# Osmium(III)o-semiquinonato complexes and their use as catalysts for the oxidation of alcohols

Ahmed M. El-Hendawy

*Chemistry Department, Faculty of Science, Damietta (Egypt)*

## Abstract

The new complexes [Os$^{III}$Cl$_2$(PPh$_3$)$_2$SQ'] (SQ'=$o$-semiquinone; 1,2-benzosemiquinone (SQ), 4-methyl-1,2-benzosemiquinone, 3,5-di(tert-butyl)-1,2-benzosemiquinone, tetrachloro(tetrabromo)-1,2-benzosemiquinone and 2,3-naphthosemiquinone) have been isolated. They were characterised by spectroscopic techniques and investigated by cyclic voltammetry. The complex [OsCl$_2$(PPh$_3$)$_2$SQ] was found to be more efficient than the reported [Os$^{III}$Cl$_2$(PPh$_3$)$_2$acac] as a catalyst for the oxidation of primary alcohols to aldehydes and of secondary alcohols to ketones in the presence of *N*-methylmorpholine-*N*-oxide as co-oxidant.

## Introduction

It is known that the 'non-innocent' ligand catechol may coordinate in three different formal oxidation states; catecholato($-2$), semiquinonato($-1$) and quinonato(0) [1]. The reaction of $o$-quinones with RuCl$_2$(PPh$_3$)$_3$ has been studied and found to give six-coordinate complexes of the type [Ru$^{IV}$Cl$_2$(PPh$_3$)$_2$($o$-diolato)] of magnetic moment near 2.7 BM [2]. Treatment of OsO$_4$ with catechol or substituted catechols Rcat in chloroform yielded the diamagnetic Os$^{VI}$(Rcat)$_3$ species [3]. The complexes *trans*-[OsO$_2$(Rcat)$_2$]$^{2-}$ were also prepared from OsO$_4$ and catechol in alkaline medium, and *trans*-[OsO$_2$(Rcat)py$_2$] from OsO$_4$, pyridine and catechol [3].

We now report the preparation of the new complexes [Os$^{III}$Cl$_2$(PPh$_3$)$_2$SQ'] (SQ'=$o$-semiquinonate of catechol (SQ), 4-methylcatechol (4-MeSQ), 3,5-di(tert-butyl)catechol (DBSQ), tetrachlorocatechol($o$-Cl$_4$SQ), tetrabromocatechol ($o$-Br$_4$SQ) and 2,3-dihydroxynaphthalene (2,3-NaphSQ), starting with [OsCl$_3$(PPh$_3$)$_2$MeOH] [4] and the corresponding catechol. We also report their spectroscopic and electrochemical behaviour and the behaviour of [Os$^{III}$Cl$_2$(PPh$_3$)$_2$SQ] as a catalyst for the oxidation of alcohols in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidant, comparing it with the catalytic oxidation behaviour of [M$^{III}$Cl$_2$(PPh$_3$)$_2$acac]/NMO (M=Ru [5], Os [4]).

## Results and discussion

The complex [OsCl$_3$(PPh$_3$)$_2$MeOH] (I) was reported [4] to be a precursor for the synthesis of [Os$^{III}$Cl$_2$(PPh$_3$)$_2$L] (L=O,O-donor ligand($-1$)). We now find that reaction of I with excess catechol or substituted catechol in refluxing methanol for 1–3 h, gives crystalline products. Analytical data (Table 1) indicate that these new complexes have the formula [OsCl$_2$(PPh$_3$)$_2$SQ'] (SQ'=SQ, 4-MeSQ, DBSQ, $o$-Cl$_4$SQ, $o$-Br$_4$SQ and 2,3-NaphSQ). They are soluble only in CH$_2$Cl$_2$ and their molar conductivities are very low. Refluxing I with 3,5-di(tert-butyl)-1,2-benzoquinone under the conditions used for making [OsCl$_2$(PPh$_3$)$_2$DBSQ], gave the same green product with similar analytical, magnetic and spectroscopic properties. Similar mild conditions have been used in the literature [6] to prepare [Ru$^{II}$(bpy)$_2$DBSQ]$^+$, i.e. stirring a methanol–dichloromethane solution (1:1) of [Ru$^{II}$(bpy)$_2$DBcat] for several hours.

