

DIOXYGEN COMPLEXES OF RUTHENIUM

M. M. Taqui Khan

Department of Chemistry, Osmania University, Hyderabad 500007 (A.P.), India

Abstract - The stability constants of the dioxygen complexes of Ru(III) with amino polycarboxylic acids, HEDTA, EDTA, DTPA and TTHA have been determined in aqueous solution. The polarographic and cyclic voltametric behavior of the Ru(III) dioxygen complexes have been investigated and the complexes characterized by their electronic absorption spectra. The rate of formation of these complexes at one atmosphere of molecular oxygen are reported. Novel paramagnetic superoxo complexes of Ru(III) of the composition $K[Ru(L)(O_2^-)]$ (L = EDTAH, HEDTA) are also reported.

INTRODUCTION

The dioxygen complexes of transition metal ions have been the subject matter of extensive studies during the last decade (1-4). Though the dioxygen complex chemistry of other transition metal ions has been much developed, the dioxygen complexes of ruthenium however are much less studied. The only well established complexes of ruthenium with dioxygen are those that contain π -acidic ligands (5-7) like CO, CN⁻, NO and PPh₃ or AsPh₃ in the coordination sphere of the metal ion with the metal ion in the formal low valent state. Dioxygen complexes of ruthenium with hard lewis bases like aminopolycarboxylic acids are hitherto unknown. In an earlier paper (8) the dioxygen complexes of ruthenium(III) with EDTA and HEDTA were reported. In the present paper stability constants of Ru(III) with the series of aminopolycarboxylic acids, HIMDA (N-hydroxyethyliminodiacetic acid), NTA (nitrilotriacetic acid), EDTA, HEDTA, trans-CDTA (cyclohexanediamine-N,N'-tetraacetic acid), DTPA (diethylenetriaminepentaacetic acid), TTHA (triethylenetetraminehexaacetic acid) are reported. The dioxygen complexes of Ru(III) with EDTA, HEDTA, DTPA and TTHA are thoroughly investigated in aqueous solution with the help of potentiometry, polarography, cyclic voltametry, electronic absorption spectra and kinetic studies of dioxygen absorption. The present series of Ru(III) aminopolycarboxylic acid dioxygen complexes in aqueous solution are the only counterparts of Co(II) dioxygen carriers for which equilibrium and other data (3,9) are available in aqueous solution.

The Ru(III)-aminopolycarboxylic acid complexes $K[RuCl]$ (L = EDTAH, HEDTA) combine with superoxide ion O_2^- with the displacement of the labile Cl⁻ ion to form the paramagnetic complexes $K[RuL(O_2^-)]$ (10). These complexes possess superoxide dismutase activity.

RESULTS AND DISCUSSION

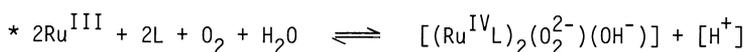
Potentiometric studies. The potentiometric titration of Ru(III) with the aminopolycarboxylic acids, HIMDA, NTA, HEDTA, EDTA, CDTA, DTPA and TTHA in a 1:1 ratio were conducted at 30°, $\mu = 0.1$ (KCl) in an atmosphere of nitrogen. The stability constants K_{ML} calculated from the titration curves are presented in Table I. The stability constants $\log K_{ML}$ are in good agreement with the Σ PKa of the ligands. It is of interest to note that the stability constants of the Ru(III) aminopolycarboxylic acid complexes are comparable with those of Fe(II) (11). This is expected because of the similarity in the ionic radii of the two ions (~ 0.91 Å).

