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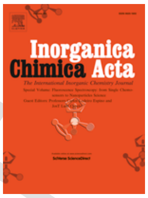

Research paper

Photochemical behavior of the quadruply metal-metal bonded $[Tc_2Cl_8]^{2-}$ anion in acetonitrile

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ABSTRACT

The photochemical behavior of $[Tc_2Cl_8]^{2-}$ was investigated in acetonitrile. The speciation of Tc before and after irradiation at 254 nm was performed by UV–vis spectroscopy. Upon irradiation at 254 nm, $[Tc_2Cl_8]^{2-}$ was unstable, the scission of the Tc≣Tc unit occurred and the complex $[TcCl_4(CH_3CN)_2]$ was identified. The disappearance rate of $[M_2Cl_8]^{2-}$ (M = Tc, Re) under irradiation has been measured and was ~7.5 time faster for Tc than for Re.

1. Introduction

Technetium is the lightest radioelement on the periodic table; it has 34 known isotopes, the most common being ^{99}Tc and ^{99m}Tc which are produced in nuclear reactors from the neutron-induced fission of ^{235}U [1]. During the past 30 years, most studies on Tc have focused on the use of ^{99m}Tc as an imaging agent, leaving substantial gaps in our knowledge of its fundamental chemistry [2,3]. Due to the radioactive nature of Tc and the relatively small number of laboratories equipped to work with this element, the coordination chemistry of Tc has lagged behind that of Re, its heavier non-radioactive congener. One illustrative example is the chemistry of complexes with multiple metal-metal bonds. As of 2015, the number of these complexes for Tc was limited and only 35 dinuclear species had been structurally characterized [4,5]. This contrasts with the chemistry of Re where more than 550 complexes are known [5,6]. In addition to the coordination chemistry, the photochemistry of Tc dinuclear complexes with multiple metal-metal bonds is underdeveloped. Study of the photochemistry of Tc dinuclear complexes can lead to a better understanding of electronic structure and reactivity of metal-metal bonds. Photochemical techniques can also be used in synthetic chemistry for the preparation of new complexes, e.g., it has been shown that the photo-induced cleavage of the Tc_2^{4+} unit ($Tc \equiv Tc$) in $[Tc_2(CH_3CN)_{10}]^{4+}$ in acetonitrile leads to the quantitative production of $[Tc(CH_3CN)_6]^{2+}$, a low spin d^5 octahedral complex [7].

For Re, the photochemistry of $[Re_2Cl_8]^{2-}$ has been extensively studied [8–11]. Photolysis of $[Re_2Cl_8]^{2-}$ at 300–366 nm in acetonitrile leads to the formation of $[ReCl_3(CH_3CN)_3]$ via the photoreactive $[ReCl_4(CH_3CN)_2]^-$ intermediate [8]. The photo reactivity of the dimer is wavelength dependent, and irradiation at 254 nm leads to the formation of $[ReCl_4(CH_3CN)_2]^-$ which is further oxidized to $[ReCl_4(CH_3CN)_2]$ and an unknown product. The photoreactivity of $[Re_2Cl_8]^{2-}$ is also solvent dependent; in CH_2Cl_2 no reaction was observed, while in $CHCl_3$ the Re(IV) dimer $[Re_2Cl_9]^-$ was formed via solvent radical formation [10].

The photochemical behavior of $[Tc_2Cl_8]^{2-}$ is unexplored. One of the questions to explore is whether photo-induced scission of the Tc_2^{6+} unit in $[Tc_2Cl_8]^{2-}$ will occur and whether similar products can be identified as was the case for the Re analogue. In the present work, we investigate the behavior of $[Tc_2Cl_8]^{2-}$ in acetonitrile under irradiation at 254 nm. The speciation of Tc before and after irradiation has been studied by UV–vis spectroscopy.

2. Experimental

Caution! Techetium-99 is a weak beta emitter ($E_{max} = 292$ keV). All manipulations were performed in radiochemistry laboratories designed for chemical synthesis using efficient HEPA-filtered fume

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hoods and following locally approved radioisotope handling and monitoring procedures.