The IR spectra of the complexes [OsCl$_2$(PPh$_3$)$_2$SQ'] showed expected bands for triphenylphosphine and coordinated SQ'. The possibility that the complexes contain coordinated catechols instead of SQ', is unlikely because no bands were observed near 1480 cm$^{-1}$ for $\nu$(C–C) vibrations which are characteristic of catecholato [3, 7], naphthalene-1,2-diolato [8] and other substituted catecholato complexes [9, 10]. No bands were found above 1550 cm$^{-1}$ consistent with the presence of oxygen bonded, reduced $o$-benzoquinone; similar behaviour was noted for Cr($o$-Cl$_4$SQ)$_3$ and M$_2$($o$-Cl$_4$SQ)$_6$ (M=Mo, W)

TABLE 1. Analytical and spectroscopic data for complexes

| Compound | Colour | Analysis: found (calc.) (%) | | IR data, wavenumbers (cm$^{-1}$) | | UV–Vis data, $\lambda_{max}$ (nm) ($\epsilon$(M$^{-1}$ cm$^{-1}$)) |
| --- | --- | --- | --- | --- | --- | --- |
| | | C | H | coordinated $o$-semiquinone bands | $\nu$(Os–C) | |
| OsCl$_2$(PPh$_3$)$_2$SQ | green | 55.8 (56.4) | 3.8 (3.8) | 15455s, 1326s, 1238vs, 1128vs | 324s | 698(6000), 449(1868), 414(2202), 336(6422), 290(15155), 263(33000), 231(48667) |
| OsCl$_2$(PPh$_3$)$_2$(4-MeSQ) | green | 56.7 (56.9) Cl; 7.7(7.8) | 3.9 (4.0) | 1533s, 1239vs | 334s | 707(10357), 450(2422), 331sh(6257), 258(42791), 227(51902) |
| OsCl$_2$(PPh$_3$)$_2$(DBSQ) | green | 59.4 (59.7) Cl; 7.0(7.1) | 4.9 (5.0) | 1537m, 1524sh, 1186vs | 317s | 696(9940), 449(2440), 334(7436), 260(39551), 230(58045) |
| OsCl$_2$(PPh$_3$)$_2$(o-Cl$_4$SQ) | blue | 48.6 (48.8) | 2.8 (2.9) | 1510m, 1240s, 1229vs | 336s 325s | 736(15083), 540(2142), 353(6275), 263(44000), 227(67917) |
| OsCl$_2$(PPh$_3$)$_2$(o-Br$_4$SQ) | blue | 41.5 (41.8) | 2.5 (2.5) | 1276s, 1213vs | 335s | 736(17747), 540(2520), 353(7382), 263(51765), 225(79902) |
| OsCl$_2$(PPh$_3$)$_2$(2,3-NaphSQ) | green | 58.1 (58.5) | 3.8 (3.8) | 1350s, 1123s | 328s | 727(9360), 525(1833), 392(6493), 367(6933), 263(53556), 235(66667) |
| Cr(o-Cl$_4$SQ)$_3$[a] Mo$_2$(o-Cl$_4$SQ)$_6$[a] W$_2$(o-Cl$_4$SQ)$_6$[a] Fe$^{III}$(DBSQ)$_3$[b] | | | | 1440, 1330, 1270, 1245, 1210 1505, 1355, 1200 1530, 1375, 1250 | | 640(4130), 430sh, 378(6170), 300(17000) |

[a]Ref. 11.   [b]Ref. 18.

[11]. Strong bands around 320–335 $cm^{-1}$ were observed, likely due to $\nu$(Os–Cl) vibrations. The bands are shifted to higher wavenumbers in comparison with those of $[Os^{III}Cl_2(PPh_3)_2L]$ (L = O,O-donor ligand(−) [4]. The most important new IR bands are listed in Table 1. The deep colours of the complexes makes them unsuitable for Raman studies.

Magnetic susceptibility measurements for the complexes $[OsCl_2(PPh_3)_2SQ']$ at room temperature showed a magnetic moment, $\mu_{eff}$ near the spin only value of one unpaired electron (1.70–1.85 BM), $S = 1/2$ (see Table 2). However the unpaired electron of Os(III) ion, $S = 1/2$ interacts with that of SQ' ($S = 1/2$) yielding an $S = 0$ ground state and $S = 1$ higher state. A contribution from the higher spin state must therefore be present in our complexes giving rise to a magnetic moment greater than that from the ground state ($S = 0$) and fortuitously near that for one unpaired electron. Lowering the temperature should decrease the $\mu_{eff}$ but unfortunately the equipment necessary to do the experiments was not available. Similar contributions from higher spin states have likewise been suggested for $Fe(o\text{-}Cl_4SQ)_3$, $Fe(9,10\text{-}phenSQ)_3$ [12] and $Mn(DBSQ)_2$ [13] which have $\mu_{eff}$ at room temperature of 3.96, 3.34 and 5.1 BM, respectively. Spin–spin coupling interaction present in those complexes in relation to ours is summarised in Scheme 1.

