Accepted Manuscript

Research paper

Oxidation studies on mustard gas, and the first crystal structure of a metal-mustard gas complex

Nimal Rajapakse, Shahram Mehraban, Andrew Pacheco, Brian O. Patrick, Brian R. James

PII:	S0020-1693(18)30485-7
DOI:	https://doi.org/10.1016/j.ica.2018.05.012
Reference:	ICA 18263

To appear in: Inorganica Chimica Acta

Received Date:31 March 2018Revised Date:8 May 2018Accepted Date:12 May 2018



Please cite this article as: N. Rajapakse, S. Mehraban, A. Pacheco, B.O. Patrick, B.R. James, Oxidation studies on mustard gas, and the first crystal structure of a metal-mustard gas complex, *Inorganica Chimica Acta* (2018), doi: https://doi.org/10.1016/j.ica.2018.05.012

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Oxidation studies on mustard gas, and the first crystal structure of a metal-mustard gas complex

Nimal Rajapakse, Shahram Mehraban, Andrew Pacheco, Brian O. Patrick, Brian R. James*

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

ABSTRACT

Attempts to selectively oxidize mustard gas [(ClCH₂CH₂)₂S, abbreviated as BCES] to the nontoxic sulfoxide using a *trans*-Ru(TMP)(O)₂/O₂ catalyst (TMP = porphyrin dianion of 5,10,15,20tetramesitylporphyrin) have led to isolation and characterization, including an X-ray structure, of *trans*-Ru(TMP)(BCES)₂, the first such report of a metal-mustard gas complex.

Keywords: Mustard Gas; Ruthenium porphyrins; Oxidations; X-ray structure

1. Introduction

About 30 years ago, reports from our group [1,2] presented studies on the catalyzed O₂oxidation of thioethers to the sulfoxide, an industrial important process [3]. Ru^{II}-porphyrins were used as catalysts, and two very different mechanistic pathways were established depending on the porphyrin used, specifically OEP and TMP (the respective dianions of 2,3,7,8,12,13,17,18octaethylporphyrin, and 5,10,15,20-tetramesitylporphyrin) [1,2,4,5]. The mechanism using the bis(thioether) species, $Ru(OEP)(R_2S)_2$ [6], involves a suggested initial 1e, 'outer-sphere' activation of O₂, with formation of Ru^{III} and superoxide that with acid (either added or present as impurity H₂O) forms the HO₂ radical that disproportionates into H₂O₂ and O₂; the H₂O₂ oxidizes the thioether to sulfoxide and the co-product H₂O then reduces the Ru^{III} back to Ru^{II} with coproduction of the sulfoxide and the regeneration of the H^+ co-catalyst [1,2]. The use of TMP (or OCP, the 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin dianion – see Fig.1) allowed for more 'sterically hindered' species, including formation (using O₂) of the corresponding *trans*-dioxo species Ru^{VI}(porp)(O)₂ [4,5] rather than the relatively inert, catalytically inactive, Ru^{IV}-O-Ru^{IV} species readily generated from OEP species [2]. These dioxo species are unique in being able to transfer catalytically both oxo ligands as O-atoms to organic substrates, including some thioethers [4]; such oxygenations have been well reviewed [7].

^{*}Corresponding author. Tel.: +1 604 822 6645; fax: +1 604 822 2847.

E-mail address: brj@chem.ubc.ca (B.R. James).

During our studies on the oxidation of thioethers to sulfoxides [1,2,4], we were contacted by the Canadian Department of Defence, and received contract grants to investigate whether such chemistry was applicable to 'Mustard Gas' [bis(β -chloroethyl) sulfide, abbreviated as BCES]; this is a treacle-like liquid, whose vapour is toxic. The key factor is that the sulfoxide (ClCH₂CH₂)₂SO is crystalline and as such is essentially non-toxic, while further oxidation generates the vesicant toxic sulphone [8]. Our studies ended in 1993, and reviews and new studies on reactivity of BCES, the simulant 2-chloroethyl(ethyl)sulfide (CEES), and other models, continue to appear [9,10]; metal-organic framework systems are becoming increasingly involved [10a,b], and include studies on catalyzed selective oxidations to the sulfoxides [10b].