2.1. Starting materials and protocols

The $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ salt was purchased from Sigma-Aldrich and used as received. HPLC grade acetonitrile (Sigma-Aldrich) was dried over activated 3 Å molecular sieves and purged with dry Ar gas for 15 min prior to use. The $(n\text{-Bu}_4\text{N})_2[\text{Tc}_2\text{Cl}_8]$ salt was synthesized according to the method reported in the literature and recrystallized two times from acetone/diethyl ether and two times from CH_2Cl_2/hexane [12]. Technetium tetrachloride was prepared in a glass sealed tube according the method reported in the literature [13]. After the preparation, the glass tube was opened, acetonitrile (2 mL) was introduced in the part of the tube that contained TcCl_4 and the solution turned immediately yellow. The yellow solution was removed from the tube, diluted (~1:10) with acetonitrile and its UV–vis spectra recorded.

Irradiations were conducted with a Spectroline 6 W lamp ($\lambda_{\text{max}} = 254$ nm). Solutions of $(n\text{-Bu}_4\text{N})_2[\text{Tc}_2\text{Cl}_8]$ (0.2 mM, 2 mL) were irradiated at room temperature in 1 cm quartz cells placed at 5 cm (fixed geometry) from the light source. After irradiations, the cells were immediately protected from light and transferred to the UV–vis spectrometer for measurement. The time between the end of an irradiation and the UV–vis measurement was ~90 s. The UV–vis measurements were performed between 200 and 800 nm using acetonitrile as a reference baseline. Measurements were performed in 1 cm matched quartz cells on a Cary 6000i spectrophotometer.

The ESI-MS measurements were performed using a Dionex MSQ plus electrospray ionization with a quadrupole mass filter detector. The solutions were introduced via syringe in a capillary (10 μL) and then diluted in a carrier solvent. In order to avoid secondary reactions of the ions in the instrument, the cone voltage was kept at 5 V with a temperature of 350 °C. This method has already been successfully used for the speciation of other ionic Tc compounds in acetonitrile [14].

3. Results

3.1. Behavior of $[\text{Tc}_2\text{Cl}_8]^{2-}$ in acetonitrile in absence of irradiation

The UV–vis spectrum of $[\text{Tc}_2\text{Cl}_8]^{2-}$ in acetonitrile exhibits bands at 675 nm (1210 $\text{M}^{-1}\,\text{cm}^{-1}$), 388 nm (6580 $\text{M}^{-1}\,\text{cm}^{-1}$) and 301 nm (8200 $\text{M}^{-1}\,\text{cm}^{-1}$). Previous studies have shown that the UV–vis spectrum of $[\text{Tc}_2\text{Cl}_8]^{2-}$ in CH_2Cl_2 exhibits bands at 679 nm (1391 $\text{M}^{-1}\,\text{cm}^{-1}$), 390 nm (8674 $\text{M}^{-1}\,\text{cm}^{-1}$) and 303 nm (10,564 $\text{M}^{-1}\,\text{cm}^{-1}$) that have been attributed to the $\delta \rightarrow \delta^*$, $\pi(\text{Cl}) \rightarrow \delta^*$ and $\pi \rightarrow \pi^*$ transitions, respectively [15,16]. The spectrum of $[\text{Tc}_2\text{Cl}_8]^{2-}$ in acetonitrile is slightly shifted to lower wavelength relative to the one in CH_2Cl_2; a similar solvatochromism has been observed for $[\text{Re}_2\text{Cl}_8]^{2-}$ in these solvents [15,17]. In the quartz cell, the $[\text{Tc}_2\text{Cl}_8]^{2-}$ acetonitrile solutions are stable for up to 1 h in the dark at room temperature.

The ESI-MS spectrum (negative mode) of a solution obtained after the dissolution of $(n\text{-Bu}_4\text{N})_2[\text{Tc}_2\text{Cl}_8]$ in acetonitrile is presented in Fig. 1. Under the experimental conditions, three species with m/z ratios centered at 240, 262 and 281 were observed. The isotopic distributions (Table S1) are consistent with the formulations $[\text{Tc}_2\text{Cl}_8]^{2-}$, $[\text{Tc}_2\text{Cl}_8(\text{CH}_3\text{CN})]^{2-}$ and $[\text{Tc}_2\text{Cl}_8(\text{CH}_3\text{CN})_2]^{2-}$. We hypothesize that acetonitrile coordinates to $[\text{Tc}_2\text{Cl}_8]^{2-}$ during the ionization process in the ESI-MS analysis. Experiments performed in the positive mode show only the presence of $(n\text{-Bu}_4\text{N})^+$ cations.

