Mixed Ligand Complexes of Ruthenium(III)edta with Pyrimidines

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Abstract

Mixed ligand complexes of ruthenium(III)edta with cytosine, uracil, 2-thiocytosine, 2-aminopyrimidine and 5-aminouracil were synthesised and characterised by elemental analysis, conductivity, infrared spectra, electronic spectra, ^{1}H NMR, ESR and polarography. Uracil acts as a monodentate ligand coordinating to the metal ion through C_2O. The ligands cytosine, 2-thiocytosine, 2-aminopyrimidine, 5-aminouracil act as bidentate ligands coordinating to the metal ion through N_3 and C_2O; N_3 and C_2SH; N_3 and C_2NH_2; C_6 and $5NH_2$, respectively. 5-Aminouracil forms an interesting organometallic complex. In this complex the C_6 carbon of 5-aminouracil forms a covalent bond with ruthenium(III), with simultaneous coordination of the nitrogen of the exocyclic amino group to a second ruthenium atom forming a 2:2 diligand bridged bimetallic complex.

Introduction

Metal complexes of purines, pyrimidines and nucleosides have been widely studied by several workers [1–8]. Very few complexes with substituted pyrimidines have been reported [9–11]. The platinum group metal complexes with purines, pyrimidines and nucleic acids are known to possess antitumour and antibacterial activity [12, 13]. Several ruthenium complexes are also known to possess antibacterial and antitumour activity [14, 15]. In the earlier work mixed ligand complexes of Ru(III)edta with purines were reported [16]. It was established that in the mixed ligand complexes of Ru(III)edta with purines such as adenine, 2,6-diaminopurine and 2-thioxanthine 2:2 complexes are formed in which edta is tetradentate. In the case of purines, guanine and hypoxanthine, however, 1:1 complexes were obtained where edta is pentadentate. In the present study mixed ligand complexes of ruthenium(III)edta with the pyrimidine bases cytosine, uracil, 2-thiocytosine, 2-aminopyrimidine and 5-aminouracil were synthesised and characterised by various physicochemical methods.

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Experimental

Materials

Hydrated ruthenium trichloride was obtained from Johnson and Mathey Company, U.S.A. Na_2edta (AR) was obtained from BDH Chemicals. All other reagents used were of AR grade. High purity nitrogen was obtained by passing the gas through alkaline pyrogallol and vanadyl sulphate solutions and finally through calcium chloride. Purines were purchased from Sigma Chemical Company, U.S.A. All solvents used were of high purity and distilled before use.

Synthesis

$K[Ru(edta\text{-}H)Cl]\cdot 2H_2O$ was prepared by the method of Ezerskaya and Solovykh [17b] as modified by Diamantis and Dubrawski [17a]. The complex $K_2[RuCl_5(H_2O)]$, prepared by a modified method of Mercer and Buckley [18], was used as the starting material in the above preparation.

Physical Measurements

Elemental analyses of the complexes were obtained from Central Drug Research Institute, Lucknow. Conductivity data were measured on a digital conductivity meter No. DI 909. Infrared and electronic spectra of the complexes were recorded on Schimadzu IR 435 and UV-160 instruments, respectively. Far infrared was recorded at RSIC, IIT, Madras. ^{1}H NMR was recorded on a Jeol 500 MHz spectrometer at TIFR, Bombay. Electron paramagnetic resonance spectra were recorded on a Brucker ESP 300 X-band band instrument at CSMCRI, Bhavnagar. Electrochemical measurements were taken at CSMCRI, Bhavnagar, on a Princeton Applied Research Electrochemical Instrument equipped with a precision X-Y recorder. A PAR 174 polarographic analyzer was used to record d.c. and differential pulse polarograms.

Preparation of Complexes

Preparation of potassium (chloroethylenediaminetetraacetato)ruthenate(III) dihydrate (1)

The complex was prepared by a modified method of Diamantis and Dubrawski [17a]. A hot solution of $Na_2(H_2edta)$ (0.373 g; 1 mM) in $HClO_4$ (5 ml; 0.001

0020-1693/90/$3.50

M) was added to a solution of $K_2[RuCl_5(H_2O)]$ (0.375 g; 1 mM) in perchloric acid (5 ml; 0.001 M) and the mixture was refluxed for 2 h. The light yellow solution obtained was concentrated to one fourth of its original volume and precipitated with ethanol when a light yellow solid was obtained. The complex was washed with a cold mixture of acetone and water (9:1) till it was free from chloride ion and finally with ethanol, then vacuum dried. $K_2[RuCl_5(H_2O)]$ used in the above preparation was prepared by a modified procedure of Mercer and Buckley [18].

