A Novel Method for Preparing of Oxoruthenates Complexes: *trans*-$[RuO_3(OH)_2]^{2-}$, $[RuO_4]^-$, $(n\text{-}Pr_4N)^+[RuO_4]^-$ and $[RuO_4]$ and Their Use as Catalytic Oxidants

Abdel-Ghany F. Shoair

Department of Chemistry, Faculty of Science, 34517 Domiat EL-gadida, Mansoura University, Egypt
**E-mail: Shoairaksm@hotmail.com*

Received June 2, 2005

The synthesis and characterization of $K_3[Ru(C_2O_4)_3]{\cdot}4H_2O$ ($C_2O_4^{2-}$ = oxalato anoin) complex are described, and its redox properties (in buffer solution of pH = 12) have been investigated. This complex is used for *in situ* generation of oxoruthenates complexes which have been characterized by electronic spectroscopy. Reaction of $K_3[Ru(C_2O_4)_3]{\cdot}4H_2O$ with excess $S_2O_8^{2-}$ in molar KOH generates *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ reagent while with excess BrO_3^- in molar Na_2CO_3 generates $[RuO_4]^-/BrO_3^-$ reagent. Avoiding the direct use of $[RuO_4]$ the organic-soluble $(n\text{-}Pr_4N)^+[RuO_4]^-$, (TPAP) has been isolated by reaction of $K_3[Ru(C_2O_4)_3]{\cdot}4H_2O$ with excess BrO_3^- in molar carbonate and *n*-Pr_4NOH. In a mixture of H_2O/CCl_4 ruthenium tetraoxide can be generated by reaction of $K_3[Ru(C_2O_4)_3]{\cdot}4H_2O$ with excess IO_4^-. The catalytic activities of oxoruthenates that have been made from $K_3[Ru(C_2O_4)_3]{\cdot}4H_2O$ towards the oxidation of benzyl alcohol, piperonyl alcohol, benzaldehyde and benzyl amine at room temperature have been studied.

Key Words : Oxoruthenates, Oxidation, *N*-Methylmorpholine-*N*-oxide (NMO)

Introduction

Oxoruthenates are effective catalytic oxidants for selective oxidation of various organic substrates.[1,2] The synthesis of oxoruthenates complexes is an area of current interest[3] and the use of $RuCl_3{\cdot}nH_2O$ or $RuO_2{\cdot}nH_2O$ for generation of oxoruthenates has been reported.[4-6] Ruthenium tetraoxide is well-defined powerful oxidizing agent; it can be made from $RuCl_3{\cdot}nH_2O$ or $RuO_2{\cdot}nH_2O$ and IO_4^- in water.[5] Such reagent is non-selective catalyst and reacts with alkenes, alcohols and alkynes causing aromatic ring rapture.[7] The organic-soluble tetrapropylammonium perruthenate; $(n\text{-}Pr_4N)^+[RuO_4]^-$ (TPAP), which is mild and selective oxidant for primary alcohols originally made by sweeping out $[RuO_4]$ into a solution of molar aqueous K_2CO_3 and *n*-Pr_4NOH.[8] Griffith *et al.*[9] have developed a convenient one-pot synthesis of $(n\text{-}Pr_4N)^+[RuO_4]^-$ (TPAP) in which *n*-Pr_4NOH is added to an aqueous solution of $[RuO_4]^-$ generated by adding $RuCl_3{\cdot}nH_2O$ to BrO_3^- in molar carbonate. The single X-ray crystal structure for the $[Ru(C_2O_4)_3]^{3-}$ anion has been reported by Beattie[11] and confirmed that the complex anion is formulated correctly as $[Ru(C_2O_4)_3]^{3-}$, with the entire oxalato group acting as bidentate ligands. So far, the use of $K_3[Ru(C_2O_4)_3]{\cdot}4H_2O$ for *in situ* generation of oxoruthenates has not been reported. Here we report the synthesis, characterization and the redox properties of $K_3[Ru(C_2O_4)_3]{\cdot}4H_2O$. The use of $K_3[Ru(C_2O_4)_3]{\cdot}4H_2O$ as a good precursor for *in situ* generation of oxoruthenates complexes has been studied. The characterization and the catalytic activity of these complexes have been investigated.