The titration of the same systems in a 1:1 ratio of the ligand to metal ion was conducted at 30° ($\mu = 0.1$ KCl) in an oxygen atmosphere. In the case of Ru(III)-HIMDA and Ru(III)-NTA systems, the titration curves in the presence of nitrogen and oxygen coincided indicating no interaction with molecular oxygen. In the case of Ru(III)-CDTA the ligand underwent oxidation with molecular oxygen. For Ru(III)-HEDTA, EDTA, DTPA and TTHA systems there was a depression of pH and the titration curves gave inflections at: (a = 3.5, 4.5-5.5 HEDTA), (a = 2.5, 3.5-4.5 EDTA), (a = 3.5, 4.5-5.5 DTPA) and (a = 4.5, 5.5-6.5 TTHA). The non-integral value of the first inflection corresponds to the liberation of one proton per two moles of metal ion and is indicative (5) of the formation of binuclear μ -hydroxo- μ -peroxo complexes λ in solution according to the equilibrium:

TABLE 1. Formation and hydrolysis constants of the μ -peroxo- μ -hydroxo binuclear aminopolycarboxylic acid chleates of Ru(III) at 30°, $\mu = 0.1$ M (KCl)

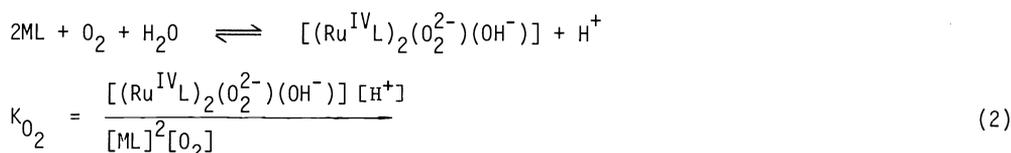
Ligand	Σ PKa	Log K_{ML}^*	Log K_1^{**}	Log K_{O_2}	-Log K_2	-Log K_3	K_d
HIMDA	10.75	10.3	-	-	-	-	-
NTA	13.85	12.1	-	-	-	-	-
HEDTA	17.30	13.6	28.1	3.9	11.1	31.8	3.47
EDTA	19.81	13.8	29.8	5.2	7.8	21.1	4.29
<u>trans</u> -CDTA	21.85	13.9	-	-	-	-	-
DTPA	27.25	14.1	28.5	3.1	12.9	16.4	-
TTHA	34.25	15.5	26.2	1.7	8.8	11.5	-

* accurate to ± 0.1 ; ** accurate to ± 0.2



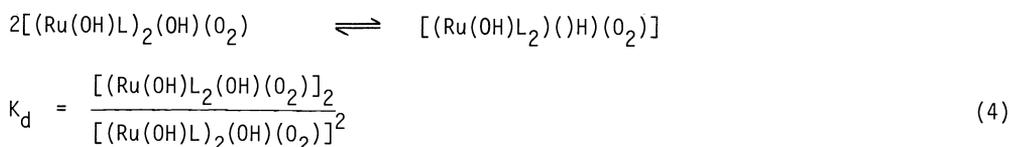
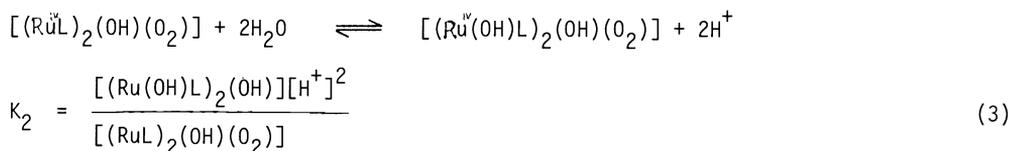
$$K_1 = \frac{[(Ru^{IV}L)_2(O_2^{2-})(OH^-)] [H^+]}{[Ru^{III}]^2 [L]^2 [O_2]} \quad (1)$$

The dioxygen complex formation constant K_{O_2} may be defined by the equilibrium:



The oxygen constant K_{O_2} was calculated from K_1 , K_{ML} and concentration of oxygen in solution $[O_2]$ at 30° and $\mu = 0.1$ (KCl). The constants are presented in Table I. The stabilities of λ decrease in the order EDTA > HEDTA > DTPA > TTHA. The stability is markedly decreased in the TTHA complex because of the repulsion of the unbound negatively charged groups in λ .