Potassium(ethylenediaminetetraacetato)-cytosineruthenate(III) dihydrate (2) and potassium(ethylenediaminetetraacetato)-uracilruthenate(III) dihydrate (3)

Potassium chloroethylenediaminetetraacetatoruthenate(III) (0.2 mM) dissolved in water was added to a solution of cytosine/uracil (0.2 mM) in water, when the yellow colour of the solutions changed to deep yellow. The pH of these solutions was between 3 and 4. The resulting solutions were refluxed for 11–15 h in an atmosphere of nitrogen and were checked by TLC for the completion of reaction. The solutions were concentrated to one fourth of the volume and were precipitated with ethanol. The complexes were filtered, washed with acetone water mixture, acetone and then vacuum dried. The complexes are soluble in water.

Potassium(ethylenediaminetetraacetato)2-thiocytosineruthenate(III) dihydrate (4) and potassium(ethylenediaminetetraacetato)2-aminopyrimidineruthenate(III) tetrahydrate (5)

Potassium chloroethylenediaminetetraacetatoruthenate(III) (0.2 mM) dissolved in water was added to solutions of 2-thiocytosine/2-aminopyrimidine (0.2 mM), when the yellow colour of the solutions changed to maroon red. The pH of these solutions was between 2 and 3. The resulting solutions were refluxed for 4 and 12 h respectively under an atmosphere of nitrogen and were checked for completion by TLC. The solutions were filtered and the filtrates were concentrated to one fourth of the volume and the complexes precipitated with ethanol. The complexes were filtered, washed with acetone water mixture, acetone and then vacuum dried. The complexes are soluble in water.

Potassium-di-μ-η′-5-aminouracil bis(ethylenediaminetetraacetatoruthenate(III)) pentahydrate (6)

Potassium chloroethylenediaminetetraacetatoruthenate(III) (0.4 mM) in water was added to a solution of 5-aminouracil (0.4 mM) in water when the yellow colour of the solution changed immediately to maroon red. The pH of the solution was between 3 and 4. The solution was refluxed in an atmosphere of nitrogen for 18 h and the completion of reaction was checked by TLC. The solution was concentrated and the complex precipitated with ethanol, filtered, washed with acetone water mixture, ethanol and then vacuum dried. The complex is soluble in water.

Results and Discussion

The analytical and conductivity data of the complexes presented in Table 1 are 1:1 electrolytes.

Infrared Spectra of the Complexes

The infrared spectra of complexes given in Table 2 in general show a broad band in the region 3400–

TABLE 1. Analytical and conductivity data of complexes

Complex no.	Complex	Analysis[a] (%)			Molar conductivity at 30 °C in H_2O (mhos cm^{-2})
		Carbon	Hydrogen	Nitrogen	
1	$K[Ru(edta\text{-}H)Cl]\cdot 2H_2O$	24.20 (24.00)	3.30 (3.39)	5.51 (5.59)	326
2	$K[Ru(edta)(cyt)]\cdot 2H_2O$	29.0 (29.2)	3.5 (3.6)	11.9 (12.2)	297
3	$K[Ru(edta)(ura)]\cdot 2H_2O$	28.02 (29.11)	3.41 (3.47)	9.2 (9.7)	310
4	$K[Ru(edta)(2\text{-thiocyt})]\cdot 2H_2O$	28.08 (28.4)	3.52 (3.55)	11.00 (11.80)	220
5	$K[Ru(edta)(2\text{-ampy})]\cdot 4H_2O$	28.0 (28.3)	4.4 (4.25)	12.5 (11.8)	224
6	$K_4[Ru(edta)(\eta'\text{-5-amura})]_2\cdot 5H_2O$	26.0 (26.3)	3.33 (3.30)	10.70 (10.97)	422

[a]Calculated value in parentheses.

