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MONO- AND DINUCLEAR MALEONITRILEDITHIOLATE AND DIBENZYLDITHIOMALEONITRILE COMPLEXES OF (bipy)₂Ru^{II}: SYNTHESIS, SPECTRAL AND ELECTROCHEMICAL STUDY

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Abstract—[Ru(bipy)$_2$\{S$_2$C$_2$(CN)$_2$\}] and [Ru(bipy)$_2$\{(C$_6$H$_5$CH$_2$)$_2$S$_2$C$_2$(CN)$_2$\}][PF$_6$]$_2$ were synthesized by the reaction of [Ru(bipy)$_2$Cl$_2$]·2H$_2$O with Na$_2$S$_2$C$_2$(CN)$_2$ or (C$_6$H$_5$CH$_2$)$_2$S$_2$C$_2$(CN)$_2$ in aqueous ethanol, and used to form dinuclear species by binding Cp(PPh$_3$)$_2$Ru^{II} or (bipy)$_2$ClRu^{II} moieties onto the CN nitrogen sites. Spectral and electrochemical properties of all complexes have been investigated. S$_2$C$_2$(CN)$_2^{2-}$ is found to introduce a low lying $d\pi$(Ru) → π*(S$_2$C$_2$(CN)$_2^{2-}$) MLCT state and an easily oxidizable centre upon complexation. (C$_6$H$_5$CH$_2$)$_2$S$_2$C$_2$(CN)$_2$ exhibits weaker π acidity and imparts a 2852 cm^{-1}, 0.35 V lower stabilization to the ruthenium $d\pi$ orbitals than the saturated chain dithioether (CH$_3$)$_2$S$_2$C$_2$H$_2$, as indicated in the Ru → bipy MLCT absorption energy and the first oxidation potential of the corresponding (bipy)$_2$Ru^{II} complexes.

Transition metal complexes of maleonitriledithiolate[1,2] (mnt^{2-}, S$_2$C$_2$(CN)$_2^{2-}$), are finding new areas of application such as electron donors in photoinduced electron transfer reactions[3–5] and chromophore sensitizers in energy conversion reactions.[6] Incorporation of mnt^{2-} in metal–diimine complexes introduces the feasibility of mnt → diimine LLCT transitions,[7–10] due to the inherent differences in the redox potentials of the two ligands, upon electronic excitation. Such an intramolecular free energy gradient is an important requirement for the photoinduced directional electron transfer and separation of the oxidative and reductive equivalents thus formed.[11–13] The energy of the LLCT transitions and the intramolecular energy gradient could be tuned by binding additional metal centres onto CN nitrogen sites or upon binding one or two aryl/alkyl fragments onto the thiolate sulphur sites. Although the alkylation of coordinated mnt^{2-} has been studied previously,[14] these aspects of the ligand have attracted little attention.

In continuation of my earlier work on diimine–ruthenium complexes possessing the RuN$_4$S$_2$ chromophore,[15,16] in this paper I describe the preparation and the spectral and electrochemical properties of mono- and dinuclear

maleonitriledithiolate and dibenzyldithiomaleonitrile [ddmn, (C$_6$H$_5$CH$_2$)$_2$S$_2$C$_2$(CN)$_2$] complexes possessing (bipy)$_2$Ru^{II} and Cp(PPh$_3$)$_2$Ru^{II} moieties.

EXPERIMENTAL

All the chemicals were of A. R. grade. Solvents were dried and degassed before use and the reactions were carried out under nitrogen. The starting compounds Na$_2$S$_2$C$_2$(CN)$_2$,[17] [Ru(bipy)$_2$Cl$_2$]·2H$_2$O,[18] [Ru(bipy)$_2$Cl(NO)][PF$_6$]$_2$[19] and [CpRu(PPh$_3$)$_2$Cl][20] were prepared by literature methods.

Preparation of [Ru(bipy)$_2$\{S$_2$C$_2$(CN)$_2$\}] (1)

[Ru(bipy)$_2$Cl$_2$]·2H$_2$O (0.53 g, 1.0 mmol) and Na$_2$S$_2$C$_2$(CN)$_2$ (0.28 g, 1.5 mmol) in a 1:1 EtOH–water mixture (200 cm^3) were heated at reflux for 2 h. The reaction solution was filtered and the volume of the filtrate was reduced to about one-third by distilling off the solvent. The resulting concentrate was cooled, whereby a black microcrystalline compound was formed, which was filtered and washed with water followed by absolute EtOH and Et$_2$O. It was recrystallized from MeCN–Et$_2$O and was

identified as [Ru(bipy)$_2${S$_2$C$_2$(CN)$_2$}] (**1**). Yield: 0.36 g, *ca* 65%.