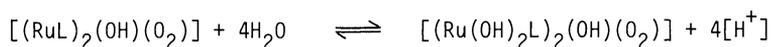
In order to compare the oxygenation of Ru(III) complexes with the dioxygen complexes of other metal ions like Fe(II) and Co(III), the reciprocal dioxygen pressure (in atmospheres⁻¹) at 50% oxygenation of the complex $P_{1/2}(O_2)^{-1}$ at pH 6 (the pH at which λ is formed to the maximum extent) are given in Table 2. It may be seen from Table 2 that the stabilities of the dioxygen complexes of ruthenium(III) are comparable to some of the μ -hydroxo- μ -peroxo complexes of Co(II) (9) and considerably higher than the picket fence complex (12) and the natural Fe(II) oxygen carriers hemoglobin and myoglobin (13,14). The stability of Ru(III)-TTHA-dioxygen complex at pH 6 is comparable to that of hemoglobin-oxygen complex in the Rest (R) state. The buffer region (2.5-4.5) for EDTA and 3.5-5.5 for HEDTA have been found to be concentration dependent. Hydrolysis and dimerization of the binuclear dioxygen complex λ were assumed to take place in this buffer region according to the equilibria:



* The charges are omitted on the ligand for the sake of clarity.

TABLE 2. Dioxygen affinities of selected complexes

No.	Complex	$(P_{1/2(O_2)})^{-1} \text{ atm}^{-1}$	Conditions	Ref.
1.	$[(\text{Ru}(\text{EDTA}))_2(\text{OH})(\text{O}_2)]$	8.7×10^8	30° , $\mu=0.1$ (KCl) calculated at pH 6	present work
2.	$[(\text{Ru}(\text{HEDTA}))_2(\text{OH})(\text{O}_2)]$	4.0×10^7	"	"
3.	$[(\text{Ru}(\text{DTPA}))_2(\text{OH})(\text{O}_2)]$	6.7×10^6	"	"
4.	$[(\text{Ru}(\text{TTHA}))_2(\text{OH})(\text{O}_2)]$	2.6×10^3	"	"
5.	$[\text{Co}(\text{en})_2]_2(\text{OH})(\text{O}_2)]$	3.4×10^{18}	25° , $\mu=0.1$ (KNO_3) calculated at pH 10	9
6.	$[(\text{Co}(\text{dien}))_2(\text{OH})(\text{O}_2)]$	7.0×10^8	"	9
7.	$[(\text{Co}(\text{trien}))_2(\text{OH})(\text{O}_2)]$	1.4×10^{12}	"	9
8.	$[(\text{Co}(\text{tren}))_2(\text{OH})(\text{O}_2)]$	7.1×10^{13}	"	9
9.	$\text{Fe}(\text{T}_{\text{PIVPP}})(1,2\text{-Me}_2\text{Im})$	2.0	toluene, 25°	12
10.	$\text{Mb}\cdot\text{O}_2$	2.6×10^3	water, pH ~ 7	14
11.	$\text{Hb}\cdot\text{O}_2$ (T)	2.9	"	14
12.	$\text{Hb}\cdot\text{O}_2$ (R)	4.5×10^3	"	15



$$K_3 = \frac{[(\text{Ru}(\text{OH})_2\text{L})_2(\text{OH})(\text{O}_2)][\text{H}^+]^4}{[(\text{RuL})_2(\text{OH})(\text{O}_2)]} \quad (5)$$

The constants K_2 , K_3 and K_d were calculated (15) for the EDTA and HEDTA complexes. The data is presented in Table 1. For Ru(III)-DTPA and Ru(III)-TTHA systems, the buffer regions 3.5-5.5, 4.5-6.5 were found to be concentration independent. Hydrolysis of the dioxygen complexes was assumed for these systems according to equations (3) and (5) and the data are presented in Table 1.

