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Monometallic rhenium(I) complexes as sensor for anions

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ABSTRACT

Three new tricarbonyl rhenium(I) polypyridine complexes containing amide, urea and thiourea derivatives of 2,2′-bipyridine ligands **L1**–**L3** have been synthesized, characterized and found to show significant UV–visible absorption spectral changes on the addition of anions CN^-, F^-, CH_3COO^- and $H_2PO_4^-$. These spectral changes and ^{1}H NMR titrations of complexes **1**–**3** with anions indicate strong binding of anions with the Re(I) complexes and the binding constants are in the range of 10^3–10^5 M^{-1}. The strong binding is attributed to the H-bond formation/deprotonation of –NH proton in the ligand and the selectivity of anion is in the order $CN^- > F^- > CH_3COO^- > H_2PO_4^-$.

There has been upsurge of interest in the detection and quantification of anions in the last decade owing to the importance of anions in various chemical, biological and environmental science processes and in the host–guest chemistry [1]. Anions are ubiquitous in biological system and their recognition is achieved through non-covalent interactions such as hydrophobic effect, electrostatic interactions, and halogen and hydrogen bonding [2]. Up to now, several anion receptors such as imidazoles [3], pyrroles [4], calixpyrroles [5], amides [6], carbamides [7], urea [8], and thiourea [9] have been developed and the labile protons of the receptors are recognized through anions by either hydrogen bonding or deprotonation [10]. In this view, the design and synthesis of receptors sensitive to the anion–receptor interactions and capable of showing either a chromogenic and/or fluorogenic response are of major concern [11]. In the past few years increasing attention has been paid to the study of anion sensing using colorimetric sensor, because the change of color is discerned by 'naked eye' which is very simple and does not require any equipment [12]. Although many reports are available for sensing of anions through organic compounds, transition metal based anion sensor is still a commendable practice [13].

Among the transition metal complexes, rhenium(I) tricarbonyl complexes with d^6 configuration have rich photophysical and photochemical behavior such as high stability and fairly strong emission in the visible region. In addition, though the application of Re(I) tricarbonyl complexes towards sensors [14], catalysis [15], light-emitting devices [16], CO_2 fixation [17], optical switches [18], and imaging [19] has been developed enormously their role as the anion sensor is very limited [20]. Lees et al. reported that the luminescent rhenium(I) tricarbonyl pyridine complexes served as receptors for anions via intramolecular hydrogen bonding with high selectivity [21]. Tzeng and co-workers also reported the anion recognition capability of Re(I)-based square containing dipyridyl-amide ligand through hydrogen bonding and it is realized using UV–vis absorption and ^{1}H NMR spectral techniques [22]. Herein we report the synthesis and characterization of three new tricarbonyl rhenium(I) complexes containing amide, urea and thiourea derivatives of 2,2′-bipyridine ligands and their role as sensor for anion through UV–vis absorption and ^{1}H NMR spectral techniques as well as naked eye.

The ligands were synthesized in good yield by a simple condensation reaction between 4-methyl-2,2′-bipyridine-4-carboxaldehyde and corresponding amine in ethanol medium. The formation of ligands was confirmed by NMR, IR, Mass spectral and elemental analysis techniques. The formation of imine linkage of the ligands **L1**–**L3** was characterized by a signal at δ 8.27, 8.25, and 8.24 (–N═CH) in ^{1}H NMR spectrum and a band at 1661, 1679 and 1593 in IR spectrum respectively. The HR-ESI-MS analysis showed a molecular ion peak at m/z = 317.14, 332.15, and 348.13 with the experimental isotope pattern matching the calculated values for the ligands **L1**–**L3** (Figs. S1–S3). The reaction of starting material $Re(CO)_5Br$ with the bidentate ligands **L1**–**L3** refluxed in toluene leads to the formation of *fac*-$[Re(CO)_3(N\text{–}N)Br]$ species which are air and moisture stable, kinetically inert and the structure of their complexes are shown in Chart 1. These complexes **1**–**3** were characterized by NMR, IR, Mass spectral and elemental analysis techniques. In IR spectra, the carbonyl region shows three peaks at 2023, 1917, and 1900 cm^{-1} which correspond to A′(1) symmetric, A′(2) asymmetric and A″ symmetric stretching frequencies [23]. The HR-ESI-MS analysis showed a molecular ion peak at m/z = 664.98, 679.99, and 695.97 with the experimental

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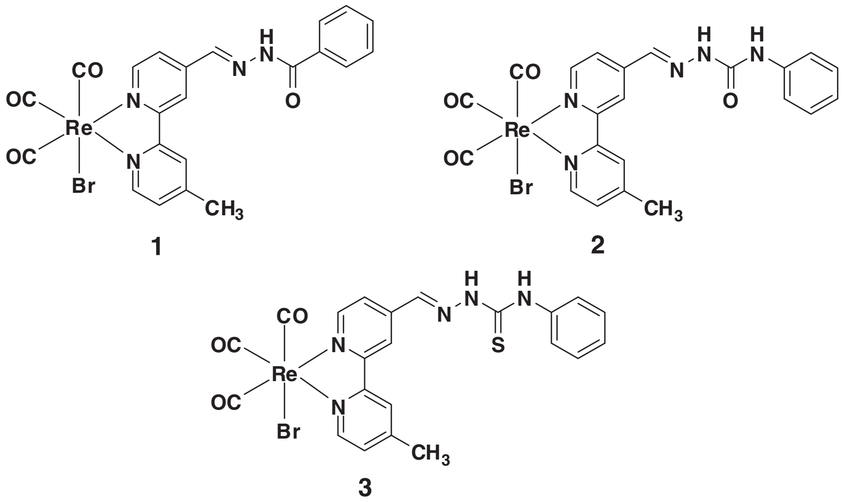

Chart 1. Structure of the rhenium(I) complexes.

isotope pattern matching the calculated values for the complexes **1**–**3** (Figs. S4–S6).

