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Synthesis, spectral and electrochemical aspects of maleonitriledithiolate and dibenzyldithiomaleonitrile complexes of cyclopentadienylruthenium(II)

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Abstract

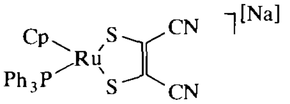
Complexes $[RuCp(PPh_3)\{S_2C_2(CN)_2\}]^-$ (**1**), $[Ru_2Cp_2(PPh_3)_4\{S_2C_2(CN)_2\}]$ (**2**) and $[RuCp(PPh_3)\{S_2(CH_2C_6H_5)_2C_2(CN)_2\}]^+$ (**3**) have been synthesized by the reaction of $[CpRu(PPh_3)_2Cl]$ with $S_2C_2(CN)_2^{2-}$ or $(C_6H_5CH_2)_2S_2C_2(CN)_2]$ in MeOH. The complex $[RuCp(PPh_3)\{S_2(CH_2\text{-}C_6H_5)_2C_2(CN)_2\}]^+$ when further reacted with $[CpRu(PPh_3)_2Cl]$ formed a dinuclear complex $[Ru_2Cp_2(PPh_3)_3\{S_2(CH_2C_6H_5)_2C_2(CN)_2\}]^{2+}$ (**4**). All these complexes have been characterized by their physical and spectral (IR; ^1H ^{31}P NMR and visible spectra) data. $S_2C_2(CN)_2^{2-}$ has been found to introduce a low lying MLCT absorption in the electronic spectra of its complexes. In CV scan these complexes exhibit an extended series of one electron transfer reactions. The metal-centred oxidation waves of the complexes have been correlated with the π acidity of ligands.

Keywords: Cyclopentadienyl; Dithioether; Electrochemistry; Maleonitriledithiolate; Ruthenium; Visible spectra

1. Introduction

A number of $Cp(PPh_3)_2Ru^{II}$ complexes with sulfur donor ligands, viz. $S_2CNR_2^-$, [1,2] S_2COR^-, [1–3] S_2CCN^-, [2,4] S_2CNCN^{2-}, [5] S_2CR^-, [6] S_x^{2-}, [7–10] MS_4^{2-}, [11], (x = 2–7; M = Mo, W) have recently been well characterized; however electronic, spectral and electrochemical studies of only a few such complexes have so far been reported [4,5,9–13]. There has been no such study reported in which the $Cp(PPh_3)_2Ru^{II}$ moiety is bound to maleonitriledithiolate, (mnt^{2-}), $S_2C_2(CN)_2^{2-}$.

Mnt^{2-} complexes with transition metal ions including organometallic complexes were extensively studied during the sixties [14,15]. Voltammetric study of $[M(mnt)_2]^{2-}$ and CpM–mnt complexes revealed an extended series of one electron transfer reactions [15] in which either an electron is added to form metal



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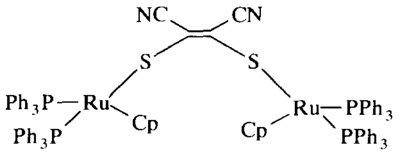

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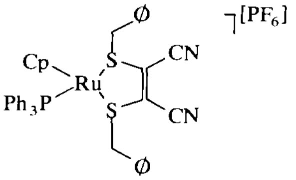

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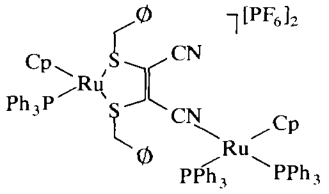

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Table 1
Physical and microanalytical data

Complex	Colour [a]	m.p. °C	Analyses: Found (Calcd.)%				Λ_M [b] Ω^{-1} cm^2 mol^{-1}
			C	H	N	S	
1	R	190–192	54.4(54.8)	3.5(3.4)	4.6(4.7)	11.8(10.8)	170
2	R	158	67.7(67.9)	4.5(4.6)	1.8(1.8)	3.9(4.2)	5
3	OY	110	54.7(55.0)	4.0(3.8)	3.2(3.1)	7.0(7.2)	135
4	YB	118	56.8(56.9)	4.1(4.0)	1.6(1.6)	3.9(3.7)	180

[a]: Colour R = red, OY = orange yellow, YB = yellow brown:
[b]: 1 × 10^{-4} M in dry acetone at room temperature.