It may be seen from Table 1 that the hydrolytic tendency of the dioxygen complexes decreases in the order DTPA > EDTA > TTHA \sim HEDTA. Except for the TTHA complex the hydrolysis decreases with an increase in the negative charge on the complex. In TTHA complex the repulsion between the negative groups may be so large as to lift some of the bound groups on the complex and expose the metal ion to hydrolysis. For the dioxygen complexes of DTPA and TTHA, the lack of dimerization of the binuclear complexes is expected because of the repulsion between the negatively charged groups. The dimerization constant K_d increases with the stability of the dioxygen complex in the order HEDTA < EDTA.

In all the dioxygen complexes of Ru(III) studied in this work, the metal ion may be assumed to get formally oxidized to Ru(IV) by the transfer of an electron to molecular oxygen which gets reduced to the bridged peroxide anion. This accounts for the increase in the stability of the dioxygen complexes as compared to the Ru(III) complexes of aminopolycarboxylic acids (Table 1). The coordination of dioxygen to Ru(III) may be considered formally as an oxidative addition reaction whereby the six coordinate d^5 Ru(III) goes to seven coordinate (16) d^4 (Ru(IV)). If the aminopolycarboxylic acid is supposed to occupy five coordination positions on the metal ion, the remaining two are available for bridging by the peroxy and hydroxo groups.

Polarographic studies. The Ru(III)-HEDTA, DTPA and TTHA dioxygen complexes give anodic polarographic waves at pH 9. The EDTA complex gives the cathodic-anodic wave at pH 9. At pH 9 the dioxygen complexes exist mostly as the dihydroxo species in solution. The anodic wave then corresponds to the oxidation of the dihydroxo dioxygen species in solution to a superoxo complex. The half-wave potential ($E^{1/2}$) for this reaction (listed in Table 3) shift to more negative potentials in the order HEDTA < EDTA < DTPA < TTHA which indicates an increasing difficulty in the oxidation of the dioxygen complex at the dropping mercury electrode

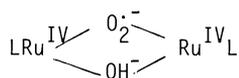
TABLE 3. Electrochemical data of the μ -peroxy- μ -hydroxo binuclear aminopoly-carboxylic acid chelates of Ru(III) at 30°, $\mu = 0.1$ (KCl)

No.	Complex	$-E^{1/2}V^*$	Cyclic Voltamograms			
			1st Redox Couple $-EP_c V^{**}$	$-EP_a V$	2nd Redox Couple $-EP_c V$	$-EP_a V$
1.	$[(Ru(HEDTA))_2(OH)(O_2)]$	0.031	0.15 ^a	0.05	-	0.58
			0.12 ^b	0.13	-	0.13
2.	$[(Ru(EDTA))_2(OH)(O_2)]^{3-}$	0.054	0.23 ^a	0.09	0.32	-
			0.14 ^b	0.05	0.28	0.23
3.	$[(Ru(DTPA))_2(OH)(O_2)]^{5-}$	0.130	0.32 ^a	0.13	0.37	-
			0.22 ^b	0.15	0.59	0.53
4.	$[(Ru(TTHA))_2(OH)(O_2)]^{7-}$	0.141	-	-	-	-

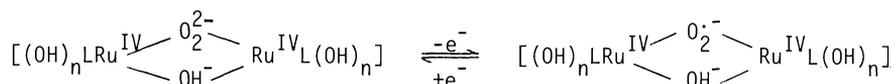
* $E^{1/2}$ calculated from anodic polarograms at pH 9. ** EP_c = electrode potential, cathode; EP_a = electrode potential, anode. ^a cyclic voltametric data at pH 9. ^b cyclic voltametric data at pH 6.

(dme). The higher negative potentials of DTPA and TTHA chelates account for the shielding of the metal and peroxy group by uncoordinated negative carboxylate groups. The Ru(III)-EDTA complex exhibits both the anodic and cathodic waves due to the enhanced stability of the complex at dme.