Fig.1. Ru(porp)L₂ species

2. Experimental

2.1. General

Our paper here describes attempted oxidations of BCES and CEES using the $Ru^{VI}(porp)(O)_2$ species, and includes the first X-ray structure of a transition metal coordination compound with BCES, namely Ru(TMP)(BCES)₂; this structure has been mentioned, but only in a short sentence within two reviews [7a,7c]. As well as the originality of our structure, the crystal data could be of value in MOF work. The general types of Ru-species discussed are shown in Fig.1, where L = oxo, thioether, or sulfoxide; for TMP, X = Y = Me, and for OCP, X = CI, Y = H.

The thioethers Et_2S and CEES, thiodiglycol, $SOCl_2$, acetone, acetonitrile, and other common chemicals (all Aldrich products), and the deuterated solvents acetone- d_6 and C_6D_6 (from MSD Isotopes), were used as received. The Ru source was obtained on loan from Johnson, Matthey Ltd. as RuCl₃•3H₂O (~40% Ru), and the H₂(TMP) and H₂(OCP) porphyrins were kindly provided by D. Dolphin of this department.

¹H and ¹³C{H} NMR spectra were measured on a Varian XL-300 or a Bruker AC200F spectrometer, with residual solvent peaks being used as internal standards.

2.2. BCES (Mustard Gas)

Small amounts of BCES (~1-2 mL) were prepared as needed, by updating an early procedure [11], and handled with extreme care in a fume-hood. The 2-stage synthesis is shown in Eq. (1);

thiodiglycol (2 mL, 2 x 10^{-2} mol) was stirred with SOCl₂ (3 mL, 4 x 10^{-2} mol) at r.t. (room temperature, ~20°C) for ~15 min., the completion of reaction being checked by ¹H NMR. The

$$S[CH_2)_2OH]_2 + 2 SOCI_2 \xrightarrow{-2 HCI} S[CH_2)_2OS(O)CI]_2 \xrightarrow{-SO_2} S[(CH_2)_2CI]_2$$
(1)

crude product mixture was then placed under vacuum for 15 min to remove gaseous by-products and any remaining SOCl₂; a GC trace in CH₂Cl₂, showed no impurities in the resulting oily BCES. ¹H NMR data in C₆D₆, and in (CD₃)₂CO, are given in Table 1; ¹³C{¹H} (C₆D₆): δ 34.4 (*C*-Cl), 43.0 (*C*-S). All glass-wear contaminated with BCES was soaked in a bleach solution (2.5% NaOCl) for at least 24 h before washing; the gloves used were soaked overnight in bleach and then discarded.

2.3. Sulfoxides and sulfones

BCESO and CEESO. H_2O_2 (5 mL of 30% aq.) was stirred with BCES (1 mL) in acetone (10 mL) at r.t. for 20 min; on removal of the acetone under reduced pressure, BCESO precipitated as a white crystalline solid (~ 0.7 g, ~ 40% yield; m.pt. 110-111°C). ¹H NMR data are given in Table 1; ¹³C(¹H} (C₆D₆): δ 36.8 (*C*-Cl), 54.5 (*C*-S). CEESO was made the same way using CEES (1 mL), the product being a liquid at r.t. ¹H NMR data are given in Table 1; ¹³C(¹H} (C₆D₆): 43.2 (Cl-C), 33.9 (Cl-C-C), 26.1 (*C*-CH₃), 14.8 (*C*H₃).