We were unable to see any credible EPR signals in $CH_2Cl_2$ frozen glasses of the complexes (concentration $5 \times 10^{-3}$ M) at −170 °C as expected from the $S = 0$ ground state, confirming that the $S = 1$ state is not occupied at this temperature.

*Electronic spectra*

The UV–Vis spectra of complexes in $CH_2CL_2$ solution (Table 1) showed similar features in the visible region. The bands above 550 nm have been assigned to ligand $(\pi) \rightarrow$ metal (d) charge transfer, and the peak at about 350 nm has been assigned to metal (d) $\rightarrow$ ligand $(\pi^*)$ charge transfer [14–17]. The ligand $\pi \rightarrow \pi^*$ transitions occur at 270 nm [17].
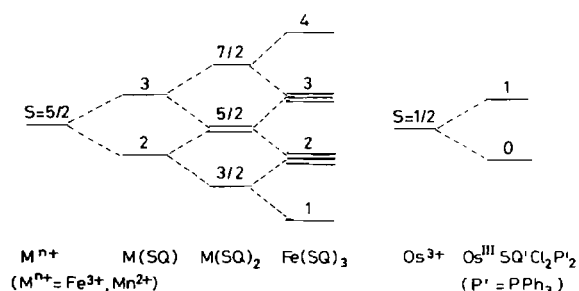


Scheme 1. Spin states arising from coupling of Fe(III) [12], Mn(II) and Os(III) ions to $S = 1/2$ semiquinone ligand.

Similar bands have been observed for $Fe^{III}(DBSQ)_3$ [18] in $CH_2Cl_2$ (Table 1).

*Redox properties*

The electrochemical properties of the complexes were investigated by cyclic voltammetric techniques. Voltammetric half wave potentials versus the Ag electrode for 0.1 M $Bu_4^nNPF_6$–$CH_2Cl_2$ solutions are presented in Table 2. The voltammograms reveal a pair of cathodic and anodic peaks in each case. The peak separation ($\Delta E$) is close to that anticipated for a Nernstian one electron process (59 mV) [19]. The wave at positive potential is due to oxidation and may presumably be assigned to an Os(III)/Os(IV) oxidation similar to those found for osmium(III) complexes, e.g. $[OsCl_2(PPh_3)_2L]$ (L = O,O-donor ligand(−1)) [4], $[OsCl_3(PPh_3)_2(CH_3CN)]$, $[OsCl_3\text{-}(PPh_3)py_2]$ [20] and $[Os^{III}X_2(PPh_3)_2L']$ (X = Cl, Br; HL' = 2-hydroxypyridine, 2-hydroxy-6-methylpyridine and picolinic acid) [21]. The other couple of peaks lies at negative potentials and seems typical to those observed for the Cat'/SQ' couple in the complexes $[Ru^{II}(bpy)_2RCat]$ (RCat = Cat, DBCat, $o\text{-}Cl_4Cat$) [6] (data in Table 2), under conditions similar to those used by us [6]. This couple is shifted to a more or less negative potential according to the nature of the coordinated semiquinonate ligand, i.e. whether it has a strong electron withdrawing ($o\text{-}Cl_4SQ$) or donating (DBSQ) character, respectively. This behaviour was similar to that found for the reduction waves in the complexes $[Cr^{III}(SQ')_3]$ (SQ' = $o\text{-}Cl_4SQ$, 9,10-phenSQ and DBSQ) [22]. In our complexes there is an approximate 0.6 V difference between the reduction waves involving DBSQ and $o\text{-}Cl_4SQ$ ligands, the latter lying at a less negative potential analogous to that of the Cat/SQ couple for the complexes $[Ru(py)_2RCat]$ [6]. So the wave at negative potentials which we have found is likely to be associated with an SQ/Cat reduction. Thus we conclude that the complexes $[OsCl_2(PPh_3)_2SQ']$ are capable of undergoing both reduction and oxidation reactions; the coordinated semiquinone ligand is reduced to catechol while Os(III) is oxidised to Os(IV). This provides electrochemical evidence for the trivalency of osmium and the presence of semiquinone ligand in our complexes.