3.2. Behavior of $\text{Tc}_2\text{Cl}_8{}^{2-}$ in acetonitrile under irradiation at 254 nm

Solutions of $[\text{Tc}_2\text{Cl}_8]^{2-}$ in acetonitrile were irradiated at 254 nm for 10 s, 1, 2, 4 and 10 min. The evolution of the UV–vis spectra in the region 200–800 nm and 500–800 nm as a function of the irradiation time are respectively presented in Fig. 2. Analysis of Fig. 2 shows that the intensity of the $\delta \rightarrow \delta^*$ transition at 675 nm dramatically decreases with the irradiation time, and after 4 min the absorption at 675 nm has disappeared. As the irradiation progresses, a new band grows in at 340 nm, reaching a maximum after 1 min of irradiation. Upon continued irradiation, the band at 340 nm then decreases in intensity simultaneously with an increase in the absorbance at 301 nm. After 10 min of irradiation, the spectrum of the yellow solution exhibits two bands (233 nm and 301 nm) and a shoulder (~400 nm) and is very similar to the one of the species ($[\text{TcCl}_4(\text{CH}_3\text{CN})_2]$) obtained after the dissolution of TcCl_4 in acetonitrile (Fig. 3). A previous study reported that the dissolution of TcCl_4 in acetonitrile lead to $[\text{TcCl}_4(\text{CH}_3\text{CN})_2]$ [18,19].

The UV–vis results unequivocally demonstrate that irradiation of $[\text{Tc}_2\text{Cl}_8]^{2-}$ at 254 nm leads to the cleavage of the Tc≣Tc quadruple bond; the predominant species after 10 min of irradiation being $[\text{TcCl}_4(\text{CH}_3\text{CN})_2]$.

3.3. Behavior of $\text{Re}_2\text{Cl}_8{}^{2-}$ in acetonitrile under irradiation at 254 nm

Irradiations of $[\text{Re}_2\text{Cl}_8]^{2-}$ solutions were performed under the same conditions as those for $[\text{Tc}_2\text{Cl}_8]^{2-}$. Solutions of $[\text{Re}_2\text{Cl}_8]^{2-}$ in acetonitrile were irradiated at 254 nm for 10 s, 1, 2, 4 and 10 min. Similar to previous reports, the irradiation leads to the disappearance of the band at 680 nm which is consistent with scission of the Re≣Re bond [8]. The spectrum after 10 min of irradiation (Fig. 4) is identical to that of $[\text{ReCl}_4(\text{CH}_3\text{CN})_2]$ which also confirm this species to be a terminal photolysis product of $[\text{Re}_2\text{Cl}_8]^{2-}$ [11].

The rate of disappearance of $[\text{Re}_2\text{Cl}_8]^{2-}$ upon irradiation at 254 nm was compared to that of $[\text{Tc}_2\text{Cl}_8]^{2-}$; the fraction of $[\text{M}_2\text{Cl}_8]^{2-}$ (M = Tc, Re) in solution as a function of the irradiation time (Fig. 5) were determined using the absorbances at 675 nm and 680 nm. The initial disappearance rate of $[\text{M}_2\text{Cl}_8]^{2-}$ (calculated for the first 10 s of irradiation) is ~7.5 time faster for Tc ($9.26 \cdot 10^{-3}$ mM.s^{-1}) than for Re

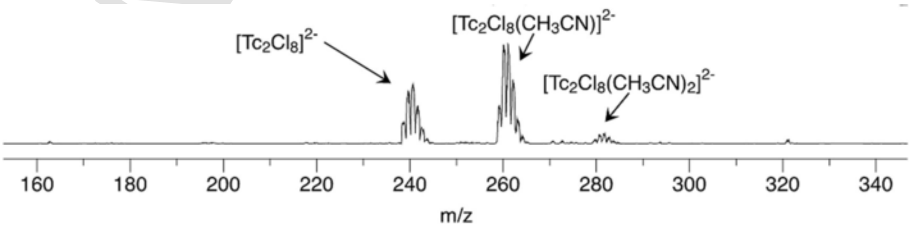

Fig. 1. ESI-mass spectrum (negative mode, 5 V) of the solution obtained after the dissolution of $(n\text{-Bu}_4\text{N})_2[\text{Tc}_2\text{Cl}_8]$ in acetonitrile.