BCESO₂ and CEESO₂. BCES was added to 1.0 mL of acetone- d_6 to a concentration of about 5 x 10⁻² M), in a 2 mL screw-cap vial, and an ozone/dioxygen mixture (~2-3 % in O₃) from a ozonator (Welsbach Model T-23) was bubbled through the solution at 0.57 L min⁻¹, using a disposable, 15 cm pasture capillary pipette (attached to the outlet tube of the ozonator); the pipette was inserted to reach the bottom of the vial to maintain a constant flow. The compositions of the resultant mixtures (sulfide, sulfoxide, and sulfone) were readily determined by a sampling technique using the ratio of integration intensities of ¹H NMR signals; the same procedure was used for O₃-oxidation of CEES. The ¹H NMR data for both sulfones are given in Table 1. Further kinetic details on the ozone oxidation of BCES and CEES, as well as dibenzyl-and methyl-*p*-tolyl sulfides, are available [12].

2.4. Ruthenium complexes

The crystallographically characterized $Ru(TMP)(MeCN)_2$ was made as reported by photolysis of Ru(TMP)CO in MeCN [4b]; heating the MeCN species under vacuum generates the 4coordinate Ru(TMP) that under O₂ then forms the isolable $Ru(TMP)(O)_2$ [4a,5b,13]. Various

Ru(TMP)L₂ species were readily made *in situ* by addition of excess L (thioethers and their respective sulfoxides) to the bis-MeCN precursor at NMR concentrations (~10⁻² M) in C₆D₆ under either N₂. ¹H NMR data for the *in situ* species are given in Table 2; assignments for the Ru(TMP)L₂ species, where L = thioether, or S- and O-bonded sulfoxide (written as S- and O-), are based on those established for the L = Et₂S, ^{*n*}Bu₂S, (decylmethyl)₂S, and Ph₂S systems [2,4]. A small amount (~10 mg) of Ru(TMP)(CEESO)₂ (Table 2) was also isolated on one occasion by treatment of Ru(TMP)(MeCN)₂ with excess CEESO in C₆H₆ solution, followed by column chromatography to remove excess sulfoxide. Calc.(found) : C, 66.08(66.2); H, 6.06 (6.1); N, 4.82 (4.7); S, 5.51 (5.5).

Crystals of Ru(TMP)(BCES)₂ were grown by slow diffusion of CH₂Cl₂, layered on the C_6H_6 solution of the *in situ* species that, like the CEES analogue, was stable toward O₂.

2.5. Reactions of BCES and CEES with Ru(porp)(O)₂ species

To a C_6D_6 solution of Ru(TMP)(O)₂ (3 x 10⁻³ M) under 1 atm O₂ at r.t. was added excess CEES or BCES (~5 x 10⁻² M), and changes were monitored by ¹H NMR; the solutions were sometimes heated to 35°C. The corresponding reactions were carried out using Ru(OCP)(O)₂. The ¹H NMR data for Ru(OCP)L₂ species (L = BECSO, CEESO), listed in Table 3, were similarly recorded from reactions of the thioethers with Ru(OCP)(O)₂ (see Results and discussion).

2.6. X-Ray Crystallographic analysis

The crystallographic data for Ru(TMP)(BCES)₂ were collected at r.t. on a Rigaku AFC6S diffractometer with graphite monochromated Cu-K α radiation. The intensities of the standard reflections, taken every 400 reflections, remained constant, and thus no decay correction was applied. The structure was solved by conventional heavy atom methods [14] and expanded using Fourier techniques [15]. Refinements were carried out using teXsan [16]. All non-H-atoms were refined anisotropically, while all H-atoms were fixed in calculated positions with C–H = 0.98 Å. The material crystallizes with two crystallographically independent half-molecules in the asymmetric unit, with each Ru-atom residing on a different inversion center. Additionally, the material crystallized as a 1:1 solvate with CH₂Cl₂. Further details of the structure analysis are given in a supplementary attachment (SI-1), while all the crystallographic data are available free of charge as the CCDC number 1585855 from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

