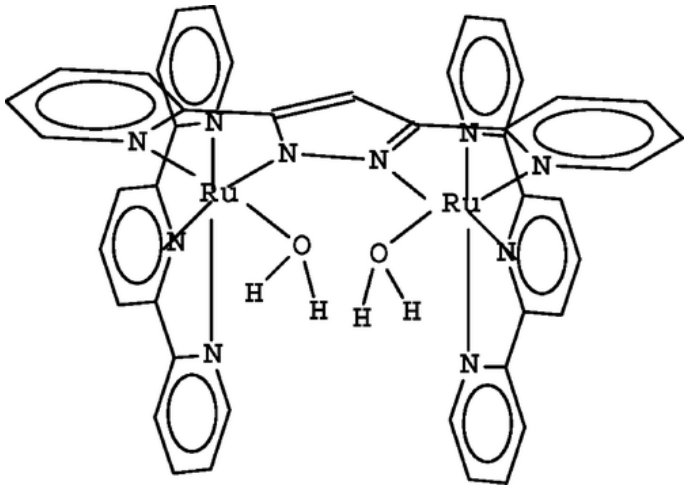
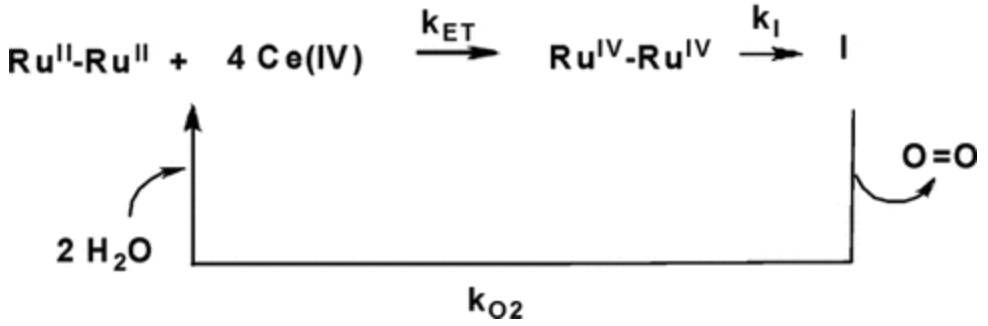
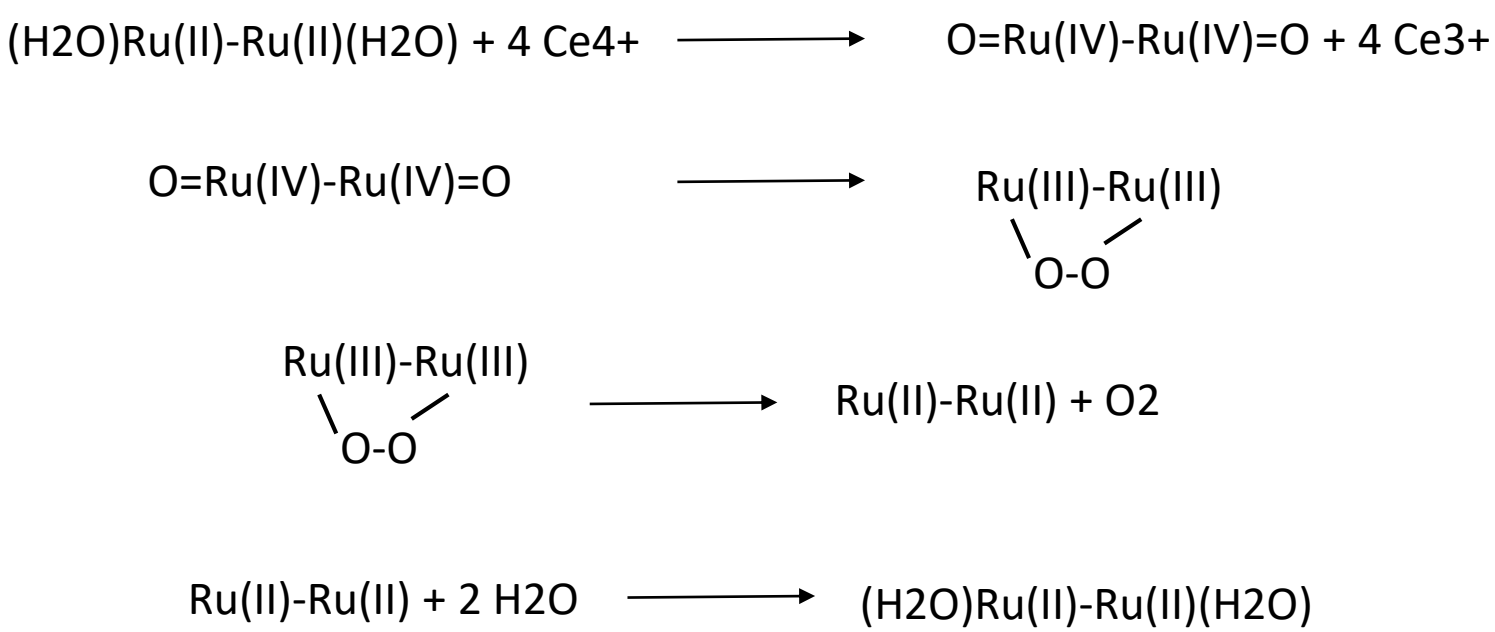
EXERCISE 1