For $[OsCl_2(PPh_3)_2(o\text{-}Cl_4SQ)]$, a representative example (Fig. 1) compared with that of ferrocene ($E_{1/2} = +0.21$ V, $\Delta E = 50$ mV) [4] under the same conditions, shows a quasi-reversible one electron oxidation wave, $E_{1/2} = +1.08$ V, $\Delta E = 110$ mV and another reduction wave of $E_{1/2} = -0.12$ V, $\Delta E = 90$ mV. For scan rate (SR) between 10–100 mV/s, the ratio $i_p/SR^{1/2}$ ($i_p$ = peak current) was constant and the ratio of the anodic to cathodic peak current is

TABLE 2. Magnetic moments and voltammetric half-wave potentials of the complexes

| Compound | $\mu_{eff}$ (BM) | $E_{1/2}$ (oxidation) Os(III)/IV | $\Delta E$ (V) | $E_{1/2}$ (reduction) SQ/Cat | $\Delta E$ | Scan rate (mV/s) |
|---|---|---|---|---|---|---|
| OsCl$_2$(PPh$_3$)$_2$SQ | 1.73 | +0.48 | 0.060 | −0.71 | 0.060 | 10, 20, 50 |
| OsCl$_2$(PPh$_3$)$_2$(4-MesQ) | 1.82 | +0.48 | 0.080 | −0.70 | 0.080 | 20, 50, 100 |
| OsCl$_2$(PPh$_3$)$_2$(DBSQ) | 1.76 | +0.50 | 0.080 | −0.73 | 0.100 | 10, 20, 50 |
| OsCl$_2$(PPh$_3$)$_2$(o-Cl$_4$SQ) | 1.85 | +1.08 | 0.110 | −0.12 | 0.090 | 20, 50, 100 |
| OsCl$_2$(PPh$_3$)$_2$(o-Br$_4$SQ) | 1.82 | +1.07 | 0.090 | −0.14 | 0.120 | 20, 50, 100 |
| OsCl$_2$(PPh$_3$)$_2$(2,3-NaphSQ) | 1.70 | +0.88 | 0.080 | −0.30 | 0.080 | 10, 20, 50 |
| Ru(bpy)$_2$Cat[a] | | +1.25[b] | | −0.75[c] | | |
| Ru(bpy)$_2$(o-Cl$_4$Cat)[a] | | +1.44[b] | | −0.22[c] | | |

[a]Ref. 6, the potentials are with respect to SCE and ferrocenium/ferrocene couple lies at +0.16 V vs. SCE [23] (CH$_2$Cl$_2$–0.1 M Bu$_4^n$PClO$_4$ solutions). [b]Corresponding to Ru(II)/Ru(III) oxidation. [c]Corresponding to Cat'/SQ' couple.
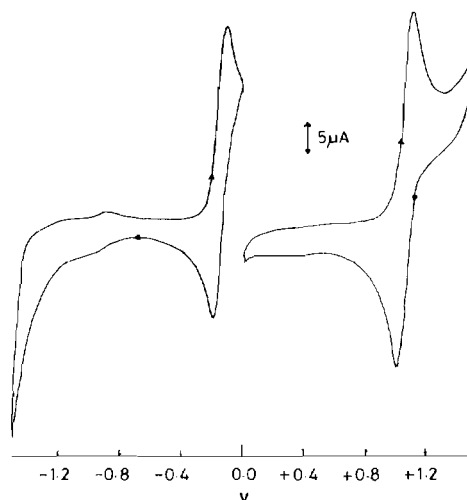


Fig. 1. Cyclic voltammogram of [OsCl$_2$(PPh$_3$)$_2$(o-Cl$_4$SQ)] ($\sim 10^{-3}$ M) in CH$_2$Cl$_2$ with 0.1 M (Bu$_4^n$N)PF$_6$ as supporting electrolyte; scan rate 50 mV/s, V vs. Ag electrode.

one, the peak separation being independent of the scan rate. This indicates that the electron transfer is reversible or approaches reversibility and that the mass transfer is limited.