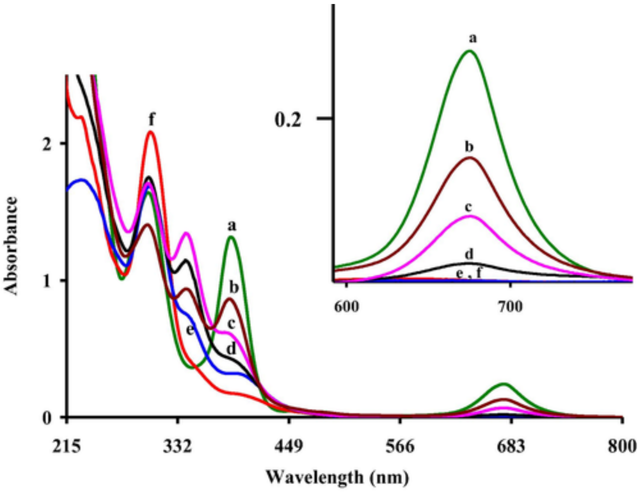

Fig. 2. Evolution of the UV–vis spectrum of a solution of $(n\text{-Bu}_4N)_2[Tc_2Cl_8]$ in acetonitrile as a function of the irradiation time. Irradiation time: a) t = 0, b) t = 10 s, c) t = 60 s, d) t = 120 s, e) t = 240 s and f) t = 600 s.

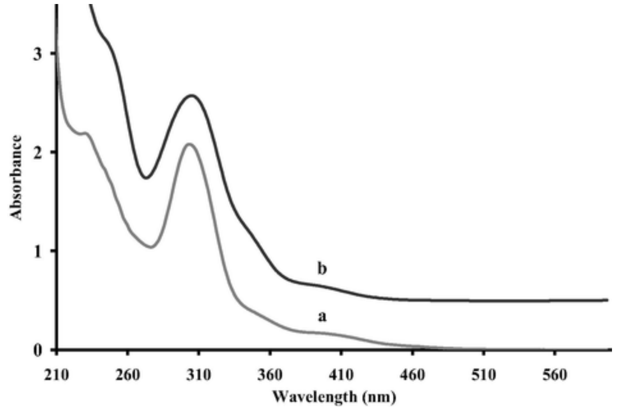

Fig. 3. UV–vis spectra of the solution obtained after: a) irradiation (600 s) of $[Tc_2Cl_8{}^{2-}]$ in acetonitrile and b) dissolution of $TcCl_4$ in acetonitrile.

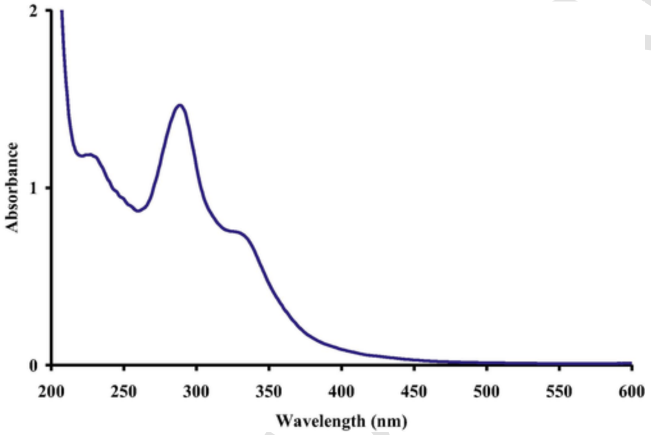

Fig. 4. UV–vis spectra of the solution obtained after the irradiation (600 s) of $[Re_2Cl_8{}^{2-}]$ at 254 nm in acetonitrile.

$(1.28\cdot10^{-3}$ mM.s$^{-1})$; $[Tc_2Cl_8]^{2-}$ to be more photoreactive than $[Re_2Cl_8]^{2-}$.