The absorption spectra of ligands **L1**–**L3** and Re(I)-tricarbonyl complexes **1**–**3** were measured and the absorption maximum values are given in Table 1. The electronic absorption spectra of Re(I)-tricarbonyl complexes reveal strong absorption bands at 194–352 nm and less intense absorption shoulders at ca. 390 nm (Table 1). The high-energy intense band in the UV region is assigned to the ligand centered (LC) π–π* transition and it is also observed for the free ligands (Fig. S7). The low energy absorption band at 390 nm is assigned to spin allowed metal to ligand charge transfer (MLCT) transition from the Re dπ- orbital to the π* orbital of the ligand [dπ (Re) → π* (ligand)] (Fig. 1) [24]. However, in complex **3** the ligand centered band was shifted to the tune of 57 nm from 295 to 352 nm compared to that in complexes **1** and **2** due to the presence of electron rich sulfur atom in thiourea moiety which may facilitate delocalization. Our complexes are non-luminescent in nature because these complexes bear imine N-atom and similar type of Re(I) complexes is reported earlier [25].

The anion-sensing ability of complexes **1**–**3** in acetonitrile has been studied by UV–vis absorption spectral titration experiments. The detectable change in the absorption spectrum can be noticed on the addition of tetrabutylammonium (TBA) salt solution of CN^-, F^-, CH_3COO^- and $H_2PO_4^-$ to the acetonitrile solution of complexes **1**–**3**. Conversely, little absorption spectral change was observed on the addition of Cl^-, Br^-, I^-, SCN^-, ClO_4^- and NO_3^- ions (Fig. 2 and Figs. S8, S9). With the addition of incremental amounts of CN^- ions to the solution of complex **1**, the absorption peak at 250 nm is slightly blue shifted to 245 nm and the peak at 316 nm is blue shifted by 19 nm to 297 nm. In addition a new peak appears in the region at 462 nm (Fig. 3). The formation of new band may be due to the hydrogen bond formation with amide proton or deprotonation of amide proton [26]. The previous literature and ^{1}H NMR studies show that the formation of new band is due to the increase in the extent of π-conjugation of the deprotonated amide moiety [26]. Similar type of results was also observed with other anions such as F^-, CH_3COO^-, and $H_2PO_4^-$ with complex **1**. Some interesting results have been observed with complex **1** on increasing concentration of F^- anion (Fig. S10). The formation of hydrogen fluoride (HF) from the reaction of complex **1** with F^- anion by deprotonation of NH proton is responsible for these spectral changes. More basicity of fluoride is responsible for selective recognition among halides, which is corroborated by previous report [27]. The observation of well-defined isosbestic point at 350 nm in this UV–vis absorption spectral changes is indicative of ground state complex formation between the anion with the amide moiety of the complex **1** [28].

The urea group contains two acidic NH protons which can be envisaged as good binding sites for anions [29]. Urea moiety is present in complex **2**. Upon addition of incremental amounts of F^- anions to the solution of complex **2**, the absorption peak at 235 nm is slightly red shifted to 245 nm and peak at 295 nm is marginally blue shifted by 4 nm to 291 nm indicating the binding of anion with the Re(I) complex. In addition to that, the formation of new peak at 486 nm (Fig. S11) is due to the deprotonation of NH proton of the urea moiety. Similar kind of results was also observed with other anions such as CN^-, CH_3COO^-, and $H_2PO_4^-$ with complex **2**. The well-defined isosbestic point at 353 nm in the UV–vis absorption spectral region is indicative of ground state interaction between the anion with the urea moiety of the complex **2**. Fabbrizzi and co-workers [30], reported intensively on

Table 1
Absorption spectral data of ligands and complexes in CH_3CN medium.

Compounds	λ_{abs}, nm (ε_{max}, dm^3 mol^{-1} cm^{-1})
1	194 (66,495), 250 (26,500), 316 (27,604), 390 (8000)
2	196 (79,565), 235 (36,863), 295 (23,981), 390 (8000)
3	194 (66,850), 248 (28,000), 300 (22,500), 352 (28,731), 391 (19,500)
L1[a]	205 (48,266), 246 (40,135), 291 (58,113)
L2[a]	205 (58,046), 240 (58,960), 286 (53,056), 303 (53,234)
L3[a]	208 (61,923), 246 (40,135), 282 (38,308), 326 (67,826)

[a] CH_3CN: THF (98:2).

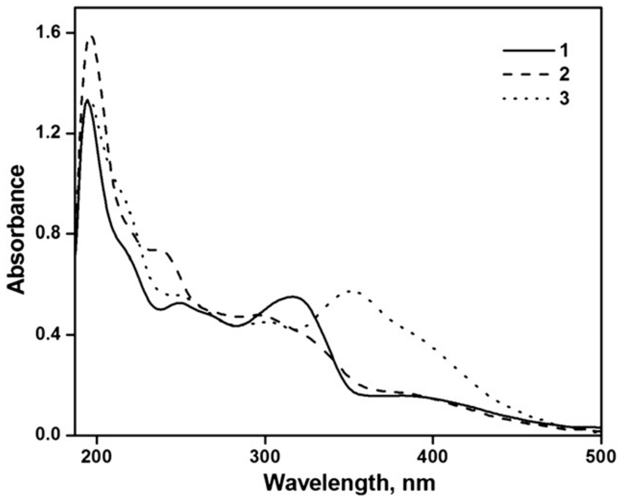

Fig. 1. Absorption spectra of complexes **1**–**3** (20 μM) in CH_3CN medium.