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## Introduction

In the past two decades, a great number of acyclic and compartmental hexadentate Schiff base ligands derived from the condensation of 3-methoxy/ethoxy salicylaldehyde with diaminoalkanes have been used for synthesis of heterodinuclear 3d–4f metal complexes.<sup>1–5</sup> They have also been well documented due to their potential applications in the field of magnetism,<sup>6–10</sup> luminescence<sup>11</sup> and asymmetric catalysis.<sup>12</sup> Hexadentate Schiff base with two different cores afford a straightforward route to synthesize heterodinuclear 3d–4f complexes. This is due to the fact that these Schiff bases contain an inner site with N- and O-donor chelating centers suitable for complexation with d-block ions (ionic radii 0.75–0.6 Å). In addition the outer coordination sites with four O-donors are larger than the inner one and are able to incorporate large oxophilic ions, such as 4f lanthanide ions (ionic radii 1.06–

Partha Pratim Chakrabarty,<sup>ab</sup> Sandip Saha,<sup>\*a</sup> Kamalika Sen,<sup>\*b</sup> Atish Dipankar Jana,<sup>c</sup> Debarati Dey,<sup>d</sup> Dieter Schollmeyer<sup>e</sup> and Santiago García-Granda<sup>f</sup>

Three heterometallic Schiff-base complexes of Cu having Pr, Nd and Sm as the heteroatoms have been synthesized. The compounds have also been characterized by their IR spectra and CHN analysis. The single crystal structures of these compounds have been studied from the X-ray crystallographic data. To the best of our knowledge the article describes the possibility of application of these compounds in the field of species dependent anion sensing for the first time. Amongst a number of anionic species, certain sulphur species were found to have greater reactivity towards a Schiff-base complex as they can incur probable changes in the molecular complexity. The  $S_2O_8^{2-}$  and  $S_2O_3^{2-}$  species could modify the spectral features of the Schiff-base complex containing Nd as the heteroatom. This particular complex was found to exhibit changes in its absorbance and fluorescence spectral features upon interaction with the anionic species  $S_2O_8^{2-}$  and  $S_2O_3^{2-}$ . The results give a strong platform for the Schiff base complexes for their analytical applications.

0.85 Å).<sup>13</sup> A large number of 3d–4f complexes have been synthesized using Schiff bases with acyclic diaminoalkanes such as ethylene diamine or propane diamine or compartmental type Schiff bases with cyclohexane-1,2-diamine or *ortho*phenylene diamine.<sup>14,15</sup> Among the different diaminoalkanes 1,2-propane diamine has rarely been used along with 3-methoxy/ethoxy salicylaldehyde to synthesize these types of 3d–4f heterometallic complexes. To the best of our knowledge only one Fe–Gd complex was reported using the hexadentate Schiff base obtained by the 1 : 2 condensation of 1,2-propane diamine and 3-methoxy salicylaldehyde.<sup>16</sup>

The synthesized compounds having practical applications are most welcome to the chemical world as they impart solutions to solving different chemical problems. Speciation analysis and anion sensing are widely popular problems in the world of analytical sciences. Little attention has been paid to solve the speciation of different anions which play vital roles in biological and environmental systems. Presence of halides in living cells induces changes in the conformation of steady state cells, anion exchange, active transport and electrodiffusion.17 Nitrates present in natural water at higher concentrations are generally associated with human activities and can cause adverse health effects on animals, human beings and plants. The toxicity of high nitrate concentrations arises from the capability of the human body to reduce it in the stomach or in the lower intestine to nitrite, which leads to methemoglobinemia.18,19 Inorganic arsenates and arsenites are well known for their chronic toxicities. Sulphate is an important anion involved in many physiological processes, having numerous biosynthetic and pharmacological functions.<sup>20</sup> It is involved in a variety of

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<sup>&</sup>lt;sup>a</sup>Department of Chemistry, Acharya Prafulla Chandra College, New Barrackpur, Kolkata-700131, India. E-mail: sandipsaha2000@yahoo.com