TABLE 2. Infrared spectral data of ruthenium(III)edta mixed ligand complexes

Complex no.	Complex	ν(M–N)	ν(M–O)	ν(C=N)	ν(C=C)	$\gamma(NH_2)$ and $\nu(COO^-)$ (antisym)	ν(C=O)
1	$K[Ru(edta\text{-}H)Cl]\cdot 2H_2O$	510	470 (320) (νM–Cl)			1650	1720 (νCOOH)
2	$K[Ru(edta)(cyt)]\cdot 2H_2O$	510	480	1420	1480	1640	1680
3	$K[Ru(edta)(ura)]\cdot 2H_2O$	500	440	1430		1640	
4	$K[Ru(edta)(2\text{-thiocyt})]\cdot 2H_2O$	580	460 440 (νM–S)	1460	1560 1510	1640	1000 (νC=S)
5	$K[Ru(edta)(2\text{-ampy})]\cdot 4H_2O$	540	490	1440		1620	
6	$K_4[Ru(edta)(\eta'\text{-}5\text{-amura})]_2\cdot 5H_2O$	495	420	1410 1370		1600 (br)	

3200 cm^{-1} due to the presence of lattice water in the complexes. The N–H and C–H stretching vibrations due to the coordinated secondary ligand were observed in the region 3100 to 2950 cm^{-1}. In complex **1**, $K[Ru(edta\text{-}H)Cl]\cdot 2H_2O$, a sharp peak at 1720 cm^{-1} and a broad peak at 1650 cm^{-1} shows the presence of the uncoordinated and coordinated carboxylic acid groups of edta, respectively [17b]. The ligational peaks of importance in the pyrimidines studied in this investigation are the ν(C=O), ν(C=C), ν(C=N) and $\delta(NH_2)$ modes. The ν(C=O) stretching frequency of coordinated cytosine in complex **2** shifts to a lower frequency by 20 cm^{-1} and is observed at 1680 cm^{-1}. The ν(C=O) stretching frequency at 1720 cm^{-1} disappears completely in complex **3** as compared to the free ligands indicating that the C=O group is involved in coordination to the metal ion in both the complexes. A broad peak at 1640 cm^{-1} is due to the coordinated carboxylate group of edta and also due to the NH_2 deformation mode of the secondary ligand in complexes **2**, **4**, **5** and **6**. The ν(C=C) and ν(C=N) stretching frequencies of pyrimidines were observed around 1600 to 1450 cm^{-1} and undergo a downward shift of about 30–40 cm^{-1} on complexation compared to the frequencies in the free ligand, indicating the involvement of ring nitrogens in coordination to the metal ion. The ν(C=S) stretching frequency in complex **4** is shifted to a lower frequency by 80 cm^{-1} as compared to the free ligand and is observed at 1000 cm^{-1} showing that 2-thiocytosine coordinates to the metal ion through sulphur. The ν(M–N) and ν(M–O) stretching frequencies are observed around 500 and 400 cm^{-1} respectively in these complexes showing that edta coordinates to the metal ion through oxygen and nitrogen.

The electronic spectra of these complexes, data given in Table 3, in general show three types of absorption bands: the LMCT band from the edta primary ligand to the metal ion, another charge transfer transition from the secondary ligand to the metal ion, the third type of absorption bands observed are due to d–d transitions of ruthenium(III). The bands around 780–800 nm in these complexes may be d–d transitions with weak MLCT character.

The ^1H NMR spectra of these complexes (Table 4) were very helpful in assigning the binding sites of the ligand to the metal ion. The ^1H NMR spectra of these complexes are not obtained in the low resolution NMR due to broadening of peaks by ruthenium(III) [19]. The spectra was therefore recorded on 500 MHz NMR with good resolution. One of the representative spectra of complex **4** is given in Fig. 1.

The ^1H NMR spectral data of complex **1** is given in Table 4. The X-ray crystal structure of the complex has been reported [20] where edta is pentadentate and the sixth position is occupied by chloride.

The ^1H NMR spectrum of complex **2** in D_2O shows two peaks at 6.21 and 7.8 ppm for C_5H and C_6H protons respectively. A downfield shift in both the protons by 0.33 and 0.11 ppm, as compared to the C_5H and C_6H protons in the ligand, infers that cytosine coordinates to the metal ion through N_3 and C_2O. The edta protons are observed at 3.1, 3.4, 3.7 and 4.0 ppm.