Materials and Methods

Chemicals. Ruthenium trichloride, *N*-methylmorpholine-*N*-oxide (NMO), tetrapropyl ammonuium hydroxide were obtained from Aldrich and used without further purification. Benzyl alcohol, benzaldehyde, piperonyl alcohol and benzyl amine were obtained from Fulka. Other chemicals and solvents were reagent grade and used as received.

Instrumentation. Infrared spectra were recorded on Mattson 5000 FT-IR and electronic spectra were recorded on UV-visible vision software V 3.2. ^1H NMR spectra were obtained using a 300 MHz Varian FT-NMR spectrometer. Microanalysis was carried out at Cairo University Micro-analytical Unit. Cyclic voltammetric studies were recorded on a potentiostat wave generator (Oxford electrodes) using a platinum-wire working electrode, platinum-wire auxiliary electrode and $Ag^+/AgCl$ reference electrode in conjunction with a Phillip PM 8043 X-Y recorder. Britton Robinson buffer of pH = 12 was used as supporting electrolyte and the solution concentration $\sim 1.0 \times 10^{-3}$ M. The half-wave potential $E_{1/2}$ was set equal to 0.5 ($E_{pa} + E_{pc}$) where E_{pa} and E_{pc} are the anodic and cathodic cyclic voltammetric peak potentials respectively. The electrochemical experiment was carried out in dinitrogen atmosphere and at room temperature.

Preparation of $Ru(OH)_3{\cdot}nH_2O$. $RuCl_3{\cdot}nH_2O$ (500 mg, 2 mmol) was dissolved in 3 cm^3 of distilled water. 2 cm^3 of 2.4 molar KOH was added dropwise with stirring. The $Ru(OH)_3{\cdot}nH_2O$ was filtered and washed several times with distilled water until the Ag^+ test showed the absence of chloride ions.

Preparation of $K_3[Ru(C_2O_4)_3]{\cdot}4H_2O$. The complex was made by a method based on that of Beattie and co-workers[11] with some modification.

To a boiling solution of oxalic acid (220 mg is dissolved in 2 cm^3 of water) 100 mg of freshly prepared $Ru(OH)_3{\cdot}nH_2O$ was added. The mixture was refluxed (*ca.* 20 min.) until the formation of olive-green solution. $K_2C_2O_4{\cdot}2H_2O$ (120 mg, 0.6 mmol) was slowly added with reflux for further 20 min. The mixture was cooled to 40 °C and then poured into 25 cm^3 of ethanol. The $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ complex was precipitated as yellow-green crystals. Yield: 70%.

Analysis: Found: C, 12.9; H, 1.4. Calcd. For $C_6H_8O_{16}K_3Ru$: C, 13; H, 1.3. I.R.: 1690 cm^{-1} ν(C=O), 475 cm^{-1} ν(Ru-O). Electronic spectrum in water: λ_{max}: 475 nm, 325 nm, 350 nm and 390 nm.

Preparation of *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ reagent. The procedure of Griffith and co-worker[4] was used with some modification.

To 100 cm^3 of molar KOH containing excess of $K_2S_2O_8$ (2700 mg, 10 mmol) $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ (30 mg, 5.4 × 10^{-2} mmol) was added. The mixture was stirred at room temperature until the orange colour appeared. The ruthenate ion was identified from its electronic spectrum: [nm (ε/dm^3 mol^{-1} cm^{-1})]: 475 (1416) and 385 (985) corresponding to that previously reported.[4]

Preparation of $[RuO_4]^-/BrO_3^-$ reagent. To 10 mL of molar Na_2CO_3 containing excess of $NaBrO_3$ (1200 mg, 0.1 mmol) $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ (11 mg, 1.98 × 10^{-2} mmol) was added with stirring at room temperature until the yellow - green colour appeared. The perruthenate ion was identified from its electronic spectrum: [nm (ε/dm^3 mol^{-1} cm^{-1})]: 388 (2525) and 320 (2610) corresponding to that previously reported.[4]

Preparation of $(n\text{-}Pr_4N)^+[RuO_4]^-$, TPAP. To 20 cm^3 of $[RuO_4]^-/ BrO_3^-$ reagent made as above 200 mg of 0.1 M *n*-Pr_4NOH was added with stirring. The deep green precipitate formed was extracted into alcohol-free CH_2Cl_2 (10 cm^3) and the solution was dried on anhydrous Na_2SO_4, concentrated *in vacou*, and recrystallized by adding CCl_4. Yield: 136 mg, 0.038 mmol (97%).

