



# Library Indian Institute of Science Education and Research Mohali



**DSpace@IISERMohali (/jspui/)**

**/ Publications of IISER Mohali (/jspui/handle/123456789/4)**

**/ Research Articles (/jspui/handle/123456789/9)**

Please use this identifier to cite or link to this item: <http://hdl.handle.net/123456789/4898>

Title:	Dangling Carboxylic Group That Participates in O–O Bond Formation Reaction to Promote Water Oxidation Catalyzed by a Ruthenium Complex: Experimental Evidence of an Oxide Relay Pathway
Authors:	Barman, Suman K. (/jspui/browse?type=author&value=Barman%2C+Suman+K.)
Keywords:	Dangling Carboxylic Group O–O Bond Formation Ruthenium Complex Oxide Relay Pathway
Issue Date:	2022
Publisher:	ACS Publications
Citation:	Inorganic Chemistry, 61(3), 1426-1437.
Abstract:	<p>Two mononuclear ruthenium(II) complexes of the types <math>[\text{Ru}(\text{trpy})(\text{HL1})(\text{OH}_2)]^{2+}</math> (1Aq) and <math>[\text{Ru}(\text{trpy})(\text{L2-}\kappa\text{-N}_2\text{O})]</math> (2) [where <math>\text{trpy} = 2,2':6',2''\text{-terpyridine}</math>, <math>\text{HL1} = 2\text{-(2-pyridyl)benzimidazole}</math>, <math>\text{H2L2} = 2\text{-(pyridin-2-yl)-1H-benzodimidazole-4-carboxylic acid}</math>] have been synthesized and thoroughly characterized by analytical and spectroscopic [UV–vis, NMR, high-resolution mass spectrometry, and IR] techniques. Complex 1Aq has been further characterized by X-ray crystallography. In an acidic aqueous medium (pH 1), complex 2 undergoes carboxylate/water exchange readily to form an aqua-ligated complex, <math>[\text{Ru}(\text{trpy})(\text{H2L2-}\kappa\text{-N}_2)(\text{OH}_2)]^{2+}</math> (2Aq), having a dangling carboxylic group. This exchange phenomenon has been followed by IR, <math>^1\text{H}</math> NMR, and UV–vis spectroscopic techniques. Electrochemical analyses of 1Aq and 2Aq (Pourbaix diagram) suggest the generation of a formal <math>\text{RuV=O}</math> species that can potentially promote the oxidation of water. A comparative study of the water oxidation activity catalyzed by 1Aq and 2Aq is reported here to see the effect of a dangling carboxylic group in the catalytic performance. Complex 2Aq shows an enormously higher rate of reaction than 1Aq. The pendant carboxylic group in 2Aq participates in an intramolecular O–O bond formation reaction with the reactive formal <math>\text{RuV=O}</math> unit to form a percarboxylate intermediate and provides an electron-deficient carbon center where water nucleophilic attack takes place. The isotope labeling experiment using <math>^{18}\text{O}</math>-labeled water verifies the attack of water at the carbon center of the carboxylic group rather than a direct attack at the oxo of the formal <math>\text{RuV=O}</math> unit. The present work provides experimental evidence of the uncommon functionality of the carboxylic group, the oxide relay, in molecular water oxidation chemistry.</p>
Description:	Only IISER Mohali authors are available in the record.
URI:	<a href="https://doi.org/10.1021/acs.inorgchem.1c03105">https://doi.org/10.1021/acs.inorgchem.1c03105</a> ( <a href="https://doi.org/10.1021/acs.inorgchem.1c03105">https://doi.org/10.1021/acs.inorgchem.1c03105</a> ) <a href="http://hdl.handle.net/123456789/4898">http://hdl.handle.net/123456789/4898</a> ( <a href="http://hdl.handle.net/123456789/4898">http://hdl.handle.net/123456789/4898</a> )
Appears in Collections:	Research Articles (/jspui/handle/123456789/9)

Files in This Item:


File	Description	Size	Format

Need To Add...Full Text\_PDF  
(/jspui/bitstream/123456789/4898/1/Need%20To%20Add%e2%80%a6Full%20Text\_PDF)

15.36    Unknown  
kB

[View/Open \(/jspui/t](#)

[Show full item record \(/jspui/handle/123456789/4898?mode=full\)](#)

 [\(/jspui/handle/123456789/4898/statistics\)](#)

Items in DSpace are protected by copyright, with all rights reserved, unless otherwise indicated.