The ^1H NMR spectrum of complex **3** shows two doublets at 5.48 and 7.7 ppm for C_5H and C_6H protons respectively. The C_6H proton shifts downfield by 0.32 ppm as compared to the ligand and the shift is only 0.04 ppm in the case of the C_5H proton, thereby inferring that uracil coordinates to the metal ion through C_2O. The edta protons due to the ethylenediamine group and methylene protons of the free carboxylates group are observed as a broad peak due to overlapping in the region 3.2 to 3.8 ppm and the methylene protons of the coordinated carboxylate group are observed at 4.2 ppm.

TABLE 3. Electronic spectral data of Ru(III)edta mixed ligand complexes and secondary ligands

Complex no.	Ligand/Complex	Absorption maxima λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	Transition
1	K[Ru(edta-H)Cl]·$2H_2O$	283	2.71×10^3	LMCT
		350	5.8×10^2	d–d
	Cytosine	267	6.11×10^4	$\pi-\pi^*$
2	K[Ru(edta)(cyt)]·$2H_2O$	272	6.11×10^3	LMCT cytosine
		354	1.16×10^3	LMCT edta
		750	4.70×10^2	d–d
		836	5.1×10^2	d–d Ru(III)
		974	2.44×10^3	d–d
	Uracil	260	1.48×10^4	$\pi-\pi^*$
3	K[Ru(edta)(ura)]·$2H_2O$	279	3.86×10^3	LMCT uracil
		354	1.25×10^3	LMCT edta
		741	4.9×10^2	d–d Ru(III)
		842	5.30×10^2	d–d
	2-Thiocytosine	242	2.355×10^4	$\pi-\pi^*$
4	K[Ru(edta)(2-thiocyt)]·$2H_2O$	235	2.206×10^4	LMCT 2-thiocytosine
		352	3.77×10^2	LMCT edta
		502	1.4×10^3	d–d
		754	1.82×10^2	d–d Ru(III)
		816	1.80×10^2	d–d
	2-Aminopyrimidine	224	1.233×10^4	
		291	2.910×10^3	$\pi-\pi^*$
5	K[Ru(edta)(2-ampy)]·$4H_2O$	220	1.083×10^4	LMCT 2-aminopyrimidine
		286	4.24×10^3	
		354	8.45×10^2	LMCT edta
		966	2.5×10	d–d Ru(III)
	5-Aminouracil	226	6.04×10^3	$\pi-\pi^*$
		290	4.89×10^3	
6	K_4[Ru(edta)(η'-5-amura)]$_2$·$5H_2O$	282	8.834×10^3	LMCT 5-aminouracil
		358	1.60×10^3	LMCT edta
		498	9.62×10^2	d–d
		799	6.48×10	d–d Ru(III)
		964	8.65×10	d–d

The NMR spectrum of complex **4** (Fig. 1) shows two doublets at 6.14 and 7.74 ppm for C_5H and C_6H protons respectively. A downfield shift in both the protons by 0.13 and 0.11 ppm which is nearly the same when compared to the ligand, infers that 2-thiocytosine coordinates to the metal ion through N_3 and C_2SH. The edta protons are observed as distinct peaks. The methylene protons of the ethylenediamine collar $N-CH_2-CH_2-N$ are observed as triplets at 3.58 and 3.9 ppm. The methylene protons of the free carboxylates are observed at 4.02 ppm and the methylene protons of the coordinated carboxylates are observed at 4.11 ppm.

The NMR spectrum of complex **5** in D_2O shows a singlet at 7.14 ppm, due to NH_2 protons, a triplet at 7.73 ppm due to the C_5H proton and a singlet at 8.64 ppm due to the C_6H proton. There is a downfield shift by 1.54 ppm in the case of amino protons and by 0.93 ppm in the case of the C_5H proton and by 0.34 ppm in the case of the C_6H proton as compared to the ligand. A large downfield shift in the case of the amino protons and C_5H proton as compared to the C_6H proton infers that 2-aminopyrimidine coordinates to the metal ion through C_2NH_2 and N_3. The edta protons are observed at 3.3, 3.5, 3.7 and 3.9 ppm.