BCES (Mustard) was synthesized in small amounts by the reaction shown in Eq.(1), and is of high purity based on ¹H and ¹³C{¹H} NMR data. Only one previous publication in 1988 has reported ¹H data, the δ values being given as 3.68 (Cl-CH₂) and 2.92 (CH₂-S) for the neat compound in the absence of solvent [17]: the multiplicities were not noted but our triplets measured in acetone- d_6 (Table 1) are in excellent agreement and, as expected, are significantly downfield (~2.5 ppm) from the CH₃ triplet of Et₂S (Table 1). Our measured two ¹³C{¹H} signals in acetone- d_6 (δ 34.4 and 43.0) are within 2 ppm of those reported for neat BCES [17], and for BCES in DMSO solution [8b]. NMR data are readily available for the simulant CEES (e.g. in CDCl₃ [8a] and in CD₃OD [9]), and our ¹H data in C₆D₆ and in acetone- d_6 solution (Table 1) are comparable; the ClCH₂ triplet of CEES is again similarly downfield from the CH₃ triplet of Et₂S.

The exciting finding, an accidental one, was isolation of crystals of $Ru(TMP)(BCES)_2$, whose structure is illustrated in Fig.2. The structure is the first to show binding of BCES to a transition



Fig. 2. Structure diagram of Ru(TMP)(BCES)₂, one centrosymmetric molecule of two in the asymmetric unit. Selected bond lengths and angles. Bond lengths (Å): Ru1–S1, 2.374(1); Ru1–N1, 2.040(3); Ru1–N2, 2.057(3); S1–C29, 1.794(5); S1–C31, 1.807(5); C11–C30, 1.783(7); C29–C30, 1.512(8); C31–C32, 1.467(8); N1–C4, 1.375(4); C4–C5, 1.406(5); C3–C4, 1.439(5); C2–C3, 1.350(5); C5–C11, 1.502(5); C11–C12, 1.398(5); C12–C17, 1.511(7). Bond angles (°): S1–Ru1–N1, 94.47(9); S1–Ru1–N2, 89.86(9); N1–Ru1–N2, 89.8(1); Ru1–S1–C29, 108.9(2); Ru1–S1–C31, 107.3(2); C29–S21–C31, 101.1(3); Ru1–N1–C1, 126.6(2); C1–N1–C4, 106.6; N1–C1–C2, 109.5; N1–C1–C10', 125.7(3); C2–C1–C10', 124.8(3); C1–C2–C3, 107.2(4); N1–C4–C3, 109.2(3); N1–C4–C5, 125.8(3); C3–C4–C5, 125.0(3); C4–C5–C11, 116.6(3); C5–C11–C12, 121.1(4); C11–C12–C13, 119.8(4).

metal; selected bond lengths and angles are given in the figure legend. No other Ru(TMP)(thioether)₂ crystal structure has been reported, structures containing Ru(TMP) being limited to species with the axial ligands (MeCN)₂ [4b], (OCHMe₂)₂ [18], and (THF)(N₂) [13]. Averaged bond lengths and angles for the Ru(TMP) moiety within all these complexes show no unusual features, with the Ru being in an essentially non-distorted porphyrin plane. The geometry details are similar to those established for other Ru(porp) species with two axial S-bonded ligands [2,19,20]: the Ru is again in an non-distorted porphyrin plane, and the S–Ru–S axes are within 5° of orthogonality to this plane. The Ru–S bond lengths within the BCES ligands are 2.374 Å, and are essentially the same as those found for the axial thioether ligands in the Ru(OEP)L₂ complexes (L = DecMS and Ph₂S), where it was noted that this distance is exactly the sum of the covalent radii for Ru and S [2]. Axial Ru–S bond lengths in porphyrin complexes appear to vary little with substituents on the S-atom (e.g. even within the S-bonded sulfoxide Ru(OEP)(Et₂SO), Ru–S is 2.319 Å) [19], and even with oxidation state of the Ru (e.g. in [Ru(OEP)(decMS)₂][BF₄], where Ru–S is 2.337 Å [20].