Analysis: Found: C, 40.4; H, 8.2; N, 3.7. Calcd. For $C_{12}H_{28}O_4N$ Ru: C, 40.1; H, 8.0; N, 4.0. I.R. 834 cm^{-1} (strong) ν^{as} (RuO_4). Electronic spectrum in CH_2Cl_2: [nm (ε/ dm^3 mol^{-1} cm^{-1})]: 375 (2256) and 318 (2481).

Catalytic oxidation by *trans*-$[RuO_3(OH)_2]^{2-}/ S_2O_8^{2-}$ or $[RuO_4]^-/BrO_3^-$ reagents. The substrate (2 mmol) was added with stirring at room temperature to 100 cm^3 of *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ solution or to 10 cm^3 of $[RuO_4]^-/ BrO_3^-$ solution. The reaction mixture was stirred at room temperature for the times listed in Table 2. The orange colour of ruthenate and the yellow green colour of perruthenate reappear when the reaction is complete. The reaction mixture was extracted with diethylether (3 × 10 cm^3) to remove the unreacted substrate. The alkaline aqueous layer was acidified with H_2SO_4 to pH 2, extracted with diethylether (3 × 10 cm^3) and dried to give the acid as a white solids (In the case of benzylamine the reaction mixture was extracted with diethylether (3 × 10 cm^3), the ether extracts dried over anhydrous Na_2SO_4 and removed to give benzonitrile as a liquid). The purity of the products were checked by ^{1}H NMR and M.P. In the case of $[RuO_4]^-/BrO_3^-$ system solid anhydrous Na_2SO_3 was added to the aqueous acidic solution to prevent interference by bromine with products.

Catalytic oxidation by $(n\text{-}Pr_4N)^+[RuO_4]^-$, TPAP/ *N*-methylmorpholine-*N*-oxide (NMO). To a solution of alcohol or benzylamine (1 mmol). *N*-methylmorpholine-*N*-oxide (NMO) (3 mmol) was added followed by the catalyst TPAP (10 mg, 2.8 × 10^{-2} mmol). The reaction mixture was stirred at room temperature for the times listed in Table 2. The mixture was reduced *in vacuo* and the residues taken up in diethylether and filtered through a bad of sillica gel. The aldehydes formed were quantified as their 2,4-dinitrophenylhydrazone derivatives.

Results and Discussion

Synthesis of $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$. The tris-oxalato ruthenate(III), $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ was made as potassium salt by reaction of freshly prepared $Ru(OH)_3\cdot nH_2O$ with oxalic acid in refluxing water. The complex was precipitated as green-olive crystals by adding the appropriate amount of potassium oxalate. Attempts were made to isolate the analogous succinato complex but were all unsuccessful since we have got ill-defined product with variable analysis. The analytical data for that complex are well agreed with its formula.

Infrared and electronic spectra of $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$. The infrared spectrum of $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ showed band at 1690 cm^{-1}, assigned to the carbonyl group of the oxalato ligand together with three bands at 1220, 1100 and 800 cm^{-1} which are typical of bidentate oxalato ligand. These bands are similar to those found for $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ complex.[12] A low frequency band appeared at 475 cm^{-1} is tentatively assigned to the ν(Ru-O). The electronic spectrum of the complex was recorded in water in concentration range 10^{-3}-10^{-5} M at ambient temperature. A low intesity band was observed at 475 nm, attributable to metal-to-ligand charge transfer transitions as similarly observed for ruthenium(III) complexes.[13,14] Three bands were also found in the region 325-400 nm, these bands are likely to be due to d-d- transitions.

