Interaction of aqua-(N-hydroxyethylethylenediaminetriacetato) ruthenate(III) complex with ortho-phenylenediamine in aqueous solution

Debabrata Chatterjee* & D Srinivas
Discipline of Coordination Chemistry, Central Salt & Marine Chemicals Research Institute, Bhavnagar 364 002, India

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Reaction of \([\text{Ru}^{III}(\text{hedtra})(\text{H}_2\text{O}))\), (1) (hedtra = N-hydroxyethylethylenediaminetriacetate) with opd (opd=ortho-phenylenediamine) results in the formation of a mixed-chelate \([\text{Ru}(\text{hedtra-H})(\text{opd})]\)Cl complex (2). Complex 2 has been isolated and characterised by UV-vis, IR and EPR methods.

The chemistry of polyaminopolycarboxylate (pac) complexes of ruthenium is of our continued research interest\(^5\). Interactions of Ru(III) -pac complexes with bidentate ligands result in the formation of mixed-chelate complexes of ruthenium(II)\(^6\),\(^7\). However, the interaction of \([\text{Ru}^{III}(\text{EDTA})(\text{H}_2\text{O}))\) (EDTA=ethylenediaminetetraacetate) with opd (orthophenylenediamine) under aerobic condition was reported\(^8\) to yield a mixed-chelate complex of ruthenium (II); not ruthenium (III). This unexpected reduction of ruthenium(III) in the reported reaction\(^8\) stimulated our interest in examining the reaction with another polyaminopolycarboxylate complex of ruthenium(III). Hence, we studied the reaction of \([\text{Ru}^{III}(\text{hedtra})(\text{H}_2\text{O}))\) (hedtra=N-hydroxyethylethylenediaminetriacetate) with opd, and, by contrast we found the formation of a ruthenium (III) complex in the reaction mixture. In this paper, we wish to report our experimental results on the synthesis and physico-chemical characterisation of this mixed-chelate \([\text{Ru}^{III}(\text{hedtra-H})(\text{opd})]\)Cl (opd) complex 2.

Experimental

\(\text{K[Ru}^{III}(\text{hedtra})\text{Cl}])\) was prepared by following the published procedure\(^9\) and characterised. On dissolution, it exists as \(\text{K[Ru}^{III}(\text{hedtra})(\text{H}_2\text{O}))\) species (1) at low pH (~3)\(^10\). All other chemicals used were of A.R. grade. Doubly distilled water was used throughout the experiments.

Synthesis of \([\text{Ru}^{III}(\text{hedtra-H})(\text{opd})]\)Cl (2).

To a stirred aqueous solution (10 ml) of \(\text{K[Ru}^{III}(\text{hedtra})\text{Cl}]\) (1 mmol) was added slowly recrystallized opd (1.1 mmol) dissolved in minimum volume of alcohol-water (1:1) mixture. The reaction mixture was stirred for 15 min (under Ar) at room temperature and then concentrated in vacuo to 2-3 ml. On addition of acetone a rose-red coloured compound separated which was filtered and washed with cold acetone-water (9:1) mixture several times and dried in vacuo (yield 90%). Analysis [Found(Calc): C 36.83 (36.89); H 4.59 (4.61); N 10.79 (10.76%)].

Physico-chemical measurements

Elemental (C H N) analysis were carried out with a Carlo Erba elemental analyser. Spectral (UV-vis) measurements were performed on a Shimadzu UV-vis 160 spectrophotometer coupled with a temperature controller (TCC 240A). IR spectra (as KBr pellets) were recorded using a Carl Zesis Specord M80 spectrometer. The EPR spectra of 2 were recorded in both powdered form (at room temperature) and frozen solution (at 77K). A Bruker ESP 300 X-band spectrometer (100 kHz field modulation) with a built in ERO 35 NMR gaussmeter (for magnetic field calibrations) was used for this purpose. The g values were determined with DPPH marker (g=2.0032). Magnetic susceptibilities of the complexes were measured at room temperature (298K) with a PAR 155 vibrating- sample magnetometer.