<sup>&</sup>lt;sup>b</sup>Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata 700009, India. E-mail: kschem@caluniv.ac.in

<sup>&</sup>lt;sup>c</sup>Department of Physics, Behala College, Parnasree, Kolkata 700 060, India

<sup>&</sup>lt;sup>d</sup>Department of Chemistry and Environment, Heritage Institute of Technology, Chowbaga Road, Anandapur, Kolkata 700107, India

<sup>&</sup>lt;sup>e</sup>Institut fur Organische Chemie, Universit at Mainz, Duesbergweg 10-14 55099, Mainz, Germany

Departamento de Química Físicay Analítica, Universidad de Oviedo, C/Julián Clavería 8, 33006 Oviedo, Spain

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Unexplored analytics of some novel 3d–4f heterometallic Schiff base complexes†

#### Paper

activation and detoxification processes. Sulfate ions are important for proper cell growth and development of living organisms. It is involved in synthesis of cell matrix and maintenance of cell membrane. Sulfites are used as food preservatives or enhancers. Sulfites occur naturally in wines and are commonly introduced to arrest fermentation at a desired time. High sulfite content in the blood and urine of babies can be caused by molybdenum cofactor deficiency disease which leads to neurological damage and early death unless treated.<sup>21</sup> Thiosulfate occurs naturally and is produced by certain biochemical processes. It is worthy for its use to halt bleaching in the papermaking industry. Sodium thiosulfate, is widely used in photography.22 Perdisulphates are used as food additives and it is used in organic chemistry as an oxidizing agent. It takes also an important role as initiator for emulsion polymerization.<sup>23</sup> The presence of these sulphur species therefore affects many systems of practical importance. Speciation of such anions and their sensing has been rarely examined. Report on chemical speciation of sulfur in heavy petroleums, using X-ray absorption near-edge structure (XANES) spectroscopy is available. This was used for approximate quantitation of different classes of sulfurcontaining compounds (e.g., sulfur, sulfides (including disulfides and polysulfides as a group), thiophenes, sulfoxides, sulfones, sulfinic acids, sulfonic acids, and sulfate) in a series of petroleums and petroleum source rocks.24 Speciation of sulphur as  $S^{2-}$ ,  $S_4^{2-}$  and  $S_6^{2-}$  in lithium batteries were performed using operand X-ray absorption spectroscopy.25 Analytical procedures for the determination of selected species of sulphur were proposed for natural water samples using the catalytic, chromatographic, ion-selective methods and absorption spectrometry.26 Anion sensing using different chemical compounds is an upcoming field. Quite a few numbers of reports can be found in the literature.27 However, in the present scenario, speciation based anion sensing solely based on chemical methods is still lacking and the large potential class of metal-Schiff base complex is highly unexplored for this purpose. In this report we have studied the possibility of application of the newly synthesized heterometallic Schiff base complexes in species dependent anion sensing of sulfur containing anions using spectral methods.

### Experimental section

### Materials

The lanthanide salts  $Pr(NO_3)_3 \cdot 6H_2O$ ,  $Nd(NO_3)_3 \cdot 6H_2O$ ,  $Sm(NO_3)_3 \cdot 6H_2O$  and solvents were purchased from Sigma-Aldrich and were used as received. All other chemicals used were of analytical grade.

#### Apparatus

IR spectra were recorded using KBr pellets within the range 4000–400 cm<sup>-1</sup> on a Perkin-Elmer Spectrum 65 FTIR Spectrometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid elemental analyzer. Horiba Jobin Yvon Fluorocube 01-NL and 291 nm Horiba nanoLED, IBH DAS-6 decay analysis software were used for Time Correlated Single Photon

Counting (TCSPC) Lifetime Spectroscopy. The UV visible spectra were obtained using an Agilent 8453 diode array spectrophotometer. Total independent data for compound **1** was collected on a STOE IPDS2T diffractometer equipped with a graphite monochromator Mo K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). Total independent data for compounds **2** and **3** were collected on a Bruker Smart Apex II CCD Area Detector equipped with a graphite monochromator Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 1.54184$  Å).

