-Ni] (1.33×10^{-4} M) with tartrate (8, 16, 24, 32 and 40 equiv.). All titrations were carried out in aqueous HEPES buffer at pH 7.0, 298 K (excitation wavelength 398 nm).



Scheme 4. Chemosensing XOR logic exercised on inputs from the [Ru-Cu] and [Ru-Ni] donor–acceptor ensembles for the detection of tartrate in neat aqueous buffer.

Conclusions

Two new trinuclear, heterodimetallic coordination donor–acceptor complexes, [Ru-Cu] and [Ru-Ni], have been synthesized and characterized. Their ability to act as chemodosimetric ensembles for the chemosensing of a series of anionic analytes in neat aqueous buffer at pH 7.0 was demonstrated. These two donor–acceptor ensembles of different stability can also work together to achieve the specific detection of tartrate by exercising XOR logic in interpreting their luminescent responses. In fact, the application of logic operation on the chemosensing outputs from an array of simple coordination donor–acceptor chemosensing ensembles of different stability seems to be a feasible way of achieving sensitive and specific analyte detection in aqueous media. However, it has to be pointed out that application of such coordination donor–acceptor chemodosimetric ensemble systems under physiological conditions may be complicated by the actual pH of the media, which may alter the relative stability of the acceptor–analyte adducts. Interference from the binding of amino acids, e.g. histidine and cysteine, to the acceptor metals may need to be evaluated. Research to address these issues is in progress.

Experimental Section

Materials and Reagents: 4,4′-Di-*tert*-butyl-2,2′-bipyridine (*t*Bubpy), 1,4,7,10-tetraazacyclododecane (cyclen), *N*-(2-hydroxyethyl)piperazine-*N*′-(2-ethanesulfonic acid) (HEPES), $RuCl_3·3H_2O$, $Cu(ClO_4)_2·6H_2O$, $Ni(ClO_4)_2·6H_2O$, sodium chloride, sodium fluoride, sodium hydrogen carbonate, sodium sulfate, sodium nitrate, sodium acetate, sodium dihydrogen phosphate, sodium cyanide, sodium pyruvate, sodium citrate, sodium tartrate and urea were obtained from commercial sources and were used without further purification. $K_2[Ru(tBubpy)(CN)_4]$ was prepared from $K_4[Ru(CN)_6]$ according to a literature method.[11] All solvents used were of analytical grade.

Physical Measurements and Instrumentation: Infrared spectra in the range 500–4000 cm^{-1} in KBr plates were recorded with a Perkin–Elmer Model FTIR-1600 spectrometer. UV/Vis spectra were measured with a Hewlett Packard 8452A ultraviolet visible diode array spectrophotometer. Emission spectra were recorded by using a Horiba FluoroMax-3 spectrofluorimeter with a 5-nm slit width and 0.5-s integration time. ^1H NMR spectra were recorded with a Varian YH300 300 MHz NMR spectrometer. Electrospray mass spectra were measured by a PE SCIEX API 365 LC/MS/MS system. Elementary analyses were performed with a Vario EL elementary analyzer.

Synthesis

$[Cu(cyclen)](ClO_4)_2$: A mixture of $Cu(ClO_4)_2·6H_2O$ (1.85 g, 5 mmol) and cyclen (0.86 g, 5 mmol) was stirred in methanol (40 mL) at room temperature for 2 h. The reaction mixture was then filtered. The blue filtrate was reduced to 5 mL and extracted with dichloromethane (100 mL). A blue solid obtained by recrystallization with acetonitrile/diethyl ether was collected. Yield: 1.74 g (80%). ES-MS (+ve mode): m/z = 334 $[M - ClO_4]^+$. $C_8H_{20}Cl_2CuN_4O_8·H_2O·CH_3CN$: calcd. C 24.32, H 5.10, N 14.18; found C 24.16, H 5.15, N 14.22.

