



SYNTHESIS, CHARACTERIZATION AND PHYSICO-CHEMICAL STUDIES OF WEAKLY INTERACTING REDOX-RESPONSIVE BINUCLEAR COMPLEXES INCORPORATING ETHYLENEDIAMINETETRAACETATORUTHANATE(III)

AMITAVA DAS*, H. C. BAJAJ and DEBABRATA CHATTERJEE*

Discipline of Coordination Chemistry, Central Salt & Marine Chemicals Research Institute, Bhavnagar 364 002, India

(Received 10 January 1995, accepted 11 April 1995)

Abstract—Novel binuclear complexes of the type $[\{\text{Ru}(\text{edtaH})\}_2\text{L}]$ [edta = ethylenediaminetetraacetate, L = pyrazine, 4,4'-bipyridyl, 3,3'-dimethyl-4,4'-bipyridyl, *trans*-1,2-bis(4-pyridyl)ethylene] have been synthesized and characterized by physico-chemical methods. All the complexes showed weak metal–metal interaction, depending on the nature of the bridging ligand, L. The electrochemical and magnetic susceptibility measurements are consistent with weak interactions between the ruthenium centres.

The study of binuclear complexes whose metal centres are linked by an unsaturated bridging ligand is of relevance to intramolecular electron transfer processes in mixed valence systems in the context of magnetic interactions between paramagnetic centres.¹ The archetypal example is the Creutz–Taube ion, which has received a great deal of attention over the past years and contributed to our understanding of electron transfer theory.² Recently, 4,4'-bipyridyl and its derivatives have been particularly popular as bridging ligands for the synthesis of redox-responsive binuclear complexes.^{1,3–5} Symmetrical binuclear complexes $[\{\text{Mo}(\text{NO})\text{L}^*\text{Cl}\}_2\text{L}]$ (L* = 3,5-dimethyl pyrazolylhydroborate, L = 4,4'-bipyridyl and its derivatives) show strong electrochemical interaction,^{3,4} where individual spins at the “ends” of molecules can correlate depending on the nature of linkages in between (e.g. saturated or unsaturated bonds) the metal centers. By contrast, a weak metal–metal interaction was reported in $[\{\text{Ru}(\text{NH}_3)_5\}_2\text{L}]^{6+}$ (L = pyrazine/H-4,4'-bipyridyl and its derivatives)^{6,7} and an even weaker interaction has also been reported for $[\{\text{Ru}(2,2'$

bipy) $_2\text{Cl}\}_2\text{L}]$.⁹ The chemistry of polyaminopolycarboxylate complexes of ruthenium(III/II) is of continued interest due to their biochemical importance and catalytic ability in oxidation and reduction reactions. To date, little attempt has been made to utilize the remarkable lability of the aqua molecule in $[\text{Ru}(\text{edtaH})\text{H}_2\text{O}]$ towards substitution reactions for design and synthesis of binuclear complexes.^{8,10} The present work stems from our interest in developing a new set of binuclear complexes of Ru(edtaH) using 4,4'-bipyridyl and its derivatives as bridging ligands. In this paper we report the preparation, characterization and physicochemical studies of binuclear complexes derived from edta complexes of ruthenium(III) using pyrazine (pyz; L₁), 4,4'-bipyridyl (bp; L₂), 3,3'-dimethyl-4,4'-bipyridyl (dmbp; L₃) and *trans*-1,2-bis(4-pyridyl)ethylene (etbp; L₄) as the bridging ligand.

EXPERIMENTAL

Materials

$\text{K}[\text{Ru}(\text{edtaH})\text{Cl}] \cdot 2\text{H}_2\text{O}$ was prepared following the published procedure.¹¹ Pyrazine, 4,4'-bipyridyl and *trans*-1,2-bis(4-pyridyl)ethylene were used as

* Authors to whom correspondence should be addressed.

received from Aldrich. 3,3'-Dimethyl-4,4'-bipyridyl was synthesized by following reported methods.⁴ $[\text{Bu}_4\text{N}][\text{ClO}_4]$ was used as background electrolyte. Solvents were purified and dried before use by standard methods and double distilled water was used throughout the experiments. Microanalyses were carried out with a Carlo Erba elemental analyser. Absorption spectra were recorded on a Shimadzu 160 UV-vis spectrophotometer. IR spectra were recorded on a Carl-Zeiss Specord M80 spectrometer as KBr pellets. EPR studies were carried out by using a Bruker ESP 300X spectrometer either at room temperature or at 77 K using a Dewar insert in the sample chamber. Electrochemical experiments were performed by using a Princeton Applied Research (PAR 174A) electrochemical instrument. A conventional three-electrode cell assembly was used. A saturated calomel electrode as reference and platinum as working electrode were used for this purpose. Magnetic susceptibility measurements were carried out in a PAR-155 vibrating magnetometer.