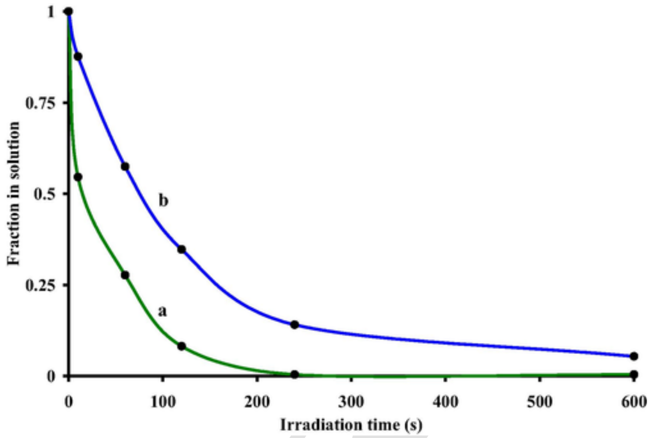

Fig. 5. Evolution of the fraction of a) $[Tc_2Cl_8{}^{2-}]$ and b) $[Re_2Cl_8{}^{2-}]$ a function of the irradiation time (seconds).

4. Discussion

The photochemistry of Re and Mo complexes with quadruple metal-metal bonds have been reviewed [20]. Photoirradiation can lead to either (i) cleavage of the metal-metal bond without change of the oxidation state, or (ii) oxidation with retention of the dinuclear metal core. The mechanism depends on many parameters such as the nature of the solvent, irradiation wavelength and the presence of ligand in solution. As noted above, irradiation of $[Re_2Cl_8]^{2-}$ in acetonitrile leads to the formation of $[ReCl_4(CH_3CN)_2]^-$ and $[ReCl_3(CH_3CN)_3]$, while no reaction is observed in CH_2Cl_2.

In acetonitrile, the speciation of Re during irradiation depends of the wavelength. Irradiation with a laser at 632.8 nm ($\delta \rightarrow \delta^*$) and at 436 nm does not lead to scission of the Re≣Re bond, while irradiation with a Pyrex filtered UV lamp (300–366 nm) leads to the formation of $[ReCl_4(CH_3CN)_2]^-$ and $[ReCl_3(CH_3CN)_3]$. In a preparative scale photolysis, $[ReCl_3(CH_3CN)_3]$ was isolated in a higher yield than $[ReCl_4(CH_3CN)_2]^-$. At 254 nm, the situation is more complicated; irradiation of $[Re_2Cl_8]^{2-}$ produced $[ReCl_4(CH_3CN)_2]^-$ as the primary product. The latter species is photosensitive and undergo a different photoreaction depending on the wavelength, i.e., irradiation with a Pyrex filtered UV lamp produced $[ReCl_3(CH_3CN)_3]$ while irradiation at 254 nm produced $[ReCl_4(CH_3CN)_2]$ and an unidentified side product [11].

The behavior of $[Tc_2Cl_8]^{2-}$ in acetonitrile upon 254 nm irradiation is similar to that of $[Re_2Cl_8]^{2-}$ and cleavage of the Tc≣Tc bond occurs. After irradiation, the UV–vis spectra was consistent with the presence of $[TcCl_4(CH_3CN)_2]$. Similar to $[Re_2Cl_8]^{2-}$, it is possible that the photolysis of $[Tc_2Cl_8]^{2-}$ at 254 nm initially produces $[TcCl_4(CH_3CN)_2]^-$ which undergoes photo-oxidation to $[TcCl_4(CH_3CN)_2]$.

The irradiation wavelength is in the range of the $\pi \rightarrow \pi^*$ transition of $[Tc_2Cl_8]^{2-}$. Previous theoretical calculations have shown that the π bonds are the strongest component of the Tc≣Tc quadruple bond [21]. Irradiation at 254 nm will promote an electron into the π^* orbitals ($\sigma^2\pi^4\delta^2 \rightarrow \sigma^2\pi^3\delta^2\pi^{*1}$), this will result in a significant weakening of the metal-metal bond and ultimately to its cleavage due to interaction with the solvent molecules.

5. Conclusions

In summary, the photophysical behavior of $[Tc_2Cl_8]^{2-}$ in acetonitrile has been studied in the dark and under irradiation at 254 nm. In the absence of irradiation, ESI-MS results are consistent with the presence of $[Tc_2Cl_8]^{2-}$, $[Tc_2Cl_8(CH_3CN)]^{2-}$ and $[Tc_2Cl_8(CH_3CN)_2]^{2-}$. Under continuous irradiation at 254 nm, $[Tc_2Cl_8]^{2-}$ is unstable, and the Tc_2^{6+} unit undergoes a photo-induced scission; the promotion of an electron into the π^* component of the Tc$\equiv$Tc quadruple bond is proposed as the origin of the cleavage of the metal-metal bond. After irradiation, the $[TcCl_4(CH_3CN)_2]$ species was identified by UV–vis spectroscopy.