The relative stabilities of Os(III), Os(IV) and coordinated SQ' or Cat' in the complexes are reflected by the reversibility of these processes:

$$[\text{Os}^{IV}\text{Cl}_2(\text{PPh}_3)_2\text{SQ}']^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$$

$$[\text{Os}^{III}\text{Cl}_2(\text{PPh}_3)_2\text{SQ}'] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\text{Os}^{III}\text{Cl}_2(\text{PPh}_3)_2\text{Cat}']$$
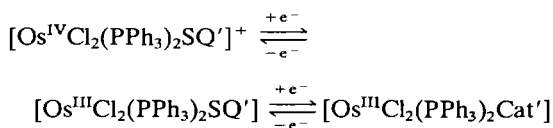
*Catalytic oxidations*

We reported the use of [Os$^{III}$Cl$_2$(PPh$_3$)$_2$acac] (II) [4] in the presence of excess NMO for catalytic oxidation of alcohols and found it is a weak oxidant but the analogous ruthenium complex [RuCl$_2$(PPh$_3$)$_2$acac] (III) was shown to be a good

oxidant for alcohols [5]. In Table 3 we summarise our results for catalytic oxidations by [Os$^{III}$Cl$_2$(PPh$_3$)$_2$SQ] (IV) for alcohols in the presence of NMO as the co-oxidant. The oxidations were carried out at room temperature in dichloromethane solution from which water was removed by using powdered molecular sieves. In no case was there detectable oxidation of an alcohol in the presence of NMO but absence of osmium complex. Primary alcohols were oxidised to aldehydes and secondary alcohols to ketones with both higher yields and turnovers like the oxidations by the ruthenium complex III. In the case of the unsaturated alcohols, e.g. cinnamyl alcohol a low yield of the corresponding aldehyde was obtained, a similar effect was noted for the catalytic oxidant (4-t-But-pyH)$_2$[RuO$_2$Cl$_4$] in presence of larger excess of Et$_4$NCl [24]. Attempts were made to use [Os$^{III}$Cl$_2$(PPh$_3$)$_2$(2,3-NaphSQ)] instead of IV for the oxidation of piperonyl alcohol and the yield of aldehyde was found to be lower than that given by IV (Table 3). It is obvious that a coordinated bulky SQ group decreases the rate of oxidation reaction.

It is of interest to note that the complex [OsCl$_2$(PPh$_3$)$_2$SQ] can act as a real catalyst for such oxidations, since the green solution of the reaction mixture does not change at all during the reaction time. It is clear that complex IV is an efficient catalytic oxidant for alcohols and we believe that a possible reason for this is the ability of the coordinated SQ ligand to be reduced to catechol as suggested by its cyclic voltammetric behaviour, and the catalytic cycle of oxidation is activated by the presence of Os(III) in the complex which is also capable of being oxidised to Os(IV).

**Experimental**

*Preparations of complexes*

All preparations used [OsCl$_3$(PPh$_3$)$_2$MeOH] which was synthesized as reported previously [4].

TABLE 3. Catalytic oxidation of alcohols by [OsCl₂(PPh₃)₂SQ]/NMO

| Alcohol | Product[a] | Time (h) | Yield (%) | Turnover[b] |
|---|---|---|---|---|
| Piperonyl | A | 6 | 96 | 60 |
| | A | 48 | 97 | 75 |
| | A[c] | 48[c] | 91[c] | 60[c] |
| Benzyl | A | 14 | 99 | 100 |
| 4-methoxybenzyl | A | 24 | 98 | 100 |
| 4-Hydroxy-3-methoxybenzyl | A | 5 | 80 | 50 |
| α-tetralol | K | 36 | 90 | 70 |
| Benzohydrol | K | 6 | 89 | 70 |
| Cinnamyl | A | 12 | 10 | 50 |

[a]A = corresponding aldehyde, K = corresponding ketone.  [b]Turnover = moles of product/moles of catalyst.  [c]Oxidation by [OsCl₂(PPh₃)₂(2,3-NaphSQ)]/NMO.

## Preparations of [OsCl₂(PPh₃)₂SQ'] (SQ' = SQ, 4-MeSQ, DBSQ, o-Cl₄SQ, o-Br₄SQ, 2,3-NaphSQ)

To [OsCl₃(PPh₃)₂MeOH] (0.43 g, 0.5 mmol) dissolved in hot methanol (140 cm³) was added catechol (0.083 g, 0.75 mmol). The mixture gave a green solution on reflux, and after 1 h green microcrystals formed which were filtered off, washed with methanol and ether, and dried in vacuo.

