Synthesis and characterization of dinuclear ruthenium(II) and ruthenium(III) acetylacetono complexes with dianion of 2,5-dihydroxy-1,4-benzoquinone as bridging ligand
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Synthesis of [{(acac)Ru}2(μ-L)] and [{(bipy)(acac)Ru}2(μ-L)] (where acac=acetylacetonato, bipy=2,2’-bipyridine) has been achieved by the reaction of K2L (where K2L=dipotasium salt of 2,5-dihydroxy-1,4-benzoquinone) with two equivalents of cis-[RuII(acac)2(CH3CN)]2 or [RuIIBr(acac)(bipy)]. The complexes have been characterized on the basis of elemental analyses, magnetic susceptibility and conductivity data, IR, UV-visible and 1H NMR spectral data and cyclic voltammetric studies.

There has been a continuing interest in complexes of ruthenium having dianion of 2,5-dihydroxy-1,4-benzoquinone as bridging ligand. The chemistry of tetraoxolene based donor site forming a five-membered ring to each metal ions in which one oxygen atom is formally quinonoidal and other is anionic, so the binding site is similar to that presented by semiquinone.

Experimental
RuCl3.nH2O was obtained from Arora-Mathey Limited, Kolkata. Tetrabutylammonium bromide was of Fluka grade. All the solvents used (analytical grade) were freshly distilled before use. HPLC-grade acetonitrile and spectroscopic grade chloroform were used for electrochemical and UV-visible spectral studies, respectively. Tetrabutylammonium perchlorate (TBAP)15, K2L16, cis-[RuII(acac)2(CH3CN)]217 and [RuIIBr(acac)(bipy)]18 were prepared by the previously reported methods. C, H and N microanalyses were obtained from RSIC, NEHU. IR spectra were recorded as compressed KBr discs on a Perkin-Elmer Model 983 spectrophotometer in 4000-400 cm⁻¹ range. Electronic absorption spectra were recorded on a Beckman DU-650 spectrophotometer in the range 800-200 nm. Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer EG and G PARC Model 155 at room temperature. 1H NMR spectra were recorded on a Bruker ACF-300, 300 MHz spectrometer, in chloroform-d. Conductivity measurements were made on a Wayne-Kerr automatic precision bridge B 905 conductivity meter with millimolar solutions. Cyclic voltammetric studies were carried out on an EG and G PARC voltameter. The experiments were carried out in acetonitrile using TBAP as supporting electrolyte in a three electrode configuration using a Pt disc as the working electrode. All potentials are referenced to the SCE. Reported potentials are uncorrected for the junction contribution.

Preparation of [{(acac)Ru}II/2(μ-L)]
To an orange coloured solution of cis-[RuII(acac)2(CH3CN)]2 (0.19 g, 0.5 mmol) in dichloromethane (30 cm³), an aqueous solution (5 cm³) of K2L (0.54 g, 0.25 mmol) was added and the
reaction mixture was refluxed on a waterbath for 5 h. A violet colour solution obtained in dichloromethane layer was separated from the aqueous solution. It was washed with water to remove unreacted K$_2$L. Violet crystals of the compound were obtained by evaporating dichloromethane at room temperature. It was washed with diethyl ether and dried in vacuo. Yield=0.14 g (76.29 %) [Found: C, 42.51; H, 4.18. Calc. for C$_{39}$H$_{30}$O$_{12}$Ru$_2$: C, 42.39; H, 4.07 %].

Preparation of [(bipy)(acac)Ru$^{II}$]$_2$(μ-L)]

A mixture of K$_2$L (0.054 g, 0.25 mmol) and [Ru$^{II}$Br(acac)(bipy)] (0.218 g, 0.5 mmol) in ethylene glycol (20 cm$^3$) was heated on a waterbath for 1 h, when the colour of the solution changed from reddish brown to green. After cooling, a green colour compound separated out. It was centrifuged and dried in vacuo. It was dissolved in dichloromethane (20 cm$^3$) and filtered to remove KBr. Green colour compound was obtained by evaporating dichloromethane at room temperature. It was washed with ethanol and dried in vacuo. Yield=0.13 g (61.17 %). [Found: C, 50.99; H, 3.87; N, 6.69. Calc. for C$_{38}$H$_{30}$N$_4$O$_8$Ru$_2$: C, 50.82; H, 3.76; N, 6.59 %].