#### Synthesis

Synthesis of the ligands. The Schiff base ligands  $H_2L$  (Scheme 1) was synthesized by refluxing 1,2-propane diamine (0.074 mL, 1 mmol) and 3-ethoxy salicylaldehyde (0.332 g, 2 mmol) in methanol (10 mL) for two h. The ligand was not isolated; instead the resulting yellow methanolic solution was subsequently used for complex formation in every case.

A clear solution of  $Cu(CH_3COOH)_2 \cdot H_2O(0.199 \text{ g}, 1 \text{ mmol})$  in methanol (10 mL) was added to a 10 mL methanolic solution of the ligand, and the mixed solution was refluxed for two hours. The resulting green colored complex was isolated and characterized by IR and CHN analysis. This complex was further used for the 3d–4f heterometallic compound preparations.

Synthesis of complexes  $[Cu(L^{2-})Pr(NO_3)_3]$  (1),  $[Cu(L^{2-})Nd(NO_3)_3(CH_3OH)]$  (2),  $Cu(L^{2-})Sm(NO_3)_3(H_2O)]$  (3). Prepared Cu-complex (0.1124 g, 0.25 mmol) was dissolved in to 10 mL acetone and mixed with 10 mL methanolic solution of praseo-dymium nitrate (0.113 g, 0.25 mmol) for complex 1, neodymium nitrate (0.1095 g, 0.25 mmol) for complex 2, and samarium nitrate (0.113 g, 0.25 mmol) for complex 3 with constant stirring for 2 h. The brown solution was filtered. On slow evaporation the dark brown block shaped single crystals of the complex 1–3 was separated out in a few days. The crystals were filtered and washed with methanol and dried in air.

Complex  $[CuL^{-2}] \cdot CH_3OH$ : yield 65%. Anal. cacld for  $C_{23}H_{31}CuN_2O_5$ : C: 51.67; H: 6.52; N: 5.85%. Found: C: 51.00; H: 7.0; N: 5.90%. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$ (CH<sub>3</sub>OH) 3400,  $\nu$ (C=N) 1631.

Complex 1: yield 65%. Anal. cacld for  $PrCuC_{21}H_{27}CuN_5O_{14}$ : C: 32.42; H:3.49; N:9.00%. Found: C: 33.0; H: 3.60; N: 8.60%. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$ (C=N) 1634,  $\nu$ (NO<sub>3</sub>) 1384.

Complex 2: yield 65%. Anal. cacld for  $NdCuC_{22}H_{28}CuN_5O_{14}$ : C: 33.32; H: 3.55; N: 8.82%. Found: C: 33.31; H: 3.60; N: 8.83%.



IR (KBr pellets, cm<sup>-1</sup>):  $\nu$ (CH<sub>3</sub>OH) 3400,  $\nu$ (C=N) 1632,  $\nu$ (NO<sub>3</sub>) 1384.

Complex 3: yield 65%. Anal. cacld for  $SmCuC_{21}H_{22}N_5O_{14}$ : C: 32.29; H:2.83; N: 8.97%. Found: C: 32.80; H: 2.90; N: 8.72%. IR (KBr pellets, cm<sup>-1</sup>):  $\nu(H_2O)$  3392,  $\nu(C=N)$  1629,  $\nu(NO_3)$  1384.