Reaction of [(bipy)$_2$Ru{S$_2$C$_2$(CN)$_2$}] *with* [CpRu(PPh$_3$)$_2$Cl]

A suspension of a stoichiometric amount of [Ru(bipy)$_2${S$_2$C$_2$(CN)$_2$}] (0.11 g, 0.2 mmol) and [CpRu(PPh$_3$)$_2$Cl] (0.145 g, 0.2 mmol) in deaerated MeOH (30 cm^3) was heated at reflux for 1.5 h. The reaction solution gradually turned from orange–red to red–brown, and was then concentrated to 5–6 cm^3 by distilling off the solvent. A few drops of concentrated methanolic solution of NH$_4$PF$_6$ were added to precipitate the product, and the resulting brown compound was filtered, washed with Et$_2$O and air dried.

Purification of the complex was carried out by adsorbing its concentrated CH$_2$Cl$_2$ solution onto an activated neutral alumina column, and eluting with a 2 : 5 MeCN–benzene mixture. The major reddish-brown band was collected, solvent was removed at reduced pressure and the residue was recrystallized from CH$_2$Cl$_2$–petroleum ether. It was identified as [Ru$_2$(bipy)$_2$(PPh$_3$){S$_2$C$_2$(CN)$_2$}Cp][PF$_6$] (**2**). Yield: 0.19 g, *ca* 70%.

Reaction of [(bipy)$_2$Ru{S$_2$C$_2$(CN)$_2$}] *with* [Ru(bipy)$_2$Cl(MeOH)]$^+$

A suspension of [Ru(bipy)$_2$Cl(NO)][PF$_6$]$_2$ (0.156 g, 0.2 mmol) and NaN$_3$ (0.013 g, 0.2 mmol) in deaerated MeOH (30 cm^3) was stirred for 30 min followed by filtration to obtain a red solution of [Ru(bipy)$_2$Cl(MeOH)]$^+$.[21] To this filtrate was added [Ru(bipy)$_2${S$_2$C$_2$(CN)$_2$}] (0.11 g, 0.2 mmol) and the mixture was heated at reflux for 2.5 h, whereupon a brownish-red solution was formed. The solution was concentrated by distilling off the solvent and a few drops of conc. methanolic NH$_4$PF$_6$ solution were added to precipitate the compound, which was filtered, washed with Et$_2$O and dried in air. The complex was purified by chromatography on alumina (eluent 1 : 2 MeCN–benzene mixture) and recrystallized as described above. The brown–red compound was identified as [Ru$_2$(bipy)$_4${S$_2$C$_2$(CN)$_2$}Cl][PF$_6$] (**3**). Yield: 0.13 g, *ca* 60%.

Preparation of [(C$_6$H$_5$CH$_2$)$_2$S$_2$C$_2$(CN)$_2$]

Na$_2$S$_2$C$_2$(CN)$_2$ (5 g, 26.9 mmol) and benzyl chloride (25 cm^3, *ca* 220 mmol) in deaerated absolute EtOH (150 cm^3) were heated at reflux for 5 h with continuous stirring. The reaction mixture was then cooled and precipitated NaCl was removed by fil-

tration. The pale yellow filtrate (specific conductance *ca* 2 mmho cm^{-1}), which comprised a *ca* 0.16 M solution of [(C$_6$H$_5$CH$_2$)$_2$S$_2$C$_2$(CN)$_2$], was used as such in its reactions.