Electrochemical properties of $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$. We investigated the electrochemical behavior of this complex by cyclic voltammetry in Britton Robinson buffer (pH = 12), (since ruthenate and perruthenate anions are stable in basic media[4,5]), to confirm the possible generation of higher oxidation states that have been generated chemically from $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$. The complex showed one reduction wave (A), two oxidation waves (B and C) and one oxidation peak (D), voltammetric data are presented in Table 1, and the voltammogram is displayed in Figure 1. The reduction wave is quasireversible, characterized by peak-to-peak separation of 120 mV. This wave remains unaltered upon changing the scan rate and is assigned to Ru(III)/Ru(II) reduction (A). The first oxidation wave is reversible ($\Delta E = 60$ mV) *versus* $Ag^+/AgCl$ electrode, that wave is corresponding to Ru^{III}/Ru^{IV} oxidation (B), the second wave is reversible ($\Delta E = 60$ mV) and attributable to $Ru^{(IV)}/Ru^{(V)}$ (C). An oxidation peak at 640 mV, the peak current of this peak is nearly twice the peak current of the

Table 1. Cyclic Voltammetric data for $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$

E_{pa} (mV)	E_{pc} (mV)	ΔE (mV)	$E_{1/2}$ (mV)	Assignment	Scan rate mVs^{-1}
−180	−300	120	−240	Ru^{III} / Ru^{II}	50
240	180	60	210	Ru^{III} / Ru^{IV}	
400	340	60	370	Ru^{IV} / Ru^{V}	
640	–	640	–	Ru^{V}/ Ru^{VI} and Ru^{VI}/ Ru^{VII}	

Conditions: supporting electrolyte Britton Robinson buffer pH =12 , the concentration of the complex; ~10^{-3} M $\Delta E = E_{pa}-E_{pc}$ and $E_{1/2} = 0.5\ (E_{pa}+E_{pc})$ where E_{pa} and E_{pc} are the anodic and cathodic cyclic voltammetric peak potentials.

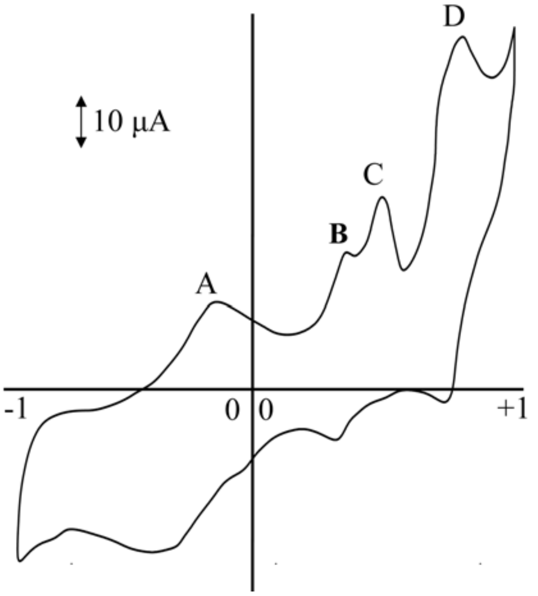

Figure 1. Cyclic voltammorgram of ~1.0 × 10^{-3} M solution of $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ in Britton Robinson buffer pH = 12, at 298 K and of scan rate 50 mVs^{-1}.

first oxidation wave. For this reason this is assigned to oxidation of $Ru^{(V)}$ to $Ru^{(VI)}$ and $Ru^{(VI)}$ to $Ru^{(VII)}$ respectively (D). These results are similar to that reported for the perruthenate anion, $[RuO_4]^-$.[15]

Synthesis of oxoruthenates. We describe here the preparation of four typical oxoruthenates using $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ as a water soluble ruthenium precursor.

The ruthenate anion trans-$[RuO_3(OH)_2]^{2-}$: It has been reported that the *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ reagent can be made from $RuCl_3\cdot nH_2O$ and excess $K_2S_2O_8$ in aqueous molar KOH.[4] The single x-ray crystal structures of *trans*-$K_2[RuO_3(OH)_2]$[16] and of *trans*-$Ba[RuO_3(OH)_2]$[17] showed that these complexes contain the trigonal bipyramidal *trans*-$[RuO_3(OH)_2]^{2-}$ anion, while $Cs_2[RuO_4]$ is tetrahedral.[18] During our attempt for the use of $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ as oxidation catalyst for some alcohols, we found that the *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ reagent can be generated from $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ and excess $K_2S_2O_8$ in molar KOH, our procedure here is similar to that used by Griffith *et al.*[4] Since a number of ruthenium(VI) complexes were made by oxidation of ruthenium(III) complexes using H_2O_2 or peracids,[19] we used H_2O_2 and *m*-chloroperbenzoic acid respectively in place of $K_2S_2O_8$ for *in situ* generation of *trans*-$[RuO_3(OH)_2]^{2-}$ anion. In the latter preparations the solutions obtained were all unstable and show no advantages over the *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ reagent.