The following Ru-based complex can catalyze the oxidation of water to form oxygen using cerium ammonium nitrate (Ce^{4+}) as oxidant. The starting catalyst is Ru(II)-Ru(II). Experiments show the sequence in the right. Moreover, isotope experiments show that both oxygen atoms of the O_2 are coming from the Ru-Ru complex. Based on this, propose a full catalytic cycle.

$$2H_2O + 4Ce^{4+} \longrightarrow O_2 + 4H^+ + 4Ce^{3+}$$



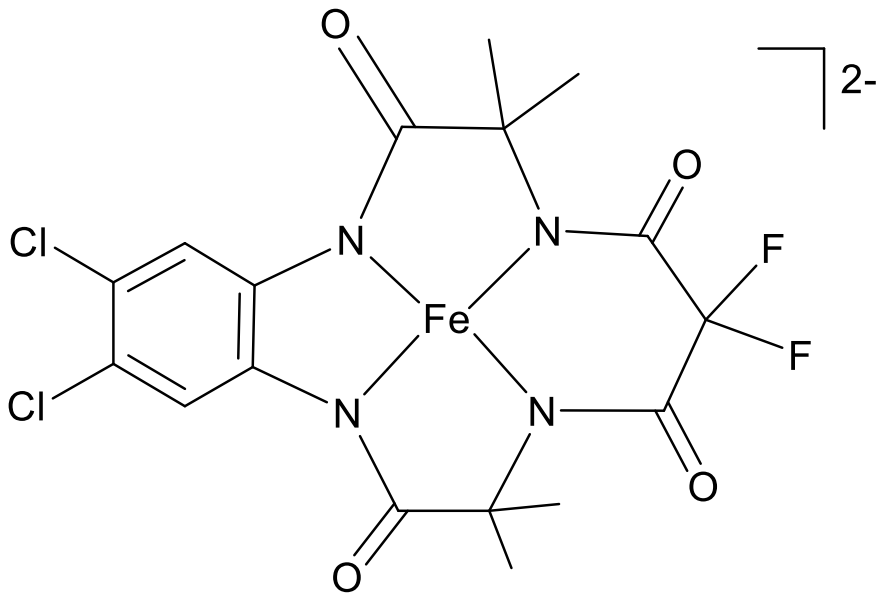



(H2O)Ru(II)-Ru(II)(H2O) + 4 Ce4+
O=Ru(IV)-Ru(IV)=O + 4 Ce3+
O=Ru(IV)-Ru(IV)=O
Ru(III)-Ru(III)
O-O
Ru(III)-Ru(III)
O-O
Ru(II)-Ru(II) + O2
Ru(II)-Ru(II) + 2 H2O
(H2O)Ru(II)-Ru(II)(H2O)

EXERCISE 2

The following scheme shows a Fe-based complex that can catalyze the oxidation of water to form oxygen using cerium ammonium nitrate (Ce^{4+}) as oxidant. The starting catalyst is Fe(II). Propose two catalytic cycles. One based on one Fe-center. One based on two Fe-centers. You are allowed to represent the tetradentate macrocyclic ligand as N_4.

$$2H_2O + 4Ce^{4+} \longrightarrow O_2 + 4H^+ + 4Ce^{3+}$$



Two metals:

$$2\ (H_2O)Fe(II) + 4\ Ce^{4+} \longrightarrow 2\ O{=}Fe(IV) + 4\ Ce^{3+}$$

$$O{=}Fe(IV) + Fe(IV){=}O \longrightarrow Fe(III)\text{-}O\text{-}O\text{-}Fe(III)$$

$$Fe(III)\text{-}O\text{-}O\text{-}Fe(III) \longrightarrow 2\ Fe(II) + O_2$$

$$2\ Fe(II) + 2\ H_2O \longrightarrow 2\ (H_2O)Fe(II)$$

One metal:

$$(H_2O)Fe(II) + 4\ Ce^{4+} \longrightarrow O{=}Fe(VI) + 4\ Ce^{3+}$$

$$O{=}Fe(VI) + OH_2 \longrightarrow Fe(IV)\text{-}OOH + H^+$$

$$Fe(IV)\text{-}OOH \longrightarrow Fe(IV)\text{-}OO + H^+$$

$$Fe(IV)\text{-}OO \longrightarrow Fe(II) + O_2$$

$$Fe(II) + H_2O \longrightarrow Fe(II)\text{-}H_2O$$