Preparation of [(bipy)$_2$Ru{S$_2$(CH$_2$C$_6$H$_5$}$_2$C$_2$(CN)$_2$)][PF$_6$]$_2$ (**4**)

[Ru(bipy)$_2$Cl$_2$]·2H$_2$O (0.2 g, 0.39 mmol) and [(C$_6$H$_5$CH$_2$)$_2$S$_2$C$_2$(CN)$_2$] solution (10 cm^3, *ca* 1.6 mmol) in a 1 : 3 EtOH–water mixture (20 cm^3) were heated at reflux for 2 h. The reaction solution gradually turned orange–red during the reflux period. It was extracted with Et$_2$O to remove excess ligand and benzyl chloride, and a few drops of conc. methanolic NH$_4$PF$_6$ solution were added to the aqueous layer to precipitate the orange–red compound. It was filtered, washed with water, EtOH and Et$_2$O successively and air dried. The complex was purified by adsorbing its conc. acetone solution onto an activated neutral alumina column and eluting with a 1 : 2 MeCN–benzene mixture. The major orange–red band was collected, solvent was removed at low pressure and the residue was recrystallized from acetone–Et$_2$O. The microcrystalline solid was dried *in vacuo* over CaCl$_2$ and was identified as [Ru(bipy)$_2${S$_2$(CH$_2$C$_6$H$_5$)$_2$C$_2$(CN)$_2$}][PF$_6$]$_2$ (**4**). Yield: 0.3 g, *ca* 75%.

Reaction of [(bipy)$_2$Ru{S$_2$(CH$_2$C$_6$H$_5$)$_2$C$_2$(CN)$_2$}][PF$_6$]$_2$ *with* [CpRu(PPh$_3$)$_2$Cl]

A suspension of [Ru(bipy)$_2${S$_2$(CH$_2$C$_6$H$_5$)$_2$C$_2$(CN)$_2$}][PF$_6$]$_2$ (0.205 g, 0.2 mmol) and [CpRu(PPh$_3$)$_2$Cl] (0.145 g, 0.2 mmol) in MeOH (30 cm^3) was heated at reflux for 2 h and the resulting solution was concentrated to approximately 5 cm^3 by distilling off the solvent. To this was added a few drops of conc. methanolic NH$_4$PF$_6$ solution to precipitate a red–brown compound, which was filtered, purified by chromatography on activated neutral alumina and recrystallized (from CH$_2$Cl$_2$–petroleum ether) as described above. The complex was identified as [Ru$_2$(bipy)$_2$(PPh$_3$)$_2$ {S$_2$(CH$_2$C$_6$H$_5$)$_2$C$_2$(CN)$_2$}Cp][PF$_6$]$_3$ (**5**). Yield: 0.28 g, *ca* 75%.

Reaction of [(bipy)$_2$Ru{S$_2$(CH$_2$C$_6$H$_5$)$_2$C$_2$(CN)$_2$}][PF$_6$]$_2$ *with* [Ru(bipy)$_2$Cl(MeOH)]$^+$

A suspension of [Ru(bipy)$_2$Cl(NO)][PF$_6$]$_2$ (0.156 g, 0.2 mmol) and NaN$_3$ (0.013 g, 0.2 mmol) in deaerated MeOH (30 cm^3) was stirred for 30 min followed by filtration to produce a red solution of [Ru(bipy)$_2$Cl(MeOH)]$^+$.[21] To this filtrate was added [Ru(bipy)$_2${S$_2$(CH$_2$C$_6$H$_5$)$_2$C$_2$(CN)$_2$}][PF$_6$]$_2$

(0.2 g, 0.2 mmol) and the suspension was heated at reflux for 3 h. The complex thus formed was precipitated, purified and recrystallized as described above. The brownish–red compound was identified as [Ru$_2$(bipy)$_4${S$_2$(CH$_2$C$_6$H$_5$)$_2$C$_2$(CN)$_2$}Cl][PF$_6$]$_3$ (6). Yield: 0.138 g, *ca* 40%.

Physical measurements

All IR spectra were recorded on a Perkin–Elmer 580 spectrophotometer, ^{1}H NMR spectra on a Varian EM 390 spectrophotometer and visible spectra on Cary 17 D or Schimadzu UV 240 spectrophotometers. Cyclic voltammograms were recorded on a Princeton Applied Research Model 175 instrument using a glassy carbon working electrode, Ag/AgCl reference and platinum wire auxiliary electrodes. Conductances were measured on an Elico conductivity bridge and the melting points were recorded on a Fisher–John melting point apparatus.