Synthesis

$[\{\text{Ru}(\text{edtaH})\}_2\text{L}]$ [$\text{L} = \text{pyz}$ (L_1), bp (L_2), dmbp (L_3), etbp (L_4)] complexes were prepared by reacting $\text{K}[\text{Ru}(\text{edtaH})\text{Cl}] \cdot 2\text{H}_2\text{O}$ with the appropriate bridging ligand (L). $\text{K}[\text{Ru}(\text{edtaH})\text{Cl}] \cdot 2\text{H}_2\text{O}$ (0.200 g, 0.4 mmol) was dissolved in the minimum volume of warm water (*ca* 10 cm^3), to which 0.2 mmol of L dissolved in 5 cm^3 of warm methanol was added dropwise with continuous stirring. The colour of the solution changed from pale to deep yellow. The stirring was continued at room temperature for another 30 min and then the reaction mixture was concentrated to 5 cm^3 *in vacuo*. Addition of 15 cm^3 of acetone and cooling to 5°C produced a yellow precipitate which was filtered off and washed with water-acetone (1:9). The recrystallized product was dried *in vacuo* (yield 80–86%). Elemental analysis and spectral data are summarized in Table 1.

RESULTS AND DISCUSSION

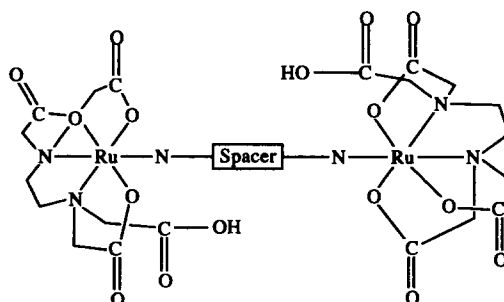
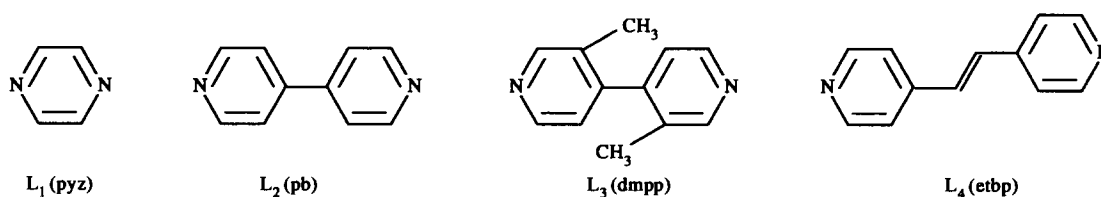
The $\text{K}[\text{Ru}(\text{edtaH})\text{Cl}] \cdot 2\text{H}_2\text{O}$ complex is rapidly aquated when dissolved in water and this aqua species undergoes a facile aqua substitution reaction with aromatic N-heterocycles.¹² We have used this reaction to synthesize the respective binuclear complexes **I–IV** (Fig. 1) using the bridging ligands L_1 , L_2 , L_3 and L_4 , respectively. Complexes **I–IV** are pale yellow in colour. Elemental analysis (Table 1) data are in good agreement with the proposed formulations (Fig. 1).

The IR spectra of all the binuclear complexes (**I–IV**) exhibited two stretching bands at 1725 and 1645 cm^{-1} , which are assigned to uncoordinated $-\text{COOH}$ and coordinated $-\text{COO}$, respectively.⁸ Complexes **I–IV** also exhibit bands at 1600 and 1460 cm^{-1} corresponding to $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching and bending¹³ of the bridging pyrazine or bipyridyl ligands in the complexes. The electronic spectral data of all binuclear complexes in water are summarized in Table 1. As in the cases of N-heterocyclic mononuclear complexes¹² of $\text{Ru}^{\text{III}}-\text{edta}$, no peaks or shoulders were observed at wavelengths greater than 320 nm for binuclear complexes.