Table 2
IR; ^{1}H and ^{31}P NMR and visible spectral data

Complex	IR ν cm^{-1}	NMR δ/ppm (Assignment)		Electronic Spectra λ_{max} nm (ϵ_{max} M^{-1} cm^{-1})
		^{1}H	^{31}P	
1	2200(CN) 850(CS)	4.7 (s, 5H, C_5H_5); 6.7–7.7 (m, 15H, Ph)	23.0	500(4200), 364(5000)
2	2200(CN) 840(CS)	4.6 (s, 10H, C_5H_5); 6.7–7.8 (m, 60H, Ph)	41.2	520(6000), 364(8500)
3	2190(CN)	6.7–7.8 (m, 25H, Ph) 4.5 (s, 5H, C_5H_5) 2.0 (s, 4H, CH_2)	40.4	342(6400)
4	2195(CN)	6.7–7.8 (m, 55H, Ph) 4.4–4.5 (d, 10H, C_5H_5) 2.0 (s, 4H, CH_2)	41.6 42.0	345(6000)

centred reduction products [15–18] or electrons are successively removed to form ligand- and metal-centred oxidation products subsequently [15]. The ease of oxidation and the stability of the adjacent oxidized and reduced forms of the bis- and tris- mnt^{2-} transition metal complexes is currently being exploited in their use as electron donors in light-induced electron transfer reactions [19–21].

This present study is aimed to synthesize mono- and dinuclear mnt^{2-} bridged complexes possessing the $Cp(PPh_3)_2Ru^{II}$ moiety, and to investigate their spectral and electrochemical properties. The MLCT absorptions and reversible oxidation steps are to be compared with those of analogous dibenzyldithiomaleonitrile (ddmn, $(C_6H_5CH_2)_2S_2C_2(CN)_2$) complexes. The $Cp(PPh_3)_2Ru^{II}$ complexes exhibit good solubility characteristics and excellent kinetic stability. These properties have enabled synthesis and characterization of four new mnt^{2-} and ddmn complexes $Na[RuCp(PPh_3)\{S_2C_2(CN)_2\}]$ (**1**) $[Ru_2Cp_2(PPh_3)_4\{S_2C_2(CN)_2\}]$ (**2**), $[RuCp_2(PPh_3)\{S_2(CH_2C_6H_5)_2C_2(CN)_2\}][PF_6]$ (**3**), $[Ru_2Cp_2(PPh_3)_3\{S_2(CH_2C_6H_5)_2C_2(CN)_2\}][PF_6]_2$ (**4**) all of which have distinctive spectral and electrochemical properties, as described in this paper.

2. Results and discussion

Complexes **1**–**4** have been synthesized and their structures deduced from their physico-chemical data. Relevant analyses, conductometric, spectrophotometric and cyclic voltammetry data for the complexes are given in Tables 1–3.

Mnt^{2-} has been converted into ddmn by reaction with an excess of benzylchloride in dry methanol. When mnt^{2-} or ddmn in 1.5 to 2.5 molar excess was treated with $[CpRu(PPh_3)_2Cl]$ in methanol it displaced Cl and one PPh_3 to give mononuclear complexes. Since the ligands mnt^{2-} and ddmn in less polar solvents (like ethanol etc.) prefer the *cis* alkene configuration [22], the (η^2-*S*,*S'*) and (η^2-*N*,*N'*) coordinations are equally

Table 3
cyclic voltammetry data [a]