The behavior of $[M_2Cl_8]^{2-}$ (M = Tc, Re) in acetonitrile under irradiation at 254 nm appears to be similar, as both complexes produced $[MCl_4(CH_3CN)_2]$. Upon irradiation, the disappearance rate of $[M_2Cl_8]^{2-}$ is faster for Tc than for Re. Further experiments in acetonitrile and CH_2Cl_2 at different wavelengths (252 nm, 675 nm and 300 nm) are needed to further probe the photochemistry of $[Tc_2Cl_8]^{2-}$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.09.041.

References

[1] K. Schwochau, Technetium: Chemistry and Radiopharmaceutical Applications, 2000.
[2] R. Alberto, H. Braband, H.W.P. N'Dongo, Curr. Radiopharm. 2 (2009) 254.
[3] A.P. Sattelberger, B.L. Scott, F. Poineau, Technetium organometallics, in: D.M. Mingos, R.H. Crabtree (Eds.), Comprehensive Organometallic Chemistry III, 5 (2007) 833.
[4] A.P. Sattelberger, Technetium, in: F.A. Cotton, C.A. Murillo, R.A. Walton (Eds.), Multiple Bonds between Metal Atoms, 3rd ed., Springer, NY, 2005. Chap. 7.
[5] F. Poineau, A.P. Sattelberger, E. Lu, S.T. Liddle, Group 7 metal–metal bonds, in: S.T. Liddle (Ed.), Molecular Metal–Metal Bonds: Compounds, Synthesis, Properties, first ed., Wiley-VCH Verlag GmbH & Co., 2015, p. 175.
[6] R.A. Walton, Rhenium, in: F.A. Cotton, C.A. Murillo, R.A. Walton (Eds.), Multiple Bonds between Metal Atoms, 3rd ed., Springer, NY, 2005. Chap. 8.
[7] F.A. Cotton, S.C. Haefner, A.P. Sattelberger, J. Am. Chem. Soc. 118 (1996) 5486.
[8] G.L. Geoffroy, H.B. Gray, G.S. Hammond, J. Am. Chem. Soc. 96 (1974) 5565.
[9] M.S. Wrighton, J.L. Graff, J.C. Luong, C.L. Reichel, J.L. Robbins, ACS Symp. Ser. 155 (1981) 85.
[10] M. Matsumura, P.E. Hoggard, Inorg. Chim. Acta 361 (2008) 2553.
[11] G.L. Geoffroy, An Investigation of the Photochemical and Exited State Properties of Selected of Second and Third Row Transition Metal Complexes (Ph.D. dissertation), California Institute of Technology, 1974.
[12] F. Poineau, E.V. Johnstone, K.R. Czerwinski, A.P. Sattelberger, Inorg. Synth. 36 (2014) 110.
[13] E.V. Johnstone, F. Poineau, P.M. Forster, L. Ma, T. Hartmann, A. Cornelius, D. Antonio, A.P. Sattelberger, K.R. Czerwinski, Inorg. Chem. 51 (2012) 8462.
[14] M. Ferrier, P.F. Weck, F. Poineau, E. Kim, A. Stebbins, L. Ma, A.P. Sattelberger, K.R. Czerwinski, Dalton Trans. 41 (2012) 6291.
[15] F. Poineau, A.P. Sattelberger, S.D. Conradson, K.R. Czerwinski, Inorg. Chem. 2008 (1991) 47.
[16] F. Poineau, L. Gagliardi, P.M. Forster, A.P. Sattelberger, K.R. Czerwinski, Dalton Trans. 30 (2009) 5954.
[17] F.A. Cotton, N.F. Curtis, B.F. Johnson, W.R. Robinson, Inorg. Chem. 4 (1965) 326.
[18] A. Hagenbach, E. Yegan, U. Abram, Inorg. Chem. 45 (2006) 7331.
[19] E. Yegan, A. Hagenbach, U. Abram, Chem. Commun. (2005) 5575.
[20] D.G. Nocera, J. Cluster Sci. 5 (1994) 185.
[21] F. Poineau, P.M. Forster, T.K. Todorova, L. Gagliardi, A.P. Sattelberger, K.R. Czerwinski, Dalton Trans. 41 (2012) 2869.