IR spectra were recorded with KBr pellets. Spectroscopic grade solvents were used for visible spectral study. CV scans were recorded using a 0.1 M tetraethylammonium perchlorate supporting electrolyte in MeCN (prepassed through activated neutral alumina). Conductances were measured in dry acetone at a fixed concentration, 1×10^{-4} mol dm^{-3}. Elemental analyses were carried out by the Regional Sophisticated Instrumentation Center, CDRI, Lucknow, India. Sulphur and halogens were estimated by standard methods.[22]

RESULTS AND DISCUSSION

Complexes 1–6 have been synthesized and their structures have been arrived at by a combination of their respective physico-chemical data and method of preparation. Relevant analytical, conductometric, spectrophotometric and cyclic voltammetry data for the complexes are given in Tables 1, 2 and 3, respectively.

Complex 1 was prepared by adopting the procedure used for the preparation of the corresponding PR$_3$ complexes,[17] by reacting [Ru(bipy)$_2$Cl$_2$]·2H$_2$O with 1.5 molar excess of Na$_2$mnt in aqueous ethanol under refluxing conditions. The Na$_2$mnt, when reacted with an excess of benzyl chloride in absolute dry ethanol, yielded its dithioether analogue, dibenzyldithiomaleonitrile [ddmn, (C$_6$H$_5$CH$_2$)$_2$S$_2$C$_2$(CN)$_2$]. Completion of the reaction was monitored through conductivity measurement, and the pale yellow solution was used as such in the further reactions after removing the precipitated NaCl, without attempting to isolate the ligand. Ddmn in 1 : 1 aqueous ethanol reacted

1

2

3

4

5

6
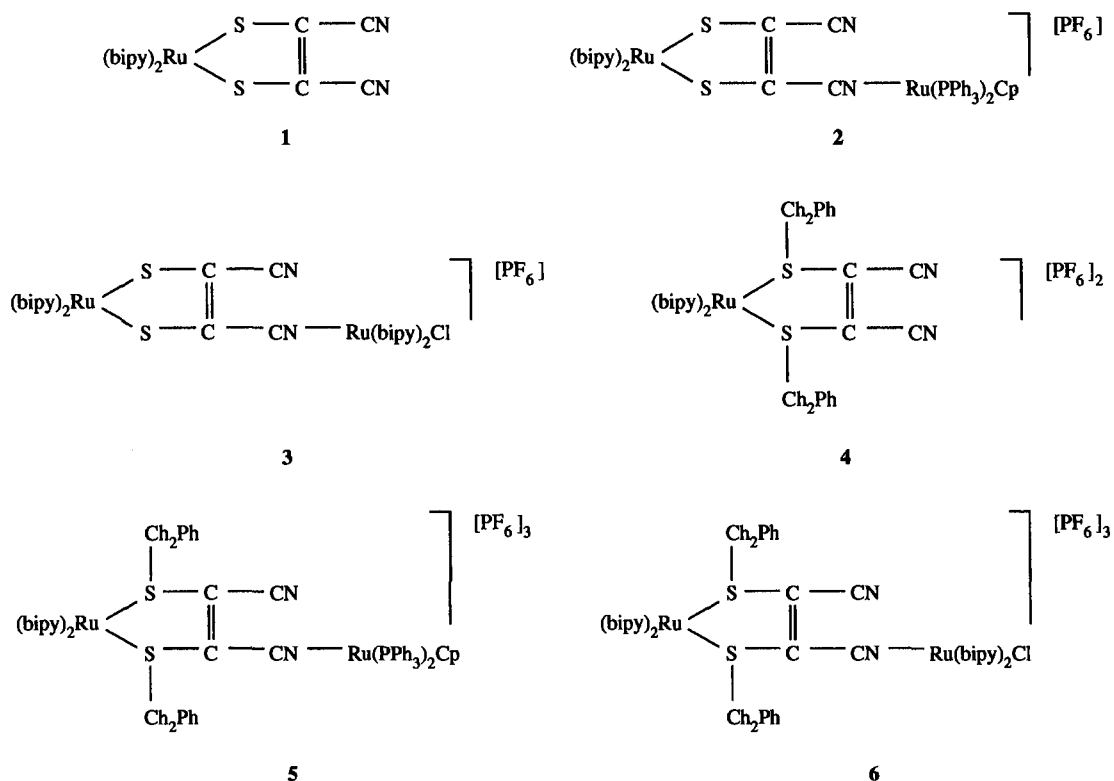
with [Ru(bipy)$_2$Cl$_2$]·2H$_2$O to give complex **4**. The ligands mnt^{2-} and ddmn are both *cis*-alkenes and have two sulphur and two nitrogen coordination sites. Therefore, they could coordinate in either η^2-S,S' or η^2-N,N' modes in complexes **1** and **4**. However, since the ruthenium(II) moiety exhibits higher affinity for soft base sulphur donors over hard base nitrogen donor ligands,[23] coordination through sulphur sites should be preferred, giving η^2-S,S' structures as the major products. The mononuclear complexes **1** and **4** upon treatment with equimolar amounts of [CpRu(PPh$_3$)$_2$Cl] or [Ru (bipy)$_2$Cl(MeOH)]$^+$ in methanol formed the dinuclear complexes **2**, **5**, **3** and **6**, respectively. Since the thioether sulphurs are capable of forming σ bonds to only one metal centre,[23,24] the second metal moiety in complexes **5** and **6** is likely to be bound onto either of the nitrogen sites. However, as the thiolate sulphurs can form one, two or three σ bonds to three different metal centres,[23,24] complexes **2** and **3** can have either $\mu(\eta^2$-S,S'; η^1-N) or $\mu(\eta^2$-S,S'; η^1-S) structures. Also, due to steric effects it is most likely that the complexes with the $\mu(\eta^2$-S,S'; η^1-N)mnt^{2-} formulation constitute the major products.