In the NMR spectrum of complex **6**, the signal due to the C_6H proton is not observed when compared to the ligand indicating coordination of the C_6 carbon to the metal ion, forming an organometallic complex. A triplet at 7.35 ppm is observed which is assigned to the protons of an amino group coordinated to the

TABLE 4. ^{1}H NMR spectral data of Ru(III)edta mixed ligand complexes and secondary ligands

Complex no.	Complex/Ligand	Pyrimidine base		edta protons		
		C_5H	C_6H	$N-CH_2-CH_2-N$	CH_2COO- (free)	CH_2COO (coordinated)
1	$K[Ru(edta\text{-}H)Cl]\cdot 2H_2O$			3.26; 3.48	3.68	4.0
	Cytosine	5.88	7.69			
2	$K[Ru(edta)(cyt)]\cdot 2H_2O$	6.21	7.80	3.1; 3.4	3.7	4.0
	Uracil	5.44	7.39			
3	$K[Ru(edta)(ura)]\cdot 2H_2O$	5.48	7.7	3.2 to	3.8	4.2
	2-Thiocytosine	6.01	7.63			
4	$K[Ru(edta)(2\text{-thiocyt})]\cdot 2H_2O$	6.14	7.74	3.58; 3.9	4.02	4.11
	2-Aminopyrimidine	6.8 5.6 (NH_2)	8.3			
5	$K[Ru(edta)(2\text{-ampy})]\cdot 4H_2O$	7.73 7.14 (NH_2 protons coordinated)	8.64	3.3; 3.5	3.7	3.9
	5-Aminouracil		8.00			
6	$K_4[Ru(edta)(\eta'\text{-}5\text{-amura})]_2\cdot 5H_2O$	7.35 (coordinated C_5NH_2)	(peak disappears)	3.1; 3.34	3.62	3.84

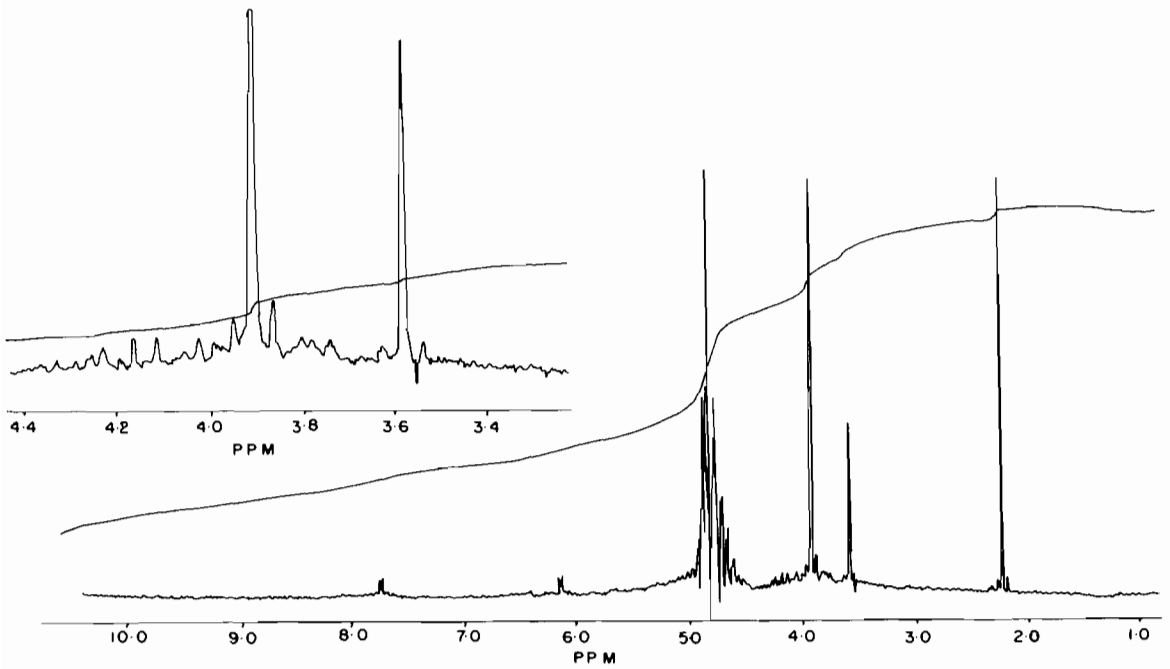

Fig. 1. ^{1}H NMR spectrum of $K[Ru(edta)(2\text{-thiocyt})]\cdot 2H_2O$.