$[Ni(cyclen)](ClO_4)_2$: A mixture of $Ni(ClO_4)_2·6H_2O$ (1.83 g, 5 mmol) and cyclen (0.86 g, 5 mmol) was stirred in methanol (40 mL) at room temperature for 2 h. The reaction mixture was then filtered. The purple filtrate was reduced to 5 mL and extracted with dichloromethane (100 mL). A purple solid obtained by recrystallization with methanol/diethyl ether was collected. Yield: 1.63 g (76%). ES-MS (+ve mode): m/z = 329 $[M - ClO_4]^+$. $C_8H_{20}Cl_2NiN_4O_8·H_2O·1/2CH_3OH$: calcd. C 22.01, H 5.21, N 12.08; found C 21.53, H 5.36, N 12.55.

{Ru(*t*Bubpy)(CN)$_4$[Cu(cyclen)]$_2$}(ClO$_4$)$_2$, [Ru-Cu]: A mixture of K_2[Ru(*t*Bubpy)(CN)$_4$] (0.03 g, 0.05 mmol) and [Cu(cyclen)](ClO$_4$)$_2$ (0.04 g, 0.1 mmol) was stirred in a mixture of water/methanol/ethanol (10 mL) with a ratio of 2:4:4 (v/v) at room temperature for 30 min and was allowed to stand overnight. The green crystalline product obtained was collected by slow evaporation. Yield: 0.04 g (50%). ES-MS (+ve mode): m/z = 1045 [M – ClO$_4$]$^+$. IR (KBr): $\tilde{\nu}_{C\equiv N}$ = 2072 cm^{-1}. $C_{38}H_{64}Cl_2Cu_2N_{14}O_8Ru\cdot 3.5H_2O$: calcd. C 37.81, H 5.93, N 16.24; found C 36.47, H 6.14, N 16.85.

{Ru(*t*Bubpy)(CN)$_4$[Ni(cyclen)]$_2$}(ClO$_4$)$_2$, [Ru-Ni]: A mixture of K_2[Ru(*t*Bubpy)(CN)$_4$] (0.03 g, 0.05 mmol) and [Ni(cyclen)](ClO$_4$)$_2$ (0.04 g, 0.1 mmol) was stirred in a mixture of water/methanol (10 mL) with a ratio of 1:9 (v/v) at room temperature for 30 min and was allowed to stand overnight. The yellow crystalline product obtained was collected by slow evaporation. Yield: 0.04 g (60%). ES-MS (+ve mode): m/z = 1035 [M – ClO$_4$]$^+$. IR (KBr): $\tilde{\nu}_{C\equiv N}$ = 2030, 2049, 2057, 2094 cm^{-1}. $C_{38}H_{64}Cl_2Ni_2N_{14}O_8Ru\cdot 3.4H_2O$: calcd. C 38.17, H 5.97, N 16.40; found C 37.99, H 5.96, N 16.48.

In Situ Synthesis of [Ru-Cu]: A mixture of K_2[Ru(*t*Bubpy)(CN)$_4$] (0.007 g, 0.013 mmol) and [Cu(cyclen)](ClO$_4$)$_2$ (0.058 g, 0.133 mmol) was stirred in aqueous HEPES buffer (100.0 mL) at pH 7.0 at room temperature for 30 min. The donor–acceptor adduct, [Ru-Cu], was not isolated, and its aqueous solution was used instead in all spectroscopic and spectrofluorimetric titrations. The stoichiometry of the adduct was determined by electrospray mass spectrometry and X-ray crystallography.

In Situ Synthesis of [Ru-Ni]: A mixture of K_2[Ru(*t*Bubpy)(CN)$_2$] (0.007 g, 0.0133 mmol) and [Ni(cyclen)](ClO$_4$)$_2$ (0.057 g, 0.133 mmol) was stirred in aqueous HEPES buffer (50.0 mL) at pH 7.0 at room temperature for 30 min. The donor–acceptor adduct, [Ru-Ni], was not isolated, and its aqueous solution was used instead in all spectroscopic and spectrofluorimetric titrations. The stoichiometry of the adduct was determined by a mole ratio plot of K_2[Ru(*t*Bubpy)$_2$(CN)$_4$] versus [Ni(cyclen)](ClO$_4$)$_2$.