The mnt^{2-} complexes in the solid state as well as in solution are air sensitive, whereas the ddmn complexes are quite stable under similar conditions at room temperature. Conductance data (Table 1) show that all, except complex **1**, are of ionic nature. Their conductances are in agreement with reported data for the respective electrolyte types in similar solvents.[25]

IR spectra

The IR spectra of all complexes exhibit a strong sharp band in the 2185–2210 cm^{-1} region due to the CN stretching vibration. The ν(CN) band, in uncoordinated mnt^{2-}, is observed at 2180 cm^{-1},[26] and shifts significantly to higher energy upon coordination in complexes **1–3**. However, contrary to this, the position of the ν(CN) band in the corresponding ddmn complexes **4–6**, between 2185 and 2190 cm^{-1}, is unchanged in comparison to that in (CH$_3$)$_2$S$_2$C$_2$(CN)$_2$, at 2190 cm^{-1}.[27] The difference in behaviour of the two ligands is due to the differences in their σ, π characteristics. Since the mnt^{2-} ion is a resonance hybrid of three structures, in the uncoordinated state it does not have any specific

demand for dithiolate formulation. However, upon coordination to a metal moiety, it being a strong σ donor and weak π acceptor, the contribution from the dithiolate formulation (**I**) is increased over the thiolate–thioketone forms (**II** and **III**), causing an increase in the ν(CN) frequency. Such a resonance interaction is not possible for ddmn, and therefore the shift in the ν(CN) band position upon coordination to a metal moiety through sulphurs is rather insignificant.

In the dinuclear $\mu(\eta^2$-S,S'; η^1-N)mnt^{2-}/ddmn complexes **2**, **3**, **5** and **6**, the two CN groups are inequivalent. By analogy to the CN-bridged complexes, where the ν(CN) frequency shifts to higher energy due to force-field[28] strengthening, the nitrogen-coordinated CN stretching frequency should be higher[29–31] than for the uncoordinated group. Therefore, two ν(CN) bands are expected in complexes **2**, **3**, **5** and **6**. However, instead they exhibit only one ν(CN) band, although it is broad and is observed at moderately higher frequency than in their corresponding mononuclear precursors **1** and **4**. It seems that the effect of force-field strengthening is partially balanced by a C≡N bond weakening effect of π back-acceptance upon coordination through nitrogen.

The ν_s(C—S) band in complex **1** is observed at 870 cm^{-1} (mnt^{2-}, 860 cm^{-1}[27]), but it is shadowed by a strong, broad PF$_6$ band in other complexes. Also, the ν(C=C) and ν_{as}(C—S) bands, which appear in mnt^{2-} at 1430 and 1120 cm^{-1}, respectively, are shadowed by the bipyridyl/phenyl bands.