Cyclic voltammetric studies of **I–IV** were carried out in water using $[\text{Bu}_4\text{N}][\text{ClO}_4]$ as supporting electrolyte; the results are summarised in Table 2. All binuclear complexes undergo two distinct one-electron reduction processes; the corresponding $E^1_{1/2}$ for $\text{Ru}^{\text{III}}-\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$ and $E^2_{1/2}$ values for $\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}-\text{Ru}^{\text{II}}$ couples are summarized in Table 2. ΔE_p ($= E_{pc} - E_{pa}$) values for both redox processes in all binuclear complexes falls in the range $120 < \Delta E_p < 140$ mV, which is indicative of the quasi-reversible nature of the redox processes. Comparison of the $E^1_{1/2}$ and $E^2_{1/2}$ values with that of $E_{1/2}(\text{Ru}^{\text{III/II}})$ for $[\text{Ru}(\text{edta})\text{py}]^-$ (which is known to undergo a nearly reversible one-electron reduction process at 0.1 V vs SCE)¹² shows that, for complexes **I–IV**, the $E^2_{1/2}$ values are slightly anodic and the $E^1_{1/2}$ values are slightly cathodic. Thus, in these symmetrical binuclear complexes, there exists a donor-acceptor type of interaction between the two redox-active ruthenium centres separated by a conjugated spacer. One of the two metal centres here acts as a donor, for which the corresponding $E_{1/2}$ value is shifted to the anodic side of the potential, while the other metal acts as an acceptor, exhibiting cathodic shift in the potential. Thus, the $\Delta E_{1/2}$ value ($E^1_{1/2} - E^2_{1/2}$) is a measure of the extent of electrochemical interaction between two redox-responsive metal centres. As expected, the $\Delta E_{1/2}$ value (Table 2), i.e. the extent of electrochemical interaction, changes with a change in nature of the bridging ligand. As the distance between the two metal centres increases, $\Delta E_{1/2}$ becomes smaller. The value of $\Delta E_{1/2}$ is lower for complex **III** than for complex **II**, demonstrating the effect of ligand planarity on the metal-metal interaction. The presence of two bulky methyl groups in dmpb inhibits the ligand planarity and consequently the interaction between the two metal centres decreases. A similar observation had also been reported earlier for the ruthenium pentamine¹⁴ and molybdenum polypyrazolyhydroborato systems.⁴ However, the observed electrochemical

Table I. Elemental analysis, UV-vis and IR spectral data for complexes I-IV

Complex	Elemental analysis		IR (cm ⁻¹)	UV-vis, nm (ϵ_{\max})
	C, H, N found	C, H, N calc.		
I	32.9, 3.7, 9.5	33.5, 3.5, 9.8	1730 (COOH) 1650 (br, COO)	305 (S) (5900), 261 (8950) 210 (17,900)
II	38.0, 3.8, 8.7	39.0, 3.7, 9.0	1725 (COOH) 1640 (br, COO)	312 (S) (900), 274 (13,500)
III	39.5, 4.0, 8.6	39.8, 4.0, 8.7	1730 (COOH) 1645 (br, COO)	304 (S) (7300) 269 (11,600) 215 (22,000)
IV	39.7, 3.9, 8.6	39.9, 3.8, 8.7	1730 (COOH) 1640 (br, COO)	314 (S) (8000), 293 (27,000), 228 (15,000)



N —	Spacer	— N	Complex
	L_1		I
	L_2		II
	L_3		III
	L_4		IV

Fig. 1. Structures of ligands and complexes I-IV.

interaction ($\Delta E_{1/2}$) is much smaller than that observed in binuclear complexes derived from $\text{MoL}^*(\text{NO})\text{Cl}$ using similar bridging ligands.^{3,4,15} For $[\text{MoL}^*(\text{NO})\text{Cl}]$ ($L = 4,4'$ -bipyridine and its derivatives) complexes, redox orbitals are significantly delocalized on the bridging bipyridyl ligands, which is not the case for Ru-edta type complexes. Further, unlike the $\text{Mo}(\text{NO})^{3+/2+}$

couple, the $E_{1/2}$ value for the $\text{Ru}^{\text{III/II}}$ couple in $[\text{Ru}(\text{edtaH})_2]\text{L}$ ($L = \text{N-donor of } \pi\text{-acid ligand}$) is not very sensitive to the nature of L . These observations support our assumption that the Ru^{III} -edta unit perhaps possesses weak π -donating ability, which was exemplified in $[\text{Ru}^{\text{III}}(\text{edtaH})(\text{PPh}_3)]^{16a}$ and $[\text{Ru}(\text{edtaH})(\text{NO})]^{16b}$ complexes. Thus, the electrochemical interaction described here for I-IV may

Table 2.