### X-ray crystal structure determination of complex 1-3

Crystal data for the compound **1–3** are given in Table 1. The structure of the complex was solved by SIR 97 (ref. 28) for compounds **1–3**. The structure refinement was also performed by full-matrix least squares based on F<sup>2</sup> with SHELXL-2014.<sup>29</sup> All non-hydrogen atoms were refined anisotropically. The C-bound H atoms were constrained to ideal geometry and were included in the refinement in the riding model approximation. Data for molecular geometry, intermolecular interactions and pictures were produced using Platon-2009 (ref. 30) and ORTEP3.2 (ref. 31) programs. All three structures possess structural disorder for the diamino moiety of the produced ligand.

# Preparation of reagent for anion sensing studies using spectral methods

10 mM methanolic solutions of the Cu-Schiff base complex, complex 1, complex 2 and complex 3 were prepared separately. 10 mM solutions of NaNO<sub>3</sub>, NaNO<sub>2</sub>, NaF, NaCl, NaBr, NaI, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, NaAsO<sub>2</sub>, Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O were each prepared by weighing. 0.5 mL solutions of different anionic species were added to 2.5 mL methanolic solution of complex 1, complex 2 and complex 3. Absorbance and fluorescence spectral measurements were done with the solutions of the complexes as well as with added anionic species.

# Time Correlated Single Photon Counting (TCSPC) Lifetime Spectroscopy

Fluorescence lifetimes of Schiff base, Schiff base-Cu complex, complex 2, and  $S_2O_8^{2-}$  and  $S_2O_3^{2-}$  treated complex 2 were determined by the method of time correlated single-photon counting (TCSPC) using a nanosecond diode laser as the light source at 291 nm. The IBH DAS-6 decay analysis software was used to deconvolute the fluorescence decays.

## **Results and discussion**

### Crystal structure descriptions

The X-ray crystal structures of the three complexes show that all the complexes are diphenoxo-bridged dinuclear neutral complexes of copper( $\pi$ ) and lanthanides( $\pi$ ) (Pr, Nd and Sm). ORTEP representations of 1–3 along with atom labels are shown in Fig. 1, 2 and 3 respectively. The selected bond lengths and angles are listed in Tables S1–S3.†

The inner salen-type  $N_2O_2$  cavity is occupied by copper(II), while lanthanide(III) is present in the open and larger  $O_4$ compartment of the dinucleating hexadentate ligand  $L^{2-}$ . The copper(II) centre in the compound 2 and 3 are penta coordinated by the two imine nitrogen atoms, two bridging phenoxo oxygen atoms and one oxygen atom in the apical position

Table 1         Crystal data and refinement parameters					
	Complex 1	Complex 2	Complex 3		
Crystal data					
Formula	Pr Cu C21H27 Cu N5 O14	Nd Cu C22H28 Cu N5 O14	Sm Cu C21H26 N5 O14		
Formula weight	777.92	794.27	786.36		
Crystal system	Monoclinic	Monoclinic	Monoclinic		
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)		
<i>a</i> , <i>b</i> , <i>c</i> [Å]	9.1341(8), 21.0076(12), 14.4523(14)	9.2033(5), 20.5226(10), 15.6347(12)	9.0452(6), 21.2587(14), 14.5234(14)		
$\alpha, \beta, \gamma [^{\circ}]$	90, 94.088(7), 90	90, 92.680(6), 90	90, 91.628(8), 90		
$V [Å^3]$	2766.1(4)	2949.8(3)	2791.6(4)		
Z	4	4	4		
D (calc) [g cm <sup>-3</sup> ]	1.872	1.786	1.866		
$\mu$ (CuK <sub><math>\alpha</math></sub> ) [mm]	2.588	14.833	17.266		
<i>F</i> (000)	1549	1580	1552		
Crystal size [mm]	$\textbf{0.06}\times\textbf{0.09}\times\textbf{0.46}$	$0.19 \times 0.26 \times 0.30$	$0.15\times0.19\times0.26$		
Data collection					
Temperature (K)	193	293	293		
Radiation [Å]	$MoK_{\alpha} 0.71073$	CuK <sub>α</sub> 1.54184	CuK <sub>α</sub> 1.54184		
Theta Min–Max [°]	2.4, 28.0	3.6, 70.8	3.7, 71.0		
Dataset	-12:10; -27:27; -19:19	-10:11; -24:25; -13:19	-10:11; -17:25; -15:17		
Tot., Uniq. Data, <i>R</i> (int)	26837, 6667, 0.169	18842, 5563, 0.120	10976, 5205, 0.113		
Observed data $[I > 2.0 \sigma(I)]$	3912	3268	2418		
Refinement					
Nref, Npar	6667, 443	5563, 401	5205, 391		
R, wR2, S	0.0805, 0.2390, 1.03	0.0610, 0.1214, 0.99	0.0797, 0.1773, 1.00		
Max. and Av. Shift/Error	0.00, 0.00	0.00, 0.00	0.24, 0.01		
Min. and Max. Resd. Dens. $[E/Å^3]$	-1.88, 1.49	-0.60, 0.62	-0.89, 0.92		