The oxidation potential for the peroxide ion in 0.1 N NaOH was reported (17) as -0.15V vs. a saturated calomel electrode (SCE). This supports the fact that the observed $E^{1/2}$ potentials in the anodic waves of the dioxygen complexes is due to the oxidation of the type



Puxeddu and Costa (18) reported anodic waves for the Co(II) Schiff base dioxygen complexes. The $E^{1/2}$ calculated for these complexes are in the range -0.1V to 0.4V vs. SCE. The electrode reaction investigated in the polarographic studies may be represented as:



Forward reaction, L = EDTA, HEDTA, DTPA, TTHA; backward reaction, L = EDTA

Cyclic voltametric studies. The results obtained from the cyclic voltamograms of Ru(III)-HEDTA, Ru(III)-EDTA and Ru(III)-DTPA complexes at pH 6 and 9 are presented in Table 3. Reliable results could not be obtained for Ru(III)-TTHA complex. Except for Ru(III)-HEDTA system at pH 6 most of the peaks were unresolved, in some cases broad.

The first step in the redox process at pH 9 seems to be the reduction of

$[(OH)_n LRu^{IV} \begin{array}{l} \diagup O_2^{2-} \\ \diagdown OH^- \end{array} Ru^{IV}L(OH)_n]$ complex to $[(OH)_n LRu^{III} \begin{array}{l} \diagup O_2^{2-} \\ \diagdown OH^- \end{array} Ru^{IV}L(OH)_n]$ species ζ . The peak potential for this wave decreases in the order HEDTA > EDTA > DTPA. The appearance of the second redox peak in these complexes corresponds to the reduction of ζ to

$[(OH)_n LRu^{III} \begin{array}{l} \diagup O_2^{2-} \\ \diagdown OH^- \end{array} Ru^{III}L(OH)_n]$ ζ species. The anodic oxidation of these species in the case of Ru(III)-EDTA and DTPA complexes results in large anodic currents. The processes are irreversible probably due to the decomposition of these complexes on oxidation.

In contrast to Ru(III)-EDTA and Ru(III)-ETPA systems, the Ru(III)-HEDTA complex shows a further one electron reduction of ζ to a possible $[(OH)_n LRu^{II} \begin{array}{l} \diagup O_2^{2-} \\ \diagdown OH^- \end{array} Ru^{III}L(OH)_n]$ ζ species

at a potential of -0.66V. This distinct behavior of HEDTA chelate may be due to the stability of the lower valent dioxygen complexes of ruthenium at pH 9. In the case of HEDTA the anodic oxidation of complexes $\tilde{2}$, $\tilde{3}$, and $\tilde{4}$ are completely reversible.

The cyclic voltammograms of the oxygenated systems at pH 6 are completely different from those at pH 9. At pH 6 the dioxygen complex species exist predominantly in the unhydrolyzed forms. All the systems EDTA, HEDTA and DTPA are completely reversible at pH 6. The reduced complexes $\tilde{2}$, $\tilde{3}$, and $\tilde{4}$ are completely reoxidized to the original complex $\tilde{1}$.

Oxygen Absorption Studies. The 1:1 Ru(III)-EDTA, Ru(III)-HEDTA, Ru(III)-DTPA and Ru(III)-TTHA systems were found to absorb oxygen when exposed to air or oxygen. The oxygen uptake measurements were conducted at pH 4.5 for EDTA and HEDTA complexes. Since the formation of the dioxygen complexes is complete at that pH (inflection point in the pH titration curve). At higher pH value the rate is lowered due to the formation of hydroxo species which are less reactive towards oxygenation. For the DTPA and TTHA complexes the rates were measured at pH 9.

In the presence of excess oxygen, the pseudo first order rate constant $k_1[O_2] \gg [Ru(III)]$ at 30° ($\mu = 0.1 M$ (KCl)) with respect to the metal ligand-dioxygen complex formation for Ru(III)-EDTA- O_2 , Ru(III)-HEDTA- O_2 , Ru(III)-DTPA- O_2 and Ru(III)-TTHA- O_2 complexes are $k_1 = 1.5 \times 10^{-3} S^{-1}$ ($t^{1/2} = 7.7$ mts), $1.2 \times 10^{-3} S^{-1}$ ($t^{1/2} = 9.7$ mts), $5.6 \times 10^{-4} S^{-1}$ ($t^{1/2} = 20.5$ mts), $4 \times 10^{-4} S^{-1}$ ($t^{1/2} = 28.8$ mts), respectively. The oxygen absorption rate decreases in the order EDTA > HEDTA > DTPA > TTHA.