Complex	$E^1_{1/2}$ (V) ^b (vs SCE)	$E^2_{1/2}$ (V) ^b (vs SCE)	$\Delta E_{1/2}$ (mV)	K_C	$\mu_{\text{eff}}/\text{Ru}$	$g_x g_y g_z$
[Ru(NH ₃) ₅] ₂ L ₁] ⁶⁺			390 ^a	4.0×10^6 ^a		2.80 2.53 g_z not observed
[Ru(2,2'-bipy) ₂] ₂ L	+0.89	+1.01		110 ^c	—	—
{[Ru(edtaH)] ₂ L ₁ }	+0.04	-0.30	360	1.2×10^6	2.2	2.60 2.30 1.93
{[Ru(edtaH)] ₂ L ₂ }	-0.07	-0.30	230	7.7×10^3	2.25	2.617 2.32 1.93
{[Ru(edtaH)] ₂ L ₃ }	-0.08	-0.26	180	1.1×10^3	2.27	2.616 2.32 1.93
{[Ru(edtaH)] ₂ L ₄ }	-0.07	-0.22	160	343	2.26	2.61 2.31 1.96

^a Ref. 6.^b $E_{\text{pc}} - E_{\text{pa}}$ values for all redox couples are 120–140 mV, representing the quasi-reversible nature of the redox process.^c Ref. 9.

be presumed to be mainly electrostatic in nature. A similar explanation has been proposed earlier for the weak interaction in the symmetrical binuclear complexes of Ru(NH₃)₅.^{5-7,15,17} However, the effect of ligand planarity (i.e. the decrease of the $\Delta E_{1/2}$ value for **III** as compared to **II**) demonstrates a certain but small contribution of weak π -interaction between Ru^{III}-edta and the bridging ligand L. The extent of π -interaction, which is low in Ru(edtaH) complexes, is expected to be even lower in {Ru(2,2'-bipy)₂]₂pyz] due to strong back-bonding between $d\pi(\text{Ru})$ and $\pi^*(\text{bipy})$ orbitals, leaving the $d\pi$ orbital less available to interact with the $\pi^*(\text{pyz})$ orbital.^{7,18} Comproportionation constants K_C ¹⁹ for all four complexes are reported in Table 2. The highest value of K_C for **I** is indicative of the fact that complex **I** is most stable in the mixed valent state.

EPR and magnetochemistry

All four binuclear complexes were found to be EPR active and exhibited broad spectra at room temperature, while at 77 K [in mixed solvent (H₂O-glycerol 1:3, v/v)], characteristic g values were observed, as reported for other complexes of Ru-edta with π -acid ligands.²⁰ The values of g_x , g_y and g_z are reported in Table 2. No ruthenium hyperfine splitting was observed. A careful analysis of the EPR spectra shows that the signal is centred at

$g = 2.47$ and is apparently split into two resonances at 2.6 and 2.3, corresponding to g_x and g_y signals. This split is presumably due to asymmetrical packing of the solvent molecules. A similar observation was also reported for {[Ru(NH₃)₅]₂pyz](OTs)₅,¹⁵ and features at 2.57 and 2.33 were assigned to g_x and g_y rather than two distinct ruthenium centres having axial symmetry. $\mu_{\text{eff}}/\text{Ru}^{21}$ values for the four homobinuclear complexes are summarized in Table 2. The reported values of μ_{eff} for K[Ru(edtaH)Cl] and Ru(edta)L (L = π -acid ligand) are 1.98 and 1.90, respectively, at room temperature.²⁰ Comparison of the $\mu_{\text{eff}}/\text{Ru}$ value of these binuclear complexes with those of mononuclear π -acid derivatives suggests the presence of a very weak interaction between the two paramagnetic ruthenium centres, which agrees well with our electrochemical observations.