Results and discussion

Upon addition of opd the pale yellow solution of complex 1 changed to a red solution. A red coloured product was isolated (see experimental) and characterised. Elemental analysis of the product corresponded to the formula \([\text{Ru}^{III}(\text{hedtra-H})(\text{opd})]\) Cl. The spectrum of the complex 2 (in \(\text{H}_2\text{O})\) display an absorption band at 501 nm (Fig. 1a). This band \((\epsilon_{max} = 3432)\) is assigned to ligand to metal charge transfer originating from opd (LMCT). Another band at 283 nm is the characteristic LMCT band of coordinated hedtra ligand. The IR spectrum of complex 2...
exhibited usual band of coordinated hedtra a broad band at 1640 cm\(^{-1}\) is assigned to coordinated COO\(^{-}\) group. A sharp band at 1720 cm\(^{-1}\) is assigned to uncoordinated and protonated COOH stretching\(^{11}\). The presence of this band at 1720 cm\(^{-1}\) indicates chelation of bidentate opd ligand. EPR spectra of complex 1 in powder form (at 298K) and frozen-glass solution (at 77K) are quite similar in nature and almost identical with the spectra reported earlier\(^{12}\) for Ru\(^{III}\)-EDTA complex. The spectra are characterised by rhombic g tensor with principal g components being \(g_1 = 2.401, g_2 = 2.345\) and \(g_3 = 1.732\). Complex 2 also exhibited similar rhombic spectra both in powder form (298K) and frozen-glass solution (77K). A representative spectrum of complex 2 in frozen-glass solution (77K) is shown in Fig. 2a. The g features \(g_1 = 2.223, g_2 = 2.147\) and \(g_3 = 1.892\) and the spectra are consistent with one unpaired electron in a lowspin \(4d^5\) electronic configuration. Further, lowering of g anisotropy in complex 2 clearly indicates the chelation of opd ligand which increases the ligand field strength.

Additional support in favour of the above arguments comes from magnetic susceptibility measurements which revealed that complex 2 is paramagnetic with \(\mu_{\text{eff.}}\) value of 1.98 B.M.

Based on the above experimental facts it is believed that interaction of pentacoordinated hedtra complex of ruthenium(III) with opd results in the formation of the paramagnetic ruthenium(III) mixed-chelate complex 2. We could not get any experimental evidences in favour of the ruthenium (II) species throughout the experiments. Further, we examined the interaction of oxidising agents with complex 2 as it was important with reference to the earlier report\(^8\) in which it is claimed that oxygen assists the reduction of Ru(III) to Ru(II) in the reaction between [Ru\(^{III}\)(EDTA) \((\text{H}_2\text{O})\)]\(^+\) and opd. We added oxidising agents like \(\text{H}_2\text{O}_2\) (or KHSO\(_5\)) to the solution of complex 2 and found spectral changes (shifting of \(\lambda_{\text{max}}\) from 501 nm to 481 nm). Similar spectral changes were also observed upon exposing the solution of complex 2 to air for a long period (4 hr). We have successfully isolated\(^{13}\) the oxidised product and out once again with a Ru(III) species. Absorption spectrum of the oxidised product in \(\text{H}_2\text{O}\) is shown in Fig. 1b. IR spectrum of the oxidised product was found to be quite similar (except for a new band at 1600 cm\(^{-1}\) assigned to \(\nu\text{C}=\text{N}\)) to that of complex 2 which indicates that the coordinated hedtra ligand in complex 2 did not get oxidised under experimental conditions. EPR spectrum of oxidised product at 77K was found to be axial (Fig. 2b) with characteristic g features \(2.332\) and \(1.785\) for a low - and spin \(d^5\) ruthenium (III) species. On the basis of the above observations it is suggested that in the interaction of complex 2 with \(\text{H}_2\text{O}_2\) (KHSO\(_5\) or \(\text{O}_2\)) coordinated opd ligand is oxidised to \(\sigma\)-benzoquinone dimine \((\sigma\text{-bqdi})\), to give [Ru\(^{III}\)(hedtra-H)(Bqdi)]\(^+\) (3) species as an oxidised product of complex 2. The value of \(\mu_{\text{eff}}\) determined for complex 3 is 1.90 B.M. This further substantiates the formation of a paramagnetic product in the oxidation of complex 2 by \(\text{H}_2\text{O}_2\) or KHSO\(_5\).

In conclusion, the reaction of Ru\(^{III}\)(hedtra) \((\text{H}_2\text{O})\) with bidentate ligand opd produces a mixed-chelate Ru(III) complex, not Ru(II). Further, oxidation of this Ru(III) species involves oxidation of coordinated ligand opd to yield another Ru(III) - complex.
[RullI (hedtra-H)(bqdi)]CI (3) was synthesized by reacting complex 2 with H2O2 (at room temperature) followed by precipitation with acetone. Anal[Found(Calc.): C 37.14 (37.03); H 4.22 (4.24); N 10.89 (10.80%)]: UV-vis λmax/εmax (nm/ mol dm\(^3\) cm\(^{-1}\)) = 481 (1725).