Results and discussion

[(acac)$_2$Ru$^{III}$]$_2$(μ-L)] and [(bipy)(acac)Ru$^{II}$]$_2$(μ-L)] have been synthesized by the reaction of K$_2$L with two equivalents of cis-[Ru$^{III}$]$_2$(CH$_3$CN)$_2$] or [Ru$^{II}$Br(acac)(bipy)] at waterbath temperature in CH$_2$Cl$_2$/H$_2$O or ethylene glycol. The formulation of the complexes were confirmed by the C, H, N analytical data. The molar conductance values of the complexes in acetonitrile (10$^{-3}$ M) at room temperature suggest non-electrolytic nature. Room temperature magnetic moment values of [(acac)$_2$Ru$^{III}$]$_2$(μ-L)] ($μ_{eff}$=1.9 BM) corresponds to the trivalent state of ruthenium (low spin d$^5$, S=1), as expected. The complex [(bipy)(acac)Ru$^{II}$]$_2$(μ-L)] is diamagnetic which corresponds to the bivalent state of ruthenium (low spin d$^6$, S=0), as expected.

The IR spectra of [(acac)$_2$Ru$^{III}$]$_2$(μ-L)] and [(bipy) (acac) Ru$^{II}$]$_2$(μ-L)] contain many sharp bands of different intensities due to vibrations arising from the coordinated acac, 2,2'-bipyridine and L$^2$ and are therefore complex in nature. No attempts have been made to assign the individual bands. However, comparison of the IR spectra of these complexes with those of the respective precursors, i.e., cis-[Ru$^{III}$]$_2$(acac)$_2$(CH$_3$CN)$_2$] or [Ru$^{II}$Br(acac)(bipy)] shows that besides small shifts in frequencies, some vibrations are common in both the spectra. Absence of the band at 2257 cm$^{-1}$ in the IR spectrum of [(acac)$_2$Ru$^{III}$]$_2$(μ-L)] confirms that both CH$_3$CN molecules have been lost from cis-[Ru$^{III}$]$_2$(acac)$_2$(CH$_3$CN)$_2$] in its reaction with K$_2$L. The spectra of complexes showed two strong and broad bands at 1516 and 1536 cm$^{-1}$, which are characteristic due to overlapping of v(C=C) or v(C=O) of chelated O-bonded acetylacetonato and diamin of 2,5-dihydroxy-1,4-benzoquinone (L$^2$) \cite{14,17,21}, as the strong band of L$^2$ shifts to lower frequency suggests the diamin of 2,5-dihydroxy-1,4-benzoquinone is bridged to the metal ions through O-atom. The IR spectrum of the complex [(bipy)(acac)Ru$^{II}$]$_2$(μ-L)], exhibits a broad band at 1630 cm$^{-1}$, which is assigned to v(C=N) of 2,2'-bipyridine \cite{14}. Besides the above, characteristics bands due to 2,2'-bipyridine are also observed \cite{21}. The IR spectral data are, therefore, in good agreement with the composition of these complexes.