^{1}H *NMR spectra*

^{1}H NMR spectral data for all complexes are given in Table 1, and are very helpful in the assignment of structures. All complexes exhibit a complex series of signals in the δ 6.7–9.8 ppm region, indicative of the presence of (bipy)$_2$Ru^{II}[32] and/or (PPh$_3$)$_2$Ru^{II}[20] moieties. In complexes **2** and **5**, cyclopentadienyl proton signals are observed at δ 4.4 and 4.5 ppm respectively, which are significantly deshielded compared to that observed in analogous isonitrile complexes (δ 4.2 ppm)[29,30] and could be attributed to the deshielding effect of the C=C double bond of the ligand, aided by the greater positive charge on complex **5**. The —S—CH$_2$— proton signals in complexes **4–6** are observed at δ 2.0 ppm.

$$^-\text{S} — \underset{\underset{\displaystyle ^-\text{S} — \text{C} — \text{C} ≡ \text{N}}{\|}}{\text{C}} — \text{C} ≡ \text{N} \qquad \underset{\underset{\displaystyle ^-\text{S} — \text{C} = \text{C} = \text{N}^-}{|}}{\text{S} = \text{C} — \text{C} ≡ \text{N}} \qquad \underset{\underset{\displaystyle \text{S} = \text{C} — \text{C} ≡ \text{N}}{|}}{^-\text{S} — \text{C} = \text{C} = \text{N}^-}$$

I **II** **III**
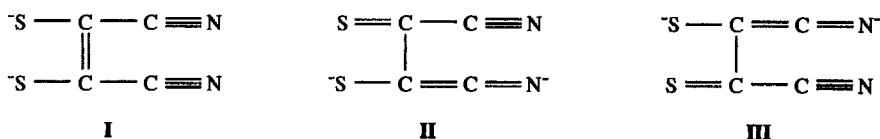
Table 1. Physical and microanalytical data

| Complex | Colour[a] | M.p. (°C) | Found (calc.)% | | | | | Δ_M[b] (Ω^{-1} cm^{2}mol^{-1}) |
			C	H	N	S	Cl	
1	B	N.M.	52.5 (52.1)	3.0 (2.9)	14.9 (15.2)	11.5 (11.6)	—	2
2	RB	182	56.0 (56.2)	3.8 (3.7)	5.9 (6.1)	4.6 (4.6)	—	175
3	BR	N.M.	46.4 (46.0)	2.9 (2.8)	12.0 (12.2)	5.4 (5.6)	3.3 (3.1)	145
4	OR	N.M.	44.6 (44.5)	3.0 (2.9)	8.4 (8.2)	6.1 (6.2)	—	190
5	RB	210	51.2 (51.0)	3.5 (3.5)	4.7 (4.4)	3.5 (3.4)	—	234
6	RB	N.M.	50.5 (50.4)	3.0 (2.8)	8.4 (8.7)	4.1 (4.0)	2.3 (2.1)	240

[a] B, black; RB, red–brown; BR, brownish-red; OR, orange-red.
[b] Concentration 1 × 10^{-4}M in dry acetone at room temperature.

Visible spectra

Visible spectral data for the complexes are given in Table 2. mnt^{2-} complexes showed three intense bands in the visible region between 400 and 500 nm, besides a moderate intensity band at longer wavelength. Because of the very nature of these complexes, a number of MLCT transitions are expected in their electronic spectra. Comparison with visible spectra of phosphine[18] and amine[33] complexes of (bipy)$_2$Ru^{II} indicates that two of the bands should arise from $d\pi$(Ru) → π^*(bipy) MLCT transitions. Upon binding a second ruthenium moiety onto complex 1, the middle band at 450 nm undergoes a bathochromic shift to 455 nm and gains intensity in complexes 2 (Fig. 1) and 3, which is a normal trend for the MLCT transitions involving a vacant π^* level of the bridging ligand.[16,34,35] Therefore, it could be assigned to a $d\pi$(Ru) → π^*(mnt^{2-}) transition. Hence the two remaining bands could be attributed to $d\pi$(Ru) → π^*(bipy) MLCT transitions. The hypsochromic shift, from 555 to 500 nm, of the lowest energy MLCT band upon displacement of chlorides in the precursor complex [Ru(bipy)$_2$Cl$_2$] by mnt^{2-} indicates significant stabilization of the $d\pi$ HOMO due to π interaction with the thiolate ligand. However, binding of the second ruthenium moiety onto the nitrogen site in complex 1 does not significantly influence the energy of the $d\pi$ HOMO level of the (bipy)$_2$(mnt)Ru^{II} moiety, indicating a poor mediatory role of the bridging ligand.