**Fig. 1** The ORTEP diagram with 30% ellipsoidal probability and atom numbering scheme for complex **1** (the disorder of the diaminopropane moiety of the ligand has been omitted for clarity).



Fig. 2 The ORTEP diagram with 30% ellipsoidal probability and atom numbering scheme for complex 2 (the disorder of the diaminopropane moiety of the ligand has been omitted for clarity).

coming from methanol molecule for compound 2 and the same oxygen atom coming from water molecule for compound 3. Thus copper( $\pi$ ) centre adopts an approximate square-pyramidal coordination environment for these two compounds. In contrast, copper( $\pi$ ) centre is tetra-coordinated by two imine nitrogen atoms and two bridging phenoxo atoms and thus



Fig. 3 The ORTEP diagram with 30% ellipsoidal probability and atom numbering scheme for complex 3 (the disorder of the diaminopropane moiety of the ligand has been omitted for clarity).

adopts an approximate square-planar coordination environment in **1**. The lanthanide(III) center is ten-coordinated with two bridging phenoxo oxygen atoms, two ethoxy oxygen atoms, and two oxygen atoms of each of the three chelating nitrates in all three compounds.

In 1, the nitrate ion as well as the central propane diamine part of the ligand is disordered over two positions (Fig. 1). Various similar bond distances of all the complexes have been jotted down in Table 2 for an easy comparison. In 1, the Cu-O bond distances fall in the range 1.904(8)-1.926(8) Å and Cu-N bond distances are 1.886(11) Å and 1.923(11) Å, respectively. The Pr-O<sub>ligand</sub> distances remain in the range 2.424(7)-2.653(9) Å and the Pr-O<sub>nitrate</sub> distance fall in the range 2.616(9)-2.626(17) Å. Similarly in 2, the observed Cu–O bond distances vary in the range 1.912(7)-2.346(11)Å and Cu-N bond distances are 1.897(9)Å and 1.913(10) Å, respectively. The Nd–O<sub>ligand</sub> distances are in the range 2.411(6)-2.554(8) Å and the Nd-O<sub>nitrate</sub> distance are observed between 2.471(9)–2.533(9) Å. In 3, the Cu–O bond distances fall in the range 1.893(11)–1.901(10) Å and Cu-N bond distances are 1.903(14) Å and 1.930(15) Å, respectively. The Sm-O<sub>ligand</sub> distances are observed between 2.566(13)-2.653(9) Å and the Sm-Onitrate distances fall in the range 2.465(18)-2.515(15) Å. A systematic variation is not observed for the Ln–O(nitrate) bond distances in three Cu(II)– Ln(III) complexes. In the compounds 1 and 2, the Ln-O(phenoxo) bond distances are shorter than the bond lengths involving ethoxy and nitrate oxygen atoms but this trend is not observed for compound 3 (see Table 2).