The $^1$H NMR spectrum of [(acac)$_2$Ru$^{III}$]$_2$(μ-L)] in CDCl$_3$ shows signals at higher chemical shift. Singlet at δ=18.55, δ=18.94, δ=21.57 and δ=21.95, confirms the presence of methyl protons of four acetylacetonato groups \cite{22,23} and another singlet at δ=5.6, may be assigned to two CH protons of L$^2$. The signals due to methine protons of acetylacetonato groups were not observed due to rapid exchange of protons with CDCl$_3$ \cite{24}. The $^1$H NMR spectrum of [(bipy)(acac)Ru$^{II}$]$_2$(μ-L)] in CDCl$_3$ showed two singlet at δ=1.82 and δ=1.95, which may be assigned to the methyl protons of the acetylacetonato groups \cite{21}. Singlets at δ 5.9 and δ 5.2, confirms the presence of two CH protons of diamin of 2,5-dihydroxy-1,4-benzoquinone \cite{13,14} and methine protons of acetylacetonato, respectively \cite{17,21}. Several signals were observed in the region δ 6.9 to δ 8.9, which may be assigned due to the aromatic protons of 2,2'-bipyridine ligands \cite{12,21}.

The cyclic voltammogram of the complex [(acac)$_2$Ru$^{III}$]$_2$(μ-L)] for a ca. 10$^{-3}$M solution in acetonitrile using TBAP (0.05M in acetonitrile) as supporting electrolyte showed one quasi-reversible, ($ΔE_p=90$ mV) wave at $E_{1/2} =+1.19$ V versus SCE, viz., Ru(II)-Ru(IV)/Ru(II)-Ru(III) couples and the cyclic voltammogram of the complex [(bipy)(acac)Ru$^{II}$]$_2$(μ-L)] for a ca. 10$^{-3}$M solution in acetonitrile using TBAP (0.05M in acetonitrile) as supporting electrolyte showed two reversible, ($ΔE_p=70-80$ mV) wave at $E_{1/2} =-0.6$ V and +0.56 V versus SCE, viz., due to bipy or L$^2$(i.e.
semiquinone–catecholate) reduction and Ru(III)–Ru(II)/Ru(II)–Ru(II) couples, respectively. In both cases, one irreversible one electron reduction wave at -1.06 and -1.2 V is observed which may be assigned to the bridging ligand reduction. Thus, metal centre of oxidation states of 3+ of [(acac)2Ru(III)]2(μ-L)] does not provide a useful probe of the π-acceptor capability of acetylacetonato or dianion of 2,5-dihydroxy-1,4-benzoquinone (bridging ligand), because of weak tendency of such ions to transfer electron density to π-acceptor ligands compared to [(bipy(acac)Ru(II)]2(μ-L)], where the oxidation states 2+ has a much higher propensity for back bonding which leads to strong metal-metal interaction. The UV visible spectrum of [(bipy(acac)Ru(II)]2(μ-L)] agrees well with its formulation and is concomitant with the fact that the closer energy matching of the π* of L2- and Ru(dπ) orbitals results a stronger π interaction.

The electronic spectra of [(acac)2Ru(III)]2(μ-L)] and [(bipy(acac)Ru(II)]2(μ-L)] in CHCl3 solutions show one or two absorption in the region 243-296 nm (ε = 4.8 × 103 - 25.3 × 103), typical of terminal and bridging ligand-centred π→π* transitions. The complex [(acac)2Ru(III)]2(μ-L)] showed one band at 344 nm (ε = 3.1 × 103) may be assigned to LMCT bands of the type acac(π)→Ru(III) transitions, whereas a lower energy broad band at 596 nm (ε = 2.7 × 103) may be assigned tentatively to an π(L2- or acac)→Ru(III), LMCT transition or a combination of d-d transition viz., 2T2g→A2g or 2A1g16,22,23. In case of [(bipy(acac)Ru(II)]2(μ-L)], one band at 347 nm (ε = 7.6 × 103) and another at 468 nm (ε = 5.3 × 103) are assigned to metal π(d)→bipy(π*) type of transitions. The most notable feature in case of 2,2'-bipyridine containing complexes is an intense, broad band in the region 783 nm (ε = 12.5 × 103) which may be assigned to a transition from the HOMO (both metal and bridging ligand based) to the LUMO (largely bridging ligand based) transition.

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