Similar procedures were used with 4-methylcatechol, 3,5-di(tert-butyl)-catechol o-tetrachloro-(tetrabromo)-catechol or 2,3-dihydroxynaphthalene replaces catechol.

## Catalytic oxidations by [OsCl₂(PPh₃)₂SQ] (IV)

The oxidation of benzyl alcohol is typical. To benzyl alcohol (1 mmol) was added NMO (3 mmol) in 20 cm³ of CH₂Cl₂ containing powdered 4 A molecular sieves (0.3 g) and 10⁻² mmol of compound IV. The solution was stirred for 24 h during which time the green colour did not change. The mixture was evaporated to dryness and extracted with ether (2×25 cm³). The combined ethereal extracts were filtered and evaporated to give benzaldehyde which was characterised and quantified as its 2,4-dinitrophenylhydrazone derivative.

IR spectra were measured on a Perkin-Elmer FT 1720 instrument as liquid paraffin mulls between CsI plates and as KBr discs. The electronic spectra were measured on a PUB 700 series UV–Vis spectrophotometer or Varian 634 model. Cyclic voltammetric studies were carried out on a potentiostat wave generator (Oxford Electrodes) using a platinum working electrode and silver reference electrode in conjunction with a Philips PM 8043 X-Y recorder. Magnetic measurements were made on a Johnson Matthey magnetic susceptibility balance.

## Acknowledgements

## References

1 C. G. Pierpont and R. M. Buchanan, Coord. Chem. Rev., 38 (1981) 45.
2 A. Y. Girgis, Y. S. Sohn and A. L. Balch, Inorg. Chem., 14 (1975) 2327.
3 A. J. Nielson and W. P. Griffith, J. Chem. Soc., Dalton Trans., (1978) 1501.
4 A. M. El-Hendawy, Polyhedron, 9 (1990) 2309.
5 A. M. El-Hendawy and M. S. El-Shahawy, Polyhedron, 8 (1989) 2813.
6 M. Haga, E. S. Dodsworth and A. B. P. Lever, Inorg. Chem., 25 (1986) 447.
7 W. P. Griffith, C. A. Pumphrey and T. A. Rainey, J. Chem. Soc., Dalton Trans., (1986) 1125.
8 A. M. El-Hendawy, W. P. Griffith, C. A. O'Mahoney and D. J. Williams, Polyhedron, 8 (1989) 519.
9 A. M. El-Hendawy, W. P. Griffith and C. A. Pumphrey, J. Chem. Soc., Dalton Trans., (1988) 1817.
10 A. M. El-Hendawy and W. P. Griffith, Inorg. Chim. Acta, 160 (1989) 67.
11 C. G. Pierpont, H. H. Downs and T. G. Rukavina, J. Am Chem. Soc., 96 (1974) 5573.
12 R. M. Buchanan, S. L. Kessel, H. H. Downs, C. G. Pierpont and D. N. Hendrickson, J. Am. Chem. Soc., (1978) 7894.
13 M. W. Lynch, D. N. Hendrickson, B. J. Fitzgerald and C. G. Pierpont, J. Am. Chem. Soc., (1984) 2041.
14 S. P. Cooper, Y. B. Koh and K. N. Raymond, Inorg. Chem., 104 (1982) 5092.
15 R. B. Von Dreele and R. C. Fay, J. Am. Chem. Soc., 94 (1972) 7935.
16 T. W. Hambley, C. J. Hawkins and T. A. Kabanos, Inorg. Chem., 26 (1987) 3740.
17 C. J. Hawkins and T. A. Kabanos, Inorg. Chem., 28 (1989) 1084.
18 S. E. Jones, L. E. Leon and D. T. Sawyer, Inorg. Chem., 21 (1982) 3692.

228

19 R. Nicholson and I. Shain, *Anal. Chem., 36* (1964) 706.

20 D. J. Salmon and R. A. Walton, *Inorg. Chem., 17* (1978) 2379.

21 J. E. Armstrong and R. A. Walton, *Inorg. Chem., 22* (1983) 1545.

22 H. H. Downs, R. M. Buchanan and C. G. Pierpont, *Inorg. Chem., 18* (1979) 1736.

23 R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem., 19* (1980) 2854.

24 A. C. Dengel, W. P. Griffith, A. M. El-Hendawy and J. M. Jolliffe, *Polyhedron, 9* (1990) 1751.