The perruthenate anion $[RuO_4]^-$: The tetrahedral $K[RuO_4]$ is normally made from $RuCl_3\cdot nH_2O$ or $RuO_2\ nH_2O$ and excess BrO_3^- in base.[5] We find that $[RuO_4]^-/BrO_3^-$ reagent is rapidly generated by using a low concentration of $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ (11 mg, 1.98 × 10^{-2} mmol) and excess BrO_3^- in molar Na_2CO_3 solution. However, addition of aqueous 0.1 M n-Pr_4NOH to the solution of $[RuO_4]^-/BrO_3^-$ which made originally from $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ resulted in the formation of the well-known $(n\text{-}Pr_4N)^+[RuO_4]^-$, (TPAP) in high yield. This preparation is better than that previously reported,[4,20] in that the direct use of $[RuO_4]$ is avoided

Preparation of $[RuO_4]$: Ruthenium tetraoxide is usually generated *in situ* from either $RuCl_3\cdot nH_2O$ or $RuO_2\cdot nH_2O$ followed by extraction in CCl_4. In a similar method to that used by Connick and Hurley[5] we easily generated $[RuO_4]$ from $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ and excess IO_4^- in H_2O/CCl_4 mixture.

Electronic spectra of oxoruthenates. We report here the electronic spectra of *trans*-$[RuO_3(OH)_2]^{2-}$, $[RuO_4]^-$ and $[RuO_4]$ complexes over the 300-550 nm range. The electronic spectrum for *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ solution gave two bands at 475 nm and 385 nm, clearly showing that the species is *trans*-$[RuO_3(OH)_2]^{2-}$, well known to be an effective oxidant for alcohols, and primary aromatic amines.[4,6] No bands due to $[RuO_4]$ were observed in that solution. The green-yellow solution of perruthenate show bands at 388 and 320 nm attributable to $[RuO_4]^-$, also known to be an effective oxidant for alcohols, activated alkylhalides and nitro compounds.[4] Electronic spectra of both the aqueous and the CCl_4 layers obtained by reaction of

Table 2. Catalytic Oxidiation by oxoruthenates reagents

Substrate	Product	$^{I)}$*trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$		$^{II)}$ $[RuO_4]^-/BrO_3^-$		Product	$^{III)}(n\text{-}Pr_4N)[RuO_4]$/MNO	
		Yield % (TO)	Time (h)	Yield% (TO)	Time (h)		Yield% (TO)	Time (h)
Benzylalcohol	Benzoic acid	95(38)	2	97(98)	2	Benzaldehyde	95(34)	2
Pipronylalcohol	Pipronylic acid	96(38)	2	98(99)	2	Pipronaldehyde	92(32)	2
Benzylamine	Benzonitrile	80(32)	2	–	2	Benzonitrile	70(25)	2
Benzaldehyde	Benzoic acid	93(37)	2	94(94)	2	–	–	–

I = 5.0 × 10^{-5} M of $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$; aqueous 0.1 M $K_2S_2O_8$ and 1 M KOH. II = 1.98 × 10^{-5} M of $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$; aqueous 1 M $NaBrO_3$ and 1 M Na_2CO_3. III = 2.8 × 10^{-5} M of $(n\text{-}Pr_4N)^+[RuO_4]^-$ and 3.0 × 10^{-3} M of *N*-methylmorpholine-*N*-oxide (NMO).