metal ion. The edta protons are observed as distinct peaks broadened by paramagnetism of Ru(III). The methylene protons of the ethylenediamine group are observed as two triplets at 3.1 and 3.34 ppm. The methylene protons of the free carboxylates are exhibited as broad signals at 3.62 ppm and the methylene protons of the coordinated carboxylates are observed at 3.84 ppm. 5-Aminouracil coordinates

TABLE 5. Electrochemical data for Ru(III)edta mixed ligand complexes

Complex no.	Complex	$E_{1/2}$ values		
		Ru^{3+}/Ru^{2+}	Ru^{2+}/Ru^{+}	$(H^{+}/\frac{1}{2}H_2)$
1	$K[Ru(edta)Cl]\cdot 2H_2O$	−0.220	−0.842	−1.012
2	$K[Ru(edta)(cyt)]\cdot 2H_2O$	−0.205	−0.772	−1.079
3	$K[Ru(edta)(ura)]\cdot 2H_2O$	−0.466	−0.616	−0.939
4	$K[Ru(edta)(2\text{-thiocyt})]\cdot 2H_2O$	−0.139		−0.899
5	$K[Ru(edta)(2\text{-ampy})]\cdot 4H_2O$	−0.280		−1.123
6	$K_4[Ru(edta)(\eta'\text{-}5\text{-amura})]_2\cdot 5H_2O$	−0.218	−0.750	

to the metal ion through the C_6 carbon and 5-amino group.

The electron paramagnetic resonance spectra of these complexes in general show rhombic or isotropic distortions. Complexes **2**, **4** and **5** show rhombic distortions and the g values are as follows: for complex **2** $g_1 = 2.42, g_2 = 2.30, g_3 = 1.85$, with $g_{av} = 2.20$; for complex **4** $g_1 = 2.34, g_2 = 2.26, g_3 = 2.175$, with $g_{av} = 2.26$; for complex **5** $g_1 = 2.45, g_2 = 2.329$, $g_3 = 1.94$, with $g_{av} = 2.25$. Complexes **3** and **6** show isotropic distortions with one g value of 2.184 and 2.29 respectively.

The electrochemical data for the complexes are given in Table 5. The differential pulse polarograms of complexes **2**, **3**, **4** and **5** show a single peak for the Ru^{3+}/Ru^{2+} couple at $E_{1/2}$ values of −0.205, −0.466, −0.139 and −0.280 V respectively. The potentials of complexes **2**, **4** and **5** are positive as compared to the parent complex **1** shown in Table 5, indicating the drift of electron density from the metal ion to the ligand and that the secondary ligands act as weak π acids. In the case of complex **3**, however, the $E_{1/2}$ value is more negative as compared to the parent complex indicating that the secondary ligand uracil acts as a pure σ base. The σ basicity of the ligand as seen by the $E_{1/2}$ values is as follows: uracil > cytosine > 2-thiocytosine. The $E_{1/2}$ values of these complexes for the Ru^{2+}/Ru^{+} and $H^{+}/\frac{1}{2}H_2$ couples are shown in Table 5. A single peak for the Ru^{3+}/Ru^{2+} couple in these complexes supports the formation of monomeric 1:1 complexes. The DPP of complex **6** shows a single peak for the Ru^{3+}/Ru^{2+} couple at $E_{1/2}$ value of −0.218 V and for the Ru^{2+}/Ru^{+} couple at −0.750 V. These potentials are positive as compared to the parent complex **1**, indicating the drift of electron density from the metal to the secondary ligand in the formation of a cyclic structure. A cyclic structure consisting of two 5-aminouracils and two Ruedta is proposed for the complex. Such a structure gives a strain free conformation for the molecule. In most of the 2:2 purine complexes discussed earlier [16] two potentials in the form of a split peak differing by about 0.8 to 0.16 V were usually observed, but in the present case the two peaks merge to give a broader peak for the Ru^{3+}/Ru^{2+} couple. This indicates that both the metal ions get reduced at the same potential in the 2:2 complex.