Complex	$E_{p,a}$	$E_{p,c}$	ΔE mV	$i_{p,c}/i_{p,a}$	$E_{1/2}$ V
1	0.06	0.00	60	– [b]	0.03
	0.44	0.36	80	0.60 [b]	0.40
	1.05	0.95	100	0.50	1.00
2	0.20	−0.60	80	– [b]	−0.20
	0.46	0.40	60	0.50 [b]	0.44
	0.67	0.61	60	0.60	0.64
	1.06	0.95	110	0.50	1.01
3	0.52	0.43	90	0.75	0.48
4	0.55	0.47	80	0.80	0.51
	0.92	0.84	80	0.75	0.88

[a]: Condition: 0.1M TEAP in acetonitrile at glassy carbon electrode vs. Ag/AgCl reference electrode at a scan rate of 50 mV s^{-1}
[b]: If scan is reversed after 0.50 V, $i_{p,c}/i_{p,a}$ ratios found for complex 1 are 0.97, 0.90; and for complex 2 are 0.95, 0.90.

probable. However due to the high affinity of soft acid Ru^{II} towards sulfur donor sites [23], the major products are likely to have (η^2-*S,S'*) coordination giving structures **1** and **3**. Complex **3** upon treatment with an equimolar amount of $[CpRu(PPh_3)_2Cl]$ has given the dinuclear complex which is hypothesized to have structure **4** because the thioether sulfurs can form only one σ bond to a single metal centre [24]. However as the thiolate sulfurs in mnt^{2-} are capable of forming one, two or three σ bonds to three different metal centres [24], the similar dimerization reaction for complex **1** to produce the $\mu(\eta^2$-*S,S'*; η^1-*N*)mnt^{2-} complex could not be carried out. Instead the neutral dinuclear complex **2** was synthesized by reacting $Na_2S_2C_2(CN)_2$ and $[CpRu(PPh_3)_2Cl]$ in 1:2 molar ratio in methanol. The complex is expected to have a *cis* $\mu(\eta^2$-*S,S'*; η^1-*N*) structure analogous to $[Cp_2Fe_2(CO)_4\{S_2C_2(CN)_2\}]$ [25].

All but neutral complexes show good solubility in CH_2Cl_2, MeCN, dmf, methanol, and polar organic solvents generally. The neutral complex **2** is highly soluble in benzene and toluene. The mnt^{2-} complexes are air sensitive in the solid state as well as in solution, but corresponding ddmn complexes are quite stable under ambient room conditions for an appreciable length of time. Conductance data show that all except complex **2** are of an ionic nature and their conductances are in good agreement with those of similar electrolyte types under identical conditions [26].

2.1. IR spectra

All these complexes exhibit a characteristic strong ν(CN) band in the region 2190–2210 cm^{-1}. The ν(CN) band in uncoordinated $Na_2S_2C_2(CN)_2$ is observed at 2185 cm^{-1} [22] which shifts to significantly higher frequency due to an enhanced contribution from dithiolate formulation over the thiolate-thioketone formulation upon its coordination. Such an effect being non-operational for ddmn, in complex **3** the position of the ν(CN) band is unchanged upon complexation [27]. The ν(CN) band in thioether complex **4** is observed at 2195 cm^{-1} and is slightly broad. If the dinuclear complex possesses $\mu(\eta^2$-*S,S'*; η^1-*N*) ddmn coordination the two CN groups are inequivalent, and the bridging CN stretching frequency is expected to shift to a higher frequency [28,29], thereby resulting in two ν(CN) bands. However the effect of force-field strengthening [30] could partially be countered by the C≡N bond weakening effect of the π backdonation. Thus the band appears to be a composite of two bands and has a broad contour. The ν(C=C) and ν_{as}C–S) bands [27] are masked by strong phosphine-phenyl bands, but the ν_s(C–S) in complexes **1** and **2** is observed at 850 and 840 cm^{-1} respectively, and is significantly low shifted due to binding of bulky metal centres to sulfur. In ddmn complexes this band has been shadowed by the strong broad PF_6 band.