The oxygenation studies were conducted on a Validyne Corporation differential pressure transducer calibrated with a known Co(II) dioxygen complex. The stoichiometry of oxygenation of ruthenium(III) complexes was determined as 1 mole of oxygen per two moles of the metal ion, supporting the findings of potentiometry and polarography.

Absorption Spectra of Complexes. The ligational bands characteristic of the aminopolycarboxylic acids are observed at 283 nm (2920), 312-316 nm (1718) in Ru(III)-EDTA; 296 nm (2120) 312 nm (1763) in Ru(III)-HEDTA; 246 nm (2583), 291 nm (2132 in Ru(III)-DTPA and 251 nm (2793), 310 nm (2052 in Ru(III)-TTHA systems, respectively.

The oxygenation complexes retain the ligational bands with slight shifts. In the oxygenated complexes the bands at 331 nm (663) and 345 nm (728) in EDTA; 320 nm (1612) and 345 nm (709) in HEDTA; 330 nm (1411) and 350 nm (961) in DTPA and 325 nm (1800) and 348 nm (1201) in TTHA complexes may be assigned to the $1\pi^*(O_2^-) \rightarrow d\sigma^*$ LMCT transition (18). The d-d transition bands characteristic of Ru(IV) are observed at 394 nm (2760), 431 nm (640), 455 nm (320) and 430 nm (410) in the EDTA, HEDTA, DTPA and TTHA complexes, respectively. A similar band at 472 nm (710) was observed (19) for Ru(IV) in HIO_4 medium.

The acidified solutions of the oxygenated complexes liberate one equivalent of I_2 per two moles of metal ion. This observation demonstrates the presence of peroxide ion in the acidified complexes. On heating the acidified complexes decompose to give solutions with characteristic Ru(IV) absorption spectra in the d-d region (19).

The basic solution of oxygenated EDTA, HEDTA and DTPA complexes are reversible with respect to oxygen uptake. On heating the solutions lose dioxygen to give ruthenium(III) species in solution with the electronic spectra similar to Ru(III) complexes. The oxygenated TTHA chelate was found to decompose on heating. The coordinated dioxygen cannot be removed from the complexes on purging nitrogen through the solution.

Superoxide Complexes of Ru(III). Complexes of the composition $K[RuLO_2^-]$ $\tilde{5}$ (L = EDTA, HEDTA) were obtained (10) as dark brown solids by the replacement of the labile chloride in $K[RuLCl]$ $\tilde{6}$ (20) by KO_2 in dichloromethane suspension at -40° . The complexes are stable when stored at low temperature but gradually decompose at room temperature. They exhibit the characteristic IR band of coordinated superoxide ion $\sim 1140 cm^{-1}$.

Complexes $\tilde{5}$ are paramagnetic and show two ESR signals both in the solid state at 300 K and in aqueous $\tilde{5}$ solution at 110 K. The g values obtained from these spectra are close to 2.06 and 2.26. The g value at 2.06 corresponds to the unpaired electron on superoxide ion and the one at 2.26 indicates the presence of the unpaired spin of Ru(III). The solid state ESR spectrum of $\tilde{6}$ at 300 K gave a sharp ESR signal with a g value of 2.32 which supports the assignment of the ESR peak corresponding to g value of 2.26 in $\tilde{5}$ to the unpaired spin of Ru(III). The aqueous solutions of $\tilde{5}$ when heated lose paramagnetism and the solution exhibits electronic spectra characteristic of Ru(II) complexes with a high intensity band around 280 nm and a low intensity band around 425 nm (20). This indicates that the unpaired electron on O_2^- is transferred to Ru(III) and the superoxide ion is converted to O_2 and H_2O_2 possible by a superoxide dismutase action (21).

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