Table 2 A summary of the geometrical parameters of the complexes 1-3

Complex	Cu(11)–O distance	Cu(II)–N distance	Ln–O distance	Cu…Ln	Dihedral angle between
	range (Å)	range (Å)	range (Å)	distance range (Å)	the bridging cores $(\delta, \circ)$
	1.904(8)-1.926(8)	1.886(11), 1.923(11)	2.424(7)-2.653(9)	3.485	3.8(5)
	1.912(7)-2.346(11)	1.897(9), 1.913(10)	2.411(6)-2.554(8)	3.487	8.7(4)
	1.901(10)-1.893(11)	1.930(15), 1.903(14)	2.465(18)-2.515(15)	3.451	5.5(6)

Intermolecular copper---lanthanide distances are 3.485 Å, 3.487 Å and 3.451 Å, for 1-3 respectively. These distances are again indicating that 3d-4f dinuclear cores are not well separated and these systems are not discrete dinuclear cores as the copper---lanthanide separations are less than 7 Å.15 Thus we can consider the planarity of these complexes which give some idea about the stability of these complexes in solution. The extent of planarity of the internal cores can be understood from the dihedral angles ( $\delta$ ) between the CuO(phenoxo)<sub>2</sub> and  $LnO(phenoxo)_2$  planes. The dihedral angle between the plane consisting of Cu1-O10-O23 and Pr1-O10-O23 is 3.8(5)° where O10 and O23 are bridging phenoxo O atoms in 1. The dihedral angle between the plane consisting of Cu1-O1-O2 and Nd1-O1-O2 is  $8.7(4)^\circ$  where O1 and O2 are bridging phenoxo O atoms in 2. The dihedral angle between the plane consisting of Cu1-O2-O3 and Sm1-O2-O3 is 5.5(6)° where O2 and O3 are bridging phenoxo O atoms in 3 (Table 2). From these values, it is indicated that the bridging moeity is more twisted in 2 compared to 1 and 3.15 This renders the complex more susceptible to changes upon addition of foreign ions in solution.

### Spectral studies for anion sensing analysis

The UV/Vis spectra of the Schiff base ligands and their complexes were recorded at 300 K in methanol medium. The observed bands in the absorbance spectrum are listed in Table 3, and the spectrum of the complex in CH<sub>3</sub>OH medium is shown in Fig. 4. The spectrum of the free ligand exhibits two inter ligand charge-transfer (CT) bands with  $\lambda_{max}$  227 nm which can be attributed to  $\pi$ - $\pi$ \* transition.<sup>32</sup> The  $\lambda_{max}$  of 261 nm is attributed to  $n-\pi^*$  transition. The Cu(L<sup>2-</sup>)·CH<sub>3</sub>OH complex also shows a peak at 225 nm for  $\pi$ - $\pi$ \* transition and the other two distinct peaks at 280 and 360 nm are observed for  $n-\pi^*$  and LMCT transitions. Complex 1 and 3 at same concentration with Schiff base-Cu complex show similar absorption peaks but with

 
 Table 3
 The observed bands in the absorbance spectrum of the Schiff
 base ligand and its complexes at 300 K in methanol medium

	Wavelength (nm) and $\varepsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )			
Complex	$\pi$ - $\pi^*$	$n-\pi^*$	LMCT	
H2L Cu (L <sup>2-</sup> )·CH <sub>3</sub> OH Complex 1 Complex 2	227 (1140) 225 (3130) 225 (3710) 225 (3130) 225 (3710)	261 (670) 280 (1820) 280 (3200) 263 (670) 280 (3200)	 360 (1100) 360 (1100) 350 (1200) 360 (1100)	



Fig. 4 Absorption spectra of the Schiff base and its mono-metallic and hetero-metallic complexes

higher intensities *i.e.*, 225 nm peak for  $n-\pi^*$  transition, 280 nm peak for  $\pi - \pi^*$  transition and 360 nm peak for LMCT transition. Complex 2 with Nd as the hetero atom behaves in a different way with new positions of absorption peaks. For complex 2, the absorption maxima are found at 225 nm for  $\pi$ - $\pi$ \* transition, 263 nm peak for n- $\pi^*$  transition and 350 nm peak for LMCT transition. This indicates a slightly different nature of the complex containing Nd as the heteroatom.