REFERENCES

- (a) C. Creutz, *Prog. Inorg. Chem.* 1983, **30**, 1; (b) D. E. Richardson and H. Taube, *Coord. Chem. Rev.* 1984, **60**, 107; (c) P. A. Long, R. H. Magnuson and H. Taube, *Inorg. Chem.* 1988, **27**, 23; (d) D. A. Geselowitz, W. Kutner and T. J. Meyer, *Inorg. Chem.* 1986, **25**, 2015; (e) M. S. Ram and A. Haim, *Inorg. Chem.* 1991, **30**, 1319; (f) J. T. Hupp, *J. Am. Chem. Soc.* 1990, **112**, 1563; (g) J. A. Thomas, C. J. Jones,

- J. A. McCleverty, D. Collison, F. E. Mabbs, C. J. Harding and M. G. Hutchings, *J. Chem. Soc., Chem. Commun.* 1992, 1796; (h) A. Das, J. G. Jeffery, J. P. Maher, J. A. McCleverty, E. Schatz, M. D. Ward and G. Wollerrman, *Angew. Chem., Int. Edn Engl.* 1992, **31**, 1515; *Inorg. Chem.* 1993, **32**, 2145; (i) A. C. Ribou, J. P. Launay, K. Takahashi, T. Nihira, S. Tarutani and C. W. Spangler, *Inorg. Chem.* 1994, **33**, 1325; (j) J. R. Reimers and N. S. Hush, *Inorg. Chem.* 1990, **29**, 4510.
2. B. J. Cooper, T. M. Vess, W. A. Kalsbeck and D. W. Wertz, *Inorg. Chem.* 1991, **30**, 2286 and refs 3–30 therein.
3. S. L. W. McWhinnie, C. J. Jones, J. A. McCleverty, D. Collison and F. E. Mabbs, *J. Chem. Soc., Chem. Commun.* 1990, 940 and references therein.
4. A. Das, J. P. Maher, J. A. McCleverty, J. A. Navas Badiola and M. D. Ward, *J. Chem. Soc., Dalton Trans.* 1993, 681.
5. S. Woitellier, J. P. Launay and C. W. Spangler, *Inorg. Chem.* 1989, **28**, 758.
6. C. Creutz, P. Kroger, T. Matsubara, T. L. Netzel and N. Sutin, *J. Am. Chem. Soc.* 1979, **101**, 5442.
7. (a) G. M. Tom, C. Creutz and H. Taube, *J. Am. Chem. Soc.* 1994, **96**, 7828; (b) C. Creutz, *Inorg. Chem.* 1978, **17**, 3723.
8. D. Chatterjee, H. C. Bajaj and A. Das, *Inorg. Chim. Acta* 1994, **224**, 189.
9. M. J. Powers and T. J. Meyer, *J. Am. Chem. Soc.* 1980, **102**, 1289.
10. D. Chatterjee, H. C. Bajaj and A. Das, *Inorg. Chem.* 1993, **32**, 40.
11. A. A. Diamanbis and J. V. Dubrawski, *Inorg. Chem.* 1980, **19**, 1142.
12. T. Matsubara and C. Creutz, *Inorg. Chem.* 1979, **18**, 1956.
13. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*. Wiley, New York (1963).
14. M. Tanner and A. Ludi, *Inorg. Chem.* 1981, **20**, 2350.
15. B. C. Bunker, R. S. Drago, D. N. Hendrickson, R. M. Richman and S. L. Kessel, *J. Am. Chem. Soc.* 1978, **100**, 3805.
16. (a) M. M. Taqui Khan, D. Chatterjee, M. R. H. Siddiqui, S. D. Bhatt, H. C. Bajaj, K. Venkatasubramanian and M. A. Moiz, *Polyhedron* 1993, **12**, 1443; (b) M. M. Taqui Khan, K. Venkatasubramanian, Z. Shirin and M. M. Bhadbhade, *J. Chem. Soc., Dalton Trans.* 1992, 1031.
17. A. Bino, P. A. Lay, H. Taube and J. F. Wishart, *Inorg. Chem.* 1985, **24**, 3969.
18. R. W. Callahan, G. M. Brown and T. J. Meyer, *Inorg. Chem.* 1975, **14**, 1443.
19. D. E. Richardson and H. Taube, *Inorg. Chem.* 1981, **20**, 1278.
20. (a) M. Ghatak and S. Bhattacharya, *Polyhedron* 1994, **13**, 2999; (b) M. M. Taqui Khan, A. Hussain and M. A. Moiz, *Polyhedron* 1992, **11**, 687.
21. J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Edn Engl.* 1994, **33**, 385.