2.2. NMR spectra

Three groups of proton resonance signals are observed in these complexes as follows: for phenyl protons, between δ 6.7–7.8; for cyclopentadienyl protons, δ 4.4–4.7; and for alkyl protons δ 1.2–3.2 ppm. In the neutral dinuclear complex **2** a single cyclopentadienyl proton signal is observed at δ 4.6 ppm indicating that both cyclopentadienyl rings are chemically equivalent. However contrary to what is expected from the overall charge on the complex the cyclopentadienyl protons in anionic complex **1** (δ 4.7 ppm) are more deshielded than in the neutral complex **2** (δ 4.6 ppm), possibly due to the deshielding effect of the C=C double bond of mnt^{2-} being larger in the former than in the latter complex where the distance is greater. The dinuclear thioether complex **4** showed two cyclopentadienyl proton signals at δ 4.4 and 4.5 ppm. Since the cyclopentadienyl proton signal in the mononuclear complex **3** is observed at δ 4.5 ppm, the signals in complex **4** at δ 4.4 and 4.5 ppm could tentatively be assigned to N and S bonded RuCp protons in agreement with the literature data [4,5].

The S bonded RuCp proton signals in all complexes are slightly broad possibly due to stereochemical nonrigidity of the RuS_2C_2 ring [31] and consequent spread in the deshielding effect of the dithiolene C=C double bond on cyclopentadienyl protons.

The ^{31}P NMR spectra of complex **2** exhibit only one signal at δ 41.2 ppm (vs. H_3PO_4 as external reference) indicating equivalence of the PPh_3 groups. In complex **4** two signals are observed at δ 40.6 and 42.0 ppm having intensity ratio 1:2 and are indicative of its $\mu(\eta^2$-*S,S'*; η^1-*N*) structure. The corresponding S bonded Ru–P signal in the mononuclear complex **3** is observed at δ 40.4 ppm.

2.3. Visible spectra

Visible spectra of the complexes were recorded in acetonitrile and the characteristics of their prominent peaks are listed in Table 2. The mnt^{2-} complexes **1** and **2** show intense bands at 500 nm (ϵ_{max} 4200 M^{-1} cm^{-1}) and 520 nm (ϵ_{max} 6000 M^{-1} cm^{-1}) respectively. Neither the precursor complex $[CpRu(PPh_3)_2Cl]$ [10,32] nor the ligand [22] possess any band in this region. The bathochromic shift of the band upon dimerization is a normal trend observed for such MLCT transitions that involve the vacant π^* level of the bridging ligand [4,33]. Therefore, considering their intensity and position, these bands could tentatively be assigned to $d\pi(Ru) \rightarrow \pi^*$ (mnt^{2-}) charge transfer transition. It is expected that the vacant π orbital has been made available by the valence isomerization of the Ru–mnt bond [34]. Since the thioether ddmn possess neither any low lying vacant π^* acceptor orbital, nor the capacity to undergo valence isomerization in the coordinated state, this band is missing in complexes **3** and **4**. The absorption bands in complexes **3** and **4**, which are reasonably broad and tail towards longer wavelength might arise from absorptions due to two overlapping LMCT transitions, Cp → Ru [35] and d(π)S → Ru [15].

2.4. Electrochemistry

Cyclic voltammograms were recorded in deaerated acetonitrile which was prepassed through activated neutral alumina, with 0.1 M TEAP supporting electrolyte at different scan rates. Glassycarbon working, platinum wire auxiliary and Ag/AgCl reference electrodes were used. Various electrochemical parameters obtained for the complexes are given in Table 3.

Plots of peak currents vs. the square root of the scan rate are linear, indicating that diffusion controlled processes occur at the electrode. The peak separation between anodic and cathodic waves $E_{p,a}$–$E_{p,c}$ vary in the range 60–110 mV which are larger than the theoretical Nernstian value and are normally attributed to the uncompensated solution resistance.