All the five compounds were excited at 350 nm to study their fluorescence emission properties. Only the Schiff base was found to be highly fluorescent and upon metal complexation there was a huge loss of emission intensity (Fig. 5). Metal complexation induces rigidity to the structure and prohibits delocalization of labile electrons in the molecule and hence the observed loss of emission intensity.33 Upon addition of different anionic species to complexes 1-3, the absorption spectra with complexes 1 and 3 containing Pr and Sm as the hetero-atoms respectively show negligible changes (Fig. 6 and 8). However, complex 2 with Nd as the heteroatom (Fig. 7) shows maximum changes in the absorption spectral properties only in presence of  $S_2O_8^{2-}$  and  $S_2O_3^{2-}$ . This indicates that there are some structural changes in this particular complex in presence of these sulphur species.34 With slowly increasing concentrations of  $S_2 O_8^{2-}$  ions in a solution of complex 2, the absorption maximum of 350 nm first suffers a red shift and then a new peak at 335 nm arises with a subsequent reduction of the first peak (at 385 nm) (Fig. 9). Perdisulphate being a highly oxidizing species (eqn (11)) interacts with the  $\pi$  electron system of the ligand surrounding the metal core which affects the optical properties of the ligand.35 Spectral changes of a solution of



Fig. 5 Fluorescence spectra of the Schiff base and its mono-metallic and hetero-metallic complex excited at 350 nm.



Fig. 6 Absorption spectra of the complex 1 in presence of different anions.



Fig. 7 Absorption spectra of the complex  ${\bf 2}$  in presence of different anions.

complex 2 were also observed with increasing concentrations of  $S_2O_3^{\ 2-}$  (Fig. 10). A red shifted absorbance spectrum with higher  $S_2O_3^{\ 2-}$  concentrations indicates sensitivity of complex 2 for this



Fig. 8 Absorption spectra of the complex 3 in presence of different anions.



Fig. 9 Absorption spectra of complex 2 with increasing  ${S_2}{O_8}^{2-}$  concentration.





particular species also.<sup>36</sup> This is again due to the positive oxidation potential of this particular species in solution (eqn (12)) compared to the low negative values of the other anionic species.  $S_2O_3^{2-}$  species is therefore also responsible to create changes in the structural environment of compound 2 and thus affect its optical properties. The appearance of new absorbance



Fig. 11 Absorption spectra of complex 2 with increasing  ${\rm SO_4}^{\rm 2}$  concentration.

peak at 335 nm (Fig. 9) and the red shift (Fig. 10) with  $S_2O_8^{2-}$ and  $S_2O_3^{2-}$  respectively may be due to the formation of new species of neodymium in the complex.<sup>37</sup> In presence of  $SO_4^{2-}$ and  $SO_3^{2-}$  there are no observable spectral changes excepting the dilution effect (Fig. 11 and 12). The fluorescence emission of



Fig. 12 Absorption spectra of complex 2 with increasing  ${\rm SO_3}^{2-}$  concentration.



Fig. 13 Fluorescence spectra of complex 2 with increasing  ${S_2}{O_8}^{2\cdot}$  concentration.

the complex 2 also enhances in presence of the anions  $S_2O_8^{2-}$ and  $S_2O_3^{2-}$  (Fig. 13 and 14) indicating that the complex suffers specific changes in the fluorophore environment in presence of these two particular species. There are hardly any changes of emission spectra in presence of  $SO_4^{2-}$  and  $SO_3^{2-}$  species (figure not shown). Fig. 15 shows the emission life times of the fluorescence active compounds, *i.e.*, the Schiff base ligand itself (4.378 ns), Cu-Schiff base complex (2.55 ns), complex 2 in presence of  $S_2O_8^{2-}$  (1.13 ns) and in presence of  $S_2O_3^{2-}$  (0.25 ns). The results are again indicative towards formation of different geometrical orientation which is responsible for the existence of different fluorescence active species. All these observations may also be explained on the basis of the redox potentials of these anionic species and hence their possibility to break down the hetero-metallic complex in their presence.