$K_3[Ru(C_2O_4)_3]\cdot 4H_2O$ with excess $NaIO_4$ showed the characteristic peaks of $[RuO_4]$ at 383 nm and 385 nm respectively. Our results are in well agreement with those reported for oxoruthenates.[4,5,6]

Catalytic oxidation. The oxidation of alcohols, aldehydes and amines by *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ and $[RuO_4]^-/BrO_3^-$ reagents have been reported.[4,5] In order to confirm the catalytic activities of *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ and $[RuO_4]^-/BrO_3^-$ reagents made from $K_3[Ru(C_2O_4)_3]\cdot 4H_2O$, we carried out typical experiments on oxidation of benzyl alcohol, piperonyl alcohol, benzaldehyde and benzylamine. We find that benzylalcohol, piperonyl alcohol and benzaldehyde were oxidized to their corresponding acids in 80-98% yields by these reagents. Benzylamine was oxidized to benzonitrile in 97% and 70% yields by *trans*-$[RuO_3(OH)_2]^{2-}/S_2O_8^{2-}$ and $(n\text{-}Pr_4N)^+[RuO_4]^-$, (TPAP)/NMO reagents respectively. The latter reagent oxidizes benzylalcohol, piperonyl alcohol to their corresponding aldehydes in 95% and 92% yields respectively. Benzylamine was not oxidized by $[RuO_4]^-/BrO_3^-$ reagent. Such observation has been reported in a similar oxidation reaction.[6] As with most other oxidation involving ruthenate and perruthenate as catalysts[4] these reagents are self-indicating; yellow-green colour of $[RuO_4]^-$ and the orange colour of *trans*-$[RuO_3(OH)_2]^{2-}$ becoming green or black on adding the mentioned substrates and returning to their original colours when the oxidation reaction is complete.

References

1. Griffith, W. P.; Shoair, A. G. F.; Suriaatmaja, M. *Synth. Commun.* **2001**, *30*(17), 3091.
2. Griffith, W. P.; Shoair, A. G. F.; Morley-Smith, N.; Nogueira, H. I. S.; Suriaatmaja, M.; White, A. J. P.; Williams, D. J. *J. Mol. Catal.* **2000**, *607*, 146.
3. Werle, T.; Maas, G. *Adv. Synth. Catal.* **2001**, *343*, 37.
4. Bailey, A. J.; Griffith, W. P.; Mostafa, S. I.; Sherwoud, P. *Inorg. Chem.* **1993**, *32*, 268.
5. Connick, R. E.; Hurley, C. R. *J. Am. Chem. Soc.* **1952**, *74*, 5012.
6. Griffith, W. P.; Reddy, B.; Shoair, A. G. F.; Suriaatmaja, M.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 2819.
7. Courtney, J. L. In *Organic Synthesis by Oxidation with Metal Complexes*; Mije, W. J., Dejonge, C. R. H. I., Eds.; Plenum: New York, 1986; p 445.
8. Griffith, W. P. *Trans. Met. Chem.* **1990**, *15*, 251.
9. Griffith, W. P.; Ley, S. V.; White, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun.* **1989**, 1625.
10. Griffith, W. P.; Ley, S. V. *Aldrichim Acta* **1990**, *23*, 3.
11. Kaziro, R. T.; Hambley, W.; Binstead, R. A.; Beattie, J. K. *Inorg. Chim. Acta* **1989**, *164*, 85.
12. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; 1986; p 244.
13. El-Hendawy, A. M.; Kubaisi, A. H.; Shoair, A. G. F. *Mont. Fûr Chemie* **1995**, *126*, 1291.
14. El-Hendawy, A. M.; El-Kourashy, A. G.; Shanab, M. M. *Polyhedron* **1992**, *11*, 523.
15. Lam, K. W.; Johnson, K. E.; Lee, D. G. *J. Electrochem. Soc.* **1978**, *125*, 1069.
16. (a) Fischer, D.; Hoppe, R. Z. *Z. Anorg. Chem.* **1991**, *41*, 601. (b) Elout, M. O.; Haije, W. O.; Maaskant, W. J. A. *Inorg. Chem.* **1988**, *27*, 610.
17. Nowogrocki, G.; Abrahams, F.; Trèhonx, J.; Thomas, D. *Acta Crystallogr.* **1976**, *B32*, 2413.
18. Fischer, D.; Hoppe, R. Z. *Z. Anorg. Chem.* **1990**, *87*, 591.
19. Groves, J. T.; Quinn, R. *Inorg. Chem.* **1984**, *23*, 3844.
20. Dengel, A. G.; Griffith, W. P. *Inorg. Chem.* **1991**, *30*, 869.