Crystal Structure Determination: Crystal data for {Ru(*t*Bubpy)(CN)$_4$[Cu(cyclen)]$_2$}(ClO$_4$)$_2\cdot$5H$_2$O ([Ru-Cu]·5H$_2$O): formula = $C_{38}H_{66}Cl_2Cu_2N_{14}O_{13}Ru$; F_W = 1226.10; monoclinic; space group *C*2/*c*; a = 29.1436(15), b = 15.2575(8), c = 14.3704(7) Å; α = 90°, β = 113.5440(10)°, γ = 90°; V = 5258.0(5) Å^3, Z = 4; D_c = 1.390 Mg m^{-3}; μ(Mo-K_α) = 1.129 mm^{-1}; F(000) = 2528; T = 273 K. A green crystal of dimensions 0.22 × 0.10 × 0.08 mm mounted on a glass fiber was used for data collection at 0 °C on a Bruker AXS SMART 1000 CCD area detector by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). 14336 reflections were measured, of which 5136 were unique, and R_{int} = 0.0342. 3949 reflections with $I > 2\sigma(I)$ were considered, observed and used in the structural analysis. The collected frames were processed with the software SAINT,[18] and absorption correct was applied (SADABS[19]) to the collected reflections. The structure of the complex was solved by direct methods (SHELXTL[20]) in conjunction with standard difference Fourier techniques and were subsequently refined by full-matrix least-squares on F^2. Convergence for 317 variable parameters by the least-square refinement for 5136 reflections with $I > 2\sigma(I)$ was reached at R = 0.0530 and wR = 0.1352 with a goodness-of-fit of 1.050. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.099 and –0.786 e Å^{-3}, respectively. All non-hydrogen atoms were assigned with anisotropic displacement parameters. The hydrogen atoms were generated in their idealized positions and allowed to ride on the respective carbon atoms. CCDC-665868 contains the supplementary crystallographic data for {Ru(*t*Bubpy)(CN)$_4$[Cu(cyclen)]$_2$}(ClO$_4$)$_2\cdot$5H$_2$O ([Ru-Cu]·5H$_2$O) can be obtained free of charge via www. ccdc.cam.ac.uk/data_request/cif.

Spectrofluorimetric Titrations: All solvents used in the spectrofluorimetric titrations were of analytical grade. HEPES buffer was used (10 mM, pH 7.0). For all anions, the sodium salts were used in the titrations. All the titrations were carried out in aqueous HEPES buffer at pH 7.0. Measurements were taken after equilibrium had formed between the ensembles and substrates.

Binding Ratio Determination

Mole Ratio Method: A series of acceptor complex solutions with a fixed concentration was prepared. Each of them was mixed with analyte solutions at various concentrations. The investigations were carried out in aqueous HEPES buffer at pH 7.0. The change in observed intensity of each solution I/I_0 was plotted as a function of the mole ratio of the analyte.

Binding Constant Determination: A series of acceptor complex solutions with a fixed concentration was prepared. Each of them was mixed with analyte solutions at various concentrations. The investigations were carried out in aqueous HEPES buffer at pH 7.0. According to the binding ratio between the receptor and analyte (1:2), the binding constant of receptor–analyte interaction was analyzed by the Benesi-Hildebrand Equation (1).[21] The change in observed intensity of each solution $I_0/(I - I_0)$ was plotted as a function of analyte concentration. The binding constant (K_B) was estimated from the ratio between the y intercept and the slope of the straight line.

$$\frac{I_0}{I-I_0}=\left(\frac{c}{d-c}\right)^2\left(\frac{1}{K_{\text{overall}}[\text{substrate}]^2}+1\right) \quad (1)$$

I_0 and I are luminescence intensity of the fluorogenic reagent at 606 nm in the absence and presence of the substrate, respectively; c and d are constants; [substrate] is the concentration of target analyte.

Supporting Information (see footnote on the first page of this article): Mole ratio plot for the confirmation of the donor–acceptor stoichiometry in [Ru-Ni] is presented. Infrared and electrospray mass spectra for [Ru-Cu] and [Ru-Ni] are also shown.

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