For complex **3** a single anodic wave at 0.52 V and corresponding cathodic wave at 0.43 V vs. Ag/AgCl are observed. The plots of $\log[i/(i_d - i)]$ (i = current at an applied potential E; i_d = diffusion limiting current) vs. applied potential E, are linear for both cathodic and anodic processes and exhibit slopes of 0.068 and 0.047 respectively. This is close to the value for one-electron processes [36]. The peak separation and $i_{p,c}/i_{p,a}$ ratio indicate that it is a one electron reversible oxidation reduction process. The complex **4** exhibits two reversible one-electron waves at $E_{1/2}$ 0.51 and 0.88 V vs. Ag/AgCl with $\log[i/(i_d - i)]$ vs. E slope for anodic processes 0.065 and 0.075 and for cathodic processes 0.048 and 0.044 respectively. Of this the first wave is identical to the Ru^{II}/Ru^{III} process of the $Cp(PPh_3)Ru(\eta^2$-*S,S'*-ddmn) fragment while the second one is identical to that of the $Cp(PPh_3)_2Ru$–NC fragment [32]. The oxidation data indicate that the removal of an electron from the $Cp(PPh_3)_2Ru$–NC fragment is more difficult than from $Cp(PPh_3)Ru(\eta^2$-*S,S'* – ddmn) possibly due to the poorer π stabilization imparted by ddmn to the dπ HOMO orbitals in the latter fragment.

For mnt^{2-} complexes **1** and **2** a number of anodic waves are observed between −0.40 and 2.00 V, but the corresponding cathodic waves are less prominent. However if the scan is reversed after the first two waves during the voltammetry scan of these complexes, the peaks exhibit reversible one electron transfer characteristics ($i_{p,a} - i_{p,c}$ = 60–80 mV; $i_{p,c}/i_{p,a} > 0.9$). Thus these oxidations are identical to that observed in $Na_2S_2C_2(CN)_2$ ($E_{1/2}$ 0.08 and 0.43 V vs. Ag/AgCl) [37] and could therefore tentatively be assigned to the ligand centred oxidation processes. The third oxidation is irreversible with $E_{p,a}$ observed at 1.05 V vs. Ag/AgCl expected to arise from a Ru^{II}/Ru^{III} process followed by a chemical reaction. It is observed at a significantly higher potential than in the precursor complex $RuCp(PPh_3)_2Cl$ ($E_{1/2}$ 0.06 V vs. Ag/AgCl) [32]. The relative difficulty of the Ru^{II}/Ru^{III} process in $\mathbf{1}^{2+}$ is due to extensive stabilization of the metal dπ HOMO through strong π back-acceptance by the dithioketone (i.e. two-electron oxidized mnt^{2-}) [38]. Contrary to this the thioether has vacant 4d(S) π acceptor orbitals of significantly higher energy and is therefore a poorer π acceptor than dithioketone and PPh_3 [24]. Thus the Ru^{II}/Ru^{III} oxidation process in thioether complexes **3** and **4** is observed at much lower potentials.

In conformity with the CV scan for complex **1** the four oxidation waves for the dinuclear complex **2** could tentatively be assigned to the following processes:

$$[Ru^{II}\text{–S–C=C–S–}Ru^{II}]$$

$$\underset{-0.02\ \text{V}}{\overset{\mp e}{\rightleftarrows}} [Ru^{II}\text{–S–C=C–S–}Ru^{II}]^{+}$$

$$\underset{0.44\ \text{V}}{\overset{\mp e}{\rightleftarrows}} [Ru^{II}\text{–S=C–C=S–}Ru^{II}]^{2+}$$

$$\xrightarrow[0.64\ \text{V}]{\mp e} [Ru^{II}\text{–S=C–C=S–}Ru^{III}]^{3+}$$

$$\xrightarrow[1.01\ \text{V}]{-e} [Ru^{III}\text{–S=C–C=S–}Ru^{III}]^{4+}$$

3. Experimental section

All chemicals were of analytical reagent grade and were used as received. Reactions were carried out under nitrogen atmosphere. Analyses physical and electrochemical measurements were carried out as described elsewhere [5,33]. The starting compounds, $Na_2S_2C_2(CN)_2$ [39] and $RuCp(PPh_3)_2Cl$ [40], were synthesized by literature procedures.