$$AsO_2^- + 2H_2O + 3e^- \implies As + 4OH^- E^\circ = -0.68 V$$
 (1)

$$AsO_4^{3-} + 2H_2O + 2e^- \Leftrightarrow AsO_2^- + 4OH^- E^\circ = -0.71 V$$
 (2)

$$F_2 + 2e^- \leftrightarrows 2F^- E^\circ = -2.87 \text{ V}$$
(3)



Fig. 14 Fluorescence spectra of complex 2 with increasing  ${\rm S_2O_3}^{2-}$  concentration.



Fig. 15 Emission life times of the fluorescence active compounds in study.

$$\operatorname{Cl}_2(g) + 2e^- \leftrightarrows 2\operatorname{Cl}^- E^\circ = -1.358 \operatorname{V}$$
 (4)

$$Br_2(aq) + 2e^- \leftrightarrows 2Br^- E^\circ = -1.087 \text{ V}$$
(5)

$$I_2 + 2e^- \leftrightarrows 2I^- E^\circ = -0.535 \text{ V} \tag{6}$$

$$NO_2^- + H_2O + e^- \Leftrightarrow NO + 2OH^- E^\circ = -0.46 V$$
 (7)

$$2NO_3^- + 2H_2O + 2e^- \leftrightarrows N_2O_4 + 4OH^- E^\circ = -0.85 \text{ V}$$
 (8)

$$2SO_3^{2-} + 2H_2O + 2e^- \leftrightarrows S_2O_4^{2-} + 4OH^- E^\circ = -1.12 V \quad (9)$$

$$SO_4^{2-} + H_2O + 2e^- \Leftrightarrow SO_3^{2-} + 2OH^- E^\circ = -0.92 V$$
 (10)

$$S_2O_8^{2-} + 2e^- \Leftrightarrow 2SO_4^{2-} E^\circ = +2.01 V$$
 (11)

$$S_2O_3^{2-} + 6H^+ + 2e^- \Leftrightarrow 2S + 3H_2O E^0 = 0.465 V$$
 (12)

The above redox potentials indicate that only  $S_2 O_8^{2-}/S O_4^{2-}$ and  $S_2O_3^{2/3}$  systems have higher oxidation potentials compared to the other redox systems. The complex containing Nd as heteroatom was only found susceptible to such attack. It is evident that the complex 2 containing Nd<sup>3+</sup> suffers encounters observable spectral changes with S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> species which results in a subtle geometrical reorganization of the molecule. Fluorescence activity reappears and the resulting species have different emission life time than the parent compounds. Everything happens only in presence of species like S<sub>2</sub>O<sub>8</sub><sup>2-</sup>and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> having high redox potentials. All the results of absorbance, fluorescence spectra and fluorescence life time measurements indicate that complex 2 containing Nd heteroatom is more prospective towards speciation based anion sensing of sulphur containing anion species  $S_2O_8^{2-}$  and  $S_2O_3^{2-}$ in particular.

### Conclusion

A new application of Schiff base 3d–4f heterometallic complex has been explored. The synthesized Cu–Nd compound was found to be effective in the speciation based anion sensing of sulphur anions. As the  $S_2O_8^{2-}$  and  $S_2O_3^{2-}$  species have higher redox potentials, they can modify the spectral features of the Schiff-base complex containing Nd as the heteroatom. The observations are in agreement with the single X-ray crystallographic features of the synthesized compound. The results indicate the potentiality of this huge class of heterometallic complexes towards development of analytical procedures in anion sensing applications.

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