The visible absorption spectra of the thioether complex 4 (λ_{max} 472 nm, ε_{max} 7600 M^{-1} cm^{-1}) resembles the absorption spectra of the corresponding ethane-1,2-dimethylsulphide (eds) complex, [(bipy)$_2$Ru{S$_2$(CH$_3$)$_2$C$_2$H$_4$}][PF$_6$]$_2$ (7; λ_{max} 416 nm, ε_{max} 7200 M^{-1} cm^{-1}), in which the lowest energy absorption band is assigned to a $d\pi$(Ru) → π^*(bipy) MLCT transition.[36] Replacement of eds by ddmn, to bind with the (bipy)$_2$Ru^{II} moiety, shifts the Ru → bipy MLCT transition from 416 to 472 nm. This corresponds to a 2852 cm^{-1} shift in the energy of the ruthenium $d\pi$ orbitals, and is equivalent to a 0.35 V lowering of its oxidation potential. This is in good agreement with the observed difference of 0.39 V, even though the solvation effect is ignored.

Electrochemistry

Cyclic voltammograms of complexes were recorded in acetonitrile and the results obtained are listed in Table 3. Plots of peak currents versus the square root of the scan rate are linear, indicating that diffusion-controlled processes are occurring at

Table 2. Spectrophotometric data

Complex	IR $\bar{v}$ (cm^{-1}) CN	C—S	^{1}H NMR δ (ppm)	λ_{max}, nm (ε_{max}, M^{-1} cm^{-1})[a]
1	2205	870	6.8–9.8 (m, Ar—H)	500 (9500), 450 (9600), 416 (9500)
2	2210	—	4.4 (s, 5H, C$_5$H$_5$); 6.7–9.8 (m, 46H, Ar—H)	500 (8000), 455 (9600), 430 (sh)
3	2207	—	6.8–9.8 (m, Ar—H)	500 (8200), 455 (9000), 420 (sh)
4[b]	2185	—	2.0 (s, 4H, CH$_2$); 6.8–9.5 (m, 16H, Ar—H)	472 (7600)
5	2185	—	2.0 (s, 4H, CH$_2$); 4.5 (s, 5H, C$_5$H$_5$); 6.7–9.4 (m, 56H, Ar—H)	478 (7600)
6[b]	2290	—	2.0 (s, 4H, CH$_2$); 6.8–9.8 (m, 42H, Ar—H)	473 (7200)

[a] In acetonitrile.
[b] NMR spectra in DMSO-d_6, others in CDCl$_3$.

Table 3. Cyclic voltammetry data[a]

Complex	$E_{p,a}$	$E_{p,c}$	Slope of log $(i/i_d - i)$ vs E plot $E_{p,a}$	$E_{p,c}$	$i_{p,c}/i_{p,a}$	$E_{1/2}$ (V)
1	0.12	0.04	0.065	0.042	0.72	0.08
2	0.16	0.08	0.069	0.046	0.70	0.12
	0.80	—	0.076	—	—	—
3	0.17	0.10	0.075	0.043	0.70	0.13
	0.88	0.80	0.078	0.039	0.70	0.84
4	1.06	1.00	0.062	0.047	0.62	1.04
5	0.88	—	0.072	—	—	—
	1.14	1.06	0.076	0.46	0.85	1.10
6	0.88	0.79	0.069	0.050	0.73	0.84
	1.160	1.072	0.067	0.048	0.81	1.12

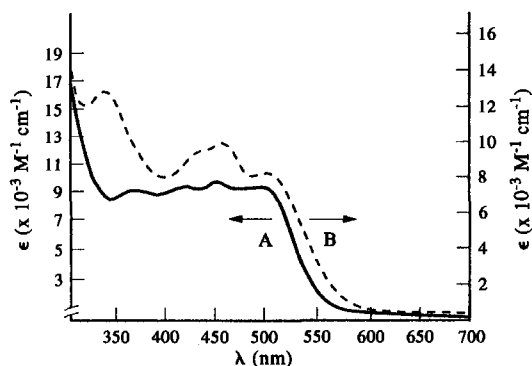[a] With 0.1 M TEAP in acetonitrile at glassy carbon electrode vs Ag/AgCl reference electrode.