Based on the above data, it is proposed that complexes **2**, **4** and **5** coordinate to the metal ion through N_3 and C_2O; N_3 and C_2SH; N_3 and C_2NH_2 respectively, where edta is tetradentate. The structure for complex **2** is given in Fig. 2. In complex **3** (Fig. 3) edta is

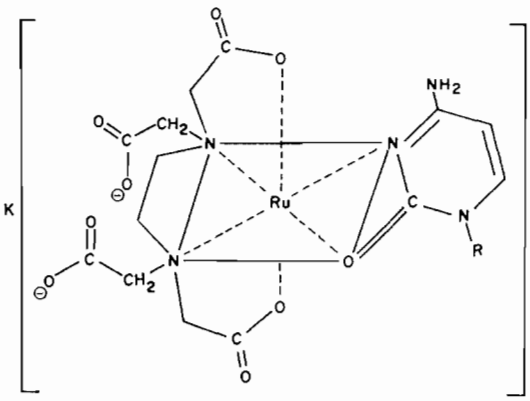

Fig. 2. Structure of $K[Ru(edta)(cyt)]\cdot 2H_2O$ (R = H).

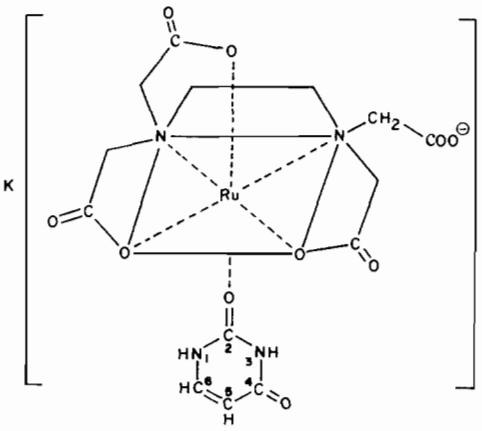

Fig. 3. Structure of $K[Ru(edta)(ura)]\cdot 2H_2O$.

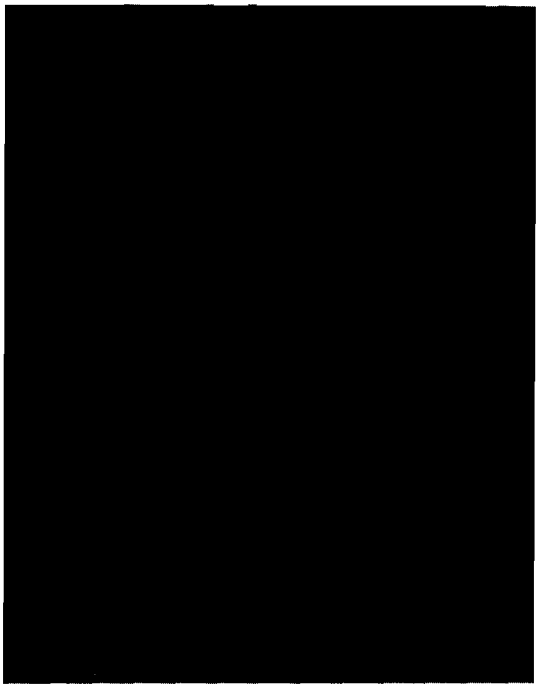

Fig. 4. Model structure of $K_4[Ru(edta)(5\text{-amura})]_2 \cdot 5H_2O$.

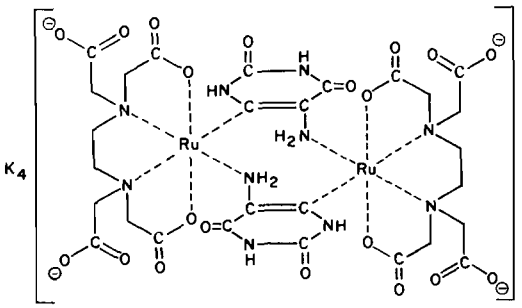

Fig. 5. Structure of $K_4[Ru(edta)(5\text{-amura})]_2 \cdot 5H_2O$.

pentadentate with uracil coordinating to the metal ion through C_2O. The model structure for complex **6** is shown in Fig. 4 and the corresponding structure shown in Fig. 5 is proposed for complex **6** where edta is four coordinate leaving the equatorial *cis* positions for coordination with the C_6 carbon of one 5-amino-uracil and the 5-amino group of the other 5-amino-uracil forming a 2:2 diligand bridged bimetallic complex.

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