3.1. Preparation of Na[RuCp(PPh$_3$){S$_2$C$_2$(CN)$_2$}] (1)

A suspension of $[CpRu(PPh_3)_2Cl]$, (0.145 g, 0.2 mmol) and $Na_2S_2C_2(CN)_2$ (0.056 g, 0.27 mmol) in deoxygenated MeOH (25 ml) was stirred at room temperature for 10 h under a nitrogen atmosphere. The resulting red solution was filtered and the solvent was removed from the filtrate at low pressure to complete dryness. The residue was washed with benzene, dissolved in the minimum quantity of CH_2Cl_2 and crystallized by adding an excess of petroleum ether. It was purified by passing through a Sephadex LH-20 column using MeOH as eluent. The red fraction was collected, the solvent was removed at low pressure and it was recrystallized from CH_2Cl_2/petroleum ether. (Yield: 0.06 g, ca. 50%).

3.2. Preparation of $[Ru_2Cp_2(PPh_3)_4\{S_2C_2(CN)_2\}]$ (2)

A suspension of $[CpRu(PPh_3)_2Cl]$; (0.29 g, 0.4 mmol) and $Na_2S_2C_2(CN)_2$ (0.037 g, 0.2 mmol) in deoxygenated MeOH (30 ml) was stirred at room temperature for 15 h. The resulting red solution was filtered, concentrated under low pressure to ca. 5 ml and was transfered to a Sephadex LH-20 column. It was eluted with MeOH and the main red band was collected. The solvent was removed at low pressure and the residue was recrystallized from CH_2Cl_2/petroleum ether to obtain a red powdery compound (yield: 0.18 g, ca. 60%).

3.3. Preparation of dibenzyldithiomaleonitrile $(C_6H_5CH_2)_2S_2C_2(CN)_2$

$Na_2S_2C_2(CN)_2$ (5.0 g, ca. 26.9 mmol) and benzylchloride (25 ml, ca. 220 mmol) in deaerated dry MeOH (150 ml) was refluxed for 5 h with continuous stirring. It was cooled, precipitated NaCl was filtered out and the pale yellow solution was used as ligand solution in further reactions.

3.4. Preparation of $[RuCp(PPh_3)[S_2(CH_2C_6H_5)_2C_2(CN)_2]]$ $[PF_6]$ (3)

A suspension of $[CpRu(PPh_3)_2Cl]$ (0.145 g, 0.2 mmol), ligand solution (3 ml, ca. 0.5 mmol) and NH_4PF_6 (0.16 g, ca. 0.98 mmol) in deoxygenated MeOH (25 ml) was stirred at room temperature for 6 h. The resultant orange solution was poured into excess water with continuous stirring whereby an orange solid separated out. It was purified and recrystallized, as described above (yield: 0.14 g, ca. 80%).

3.5. Preparation of $[Ru_2Cp_2(PPh_3)_3\{S_2(CH_2C_6H_5)_2C_2(CN)_2\}]$ $[PF_6]_2$ (4)

$[CpRu(PPh_3)_2Cl]$, (0.145 g, 0.2 mmol), $[RuCp(PPh_3)\{S_2(CH_2C_6H_5)_2C_2(CN)_2\}]$ (PF_6) (0.20 g, 0.2 mmol) and NH_4PF_6 (0.18 g, ca. 0.92 mmol) in MeOH (25 ml) was stirred at 50°C for 6 h. The solution was concentrated at low pressure and the separated orange microcrystalline solid was filtered out. It was purified and recrystallized as discribed above. (Yield: 0.24 g, ca. 70%).

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