Fig. 1. UV–vis spectra of [Ru(bipy)$_2${S$_2$C$_2$(CN)$_2$}] (1) (A) and [Ru$_2$(bipy)$_2$(PPh$_3$)$_2${S$_2$C$_2$(CN)$_2$}Cp][PF$_6$] (3) (B) in acetonitrile.

the electrode. The plots of log $(i/i_d - i)$ (i = current at an applied potential E; i_d = diffusion limiting current) versus applied potential E are linear,[37] and their slopes are in the range of one-electron processes.[34,38] The peak separations between anodic and cathodic waves, $E_{p,a} - E_{p,c}$, vary between 0.070 and 0.090 V, which are larger than the theoretical Nernstian value due to the uncompensated solution resistance.

All mnt^{2-} complexes exhibit an oxidation wave between 0.00 and 0.20 V vs Ag/AgCl, besides a wave at higher potential in the dinuclear complexes **2** and **3**. Since the mnt^{2-} in free as well as in coordinated form is found to exhibit a ligand-centred oxidation in this range,[39] the lowest oxidation wave in these complexes is attributed to a similar process. The second oxidations in complexes **2** and **3** are

similar to Ru^{II}/Ru^{III} oxidation protentials of analogous fragments [Cp(PPh$_3$)$_2$Ru—NC—]$^+$ (0.84 V vs Ag/AgCl)[30] and [(bipy)$_2$ClRu(MeCN)]$^+$ (0.85 V vs SCE)[40] under identical conditions.

The ddmn complex 4 showed reversible oxidation at $E_{1/2}$ 1.04 V vs Ag/AgCl (Fig. 2), which is 0.39 V lower than that in the corresponding eds complex [(bipy)$_2$Ru{S$_2$(CH$_3$)$_2$C$_2$H$_2$}][PF$_6$]$_2$, (7; $E_{1/2}$ 1.41 V vs SCE under similar conditions).[36] Considering this as a metal-centred Ru^{II}/Ru^{III} process, the relative ease of oxidation of the complex 4 over 7 by 0.39 V is equivalent to a 3144 cm^{-1} lowering of the Ru → bipy MLCT transition energy due to lesser stabilization of the Ru^{II} $d\pi$ orbitals, which is in good agreement with the observed difference ($\Delta\bar{\nu}$ = 2852 cm^{-1}). Complexes 5 and 6 exhibit one more oxidation wave besides the wave due to the [(bipy)$_2$Ru(η^2-S,S'-ddmn)]$^{2+}$ fragment, corresponding to oxidation of nitrogen-coordinated fragments [Cp(PPh$_3$)$_2$Ru—NC—]$^+$ or [(bipy)$_2$ClRu (MeCN)]$^+$. The oxidation potentials of these nitrogen-coordinated Ru^{II} moieties are nearly independent of the overall charge on the complex, possibly due to a small withdrawal of electron density from the $d\pi$ orbitals of the η^2-S, S'-coordinated Ru^{II}.

CONCLUSION

The (bipy)$_2$Ru^{II} complexes possessing mnt^{2-} or ddmn are good chromophores. The spectral and electrochemical properties of complexes 2, 3, 5 and 6 indicate that these ligands acting as bridging groups bring about only slight changes in the orbital energies of the two metal centres and therefore facilitate negligible metal–metal interaction.
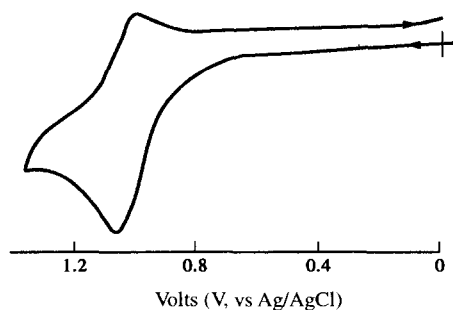
Fig. 2. Cyclic voltammogram of [(bipy)$_2$Ru {S$_2$(CH$_2$C$_6$H$_5$)$_2$C$_2$(CN)$_2$}] [PF$_6$]$_2$ (4) in acetonitrile with 0.1 M TEAP supporting electrolyte, glassy carbon working electrode and Ag/AgCl reference electrode.

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