The synthetic oxidations of BCES and CEES to the respective sulfoxides were carried at using aqueous H_2O_2 at r.t., the use of H_2O_2 in acetic acid being noted 100 years ago [21]. Oxidations using O_3 in acetone- d_6 generated the sulfones *in situ*, a well-established process [22]. The sulfoxides and sulfones are readily identified by ¹H NMR data shown in Table 1 together with corresponding data for the Et₂S species [4a,4b]. The data for the sulfoxides sometimes reveal the magnetic inequivalence of the CH₂ protons, first described for Et₂SO [23].

The white crystalline BCESO on storage at r.t. in an N_2 glove-box turned (over ~3 months) into a liquid that contained BCES as the major product (¹H NMR data); a minor component was not identified, but was not the sulfone. When stored in air, BCESO again decomposed to mainly BCES but much slower than the N₂-stored sulfoxide; a similar decomposition to non-specified products has been noted previously [24], and a BCESO sample heated under vacuum has been reported to contain BCES and BCESO, but again no sulfone [25]. To the best of our knowledge, such observations on CEESO, a colourless liquid, have not been reported.

Catalytic O₂-oxidations of alkyl and aryl thioethers (without Cl substituents) to the sulfoxides by O-atom transfer from Ru(porp)(O)₂ species are well documented; also well-known are the methodologies for synthesizing the sulfoxides (R₂SO) and sulfones (R₂SO₂), and the respective Ru(porp)L₂ complexes where L is the O- or S-bonded sulfoxide or sulfone [4,7]. Kinetic and spectroscopic studies have established the mechanism of Scheme 1 for the stoichiometric oxidation (under N₂) of thioethers by the dioxo species (1) to products of types 2, 3 and 4 [4]. In the presence of excess R₂S under O₂, catalysis occurs via reaction of 2 with O₂ (at 1 atm), this

$$\underbrace{\frac{\mathrm{Ru}(\mathrm{O})_2}{\mathrm{K_1}}}_{1} \xrightarrow{\mathrm{Ru}(\mathrm{O})(\mathrm{OSR}_2)} \underbrace{\frac{\mathrm{SR}_2}{\mathrm{fast}}}_{2} \xrightarrow{\mathrm{Ru}(\mathrm{OSR}_2)_2} \underbrace{\frac{k_2}{\mathrm{K_2}}}_{2} \xrightarrow{\mathrm{Ru}(\mathrm{OSR}_2)(\mathrm{OSR}_2)} \underbrace{\frac{k_3}{\mathrm{K_3}}}_{4} \operatorname{Ru}(\mathrm{OSR}_2)_2$$

Scheme 1. <u>Ru</u> = Ru(TMP) (**1a**) or Ru(OCP) (**1b**); R₂ = Et₂, ^{*n*}Bu₂, Me(^{*n*}decyl); k_1 is a measured 2^{*n*d}-order rate constant; k_2 , k_3 are non-measured 1^{*s*t}-order rate constants; *O* means oxygen-bonded, and *S* is sulfur-bonded [4,6].

regenerating **1** and free sulfoxide that was present in **2** as labile, oxygen-bonded ligands; however, the total turn-overs (t.o.) are limited. For example, with $Ru(TMP)(O)_2$, Et₂S and 1 atm O_2 at 20 °C, the t.o. for formation of Et₂SO is ~5 after 20 min, but at this stage the substitution-inert, S-bonded species **4** is present; at 65 °C, a higher t.o. of ~15 is observed, but the porphyrin ligand within $Ru(TMP)(O)_2$ undergoes degradation [4]. The corresponding OCP system provides effective catalysis, but again the porphyrin dianion slowly degrades [4b].

The Ru(porp)(O)₂ systems were tested as catalysts with CEES and BCES as substrates, using conditions (in C₆D₆ solution at r.t. under 1 atm O₂) similar to those used for the Et₂S systems [4a], the reactions being monitored by¹H NMR. For CEES with 1a, after 24 h only Ru(TMP)(CEESO)₂ (type 2) and Ru(TMP)(CEESO)(CEESO) (type 3) in a 2:1 ratio were seen, with 2 (also isolated) isomerizing slowly to 3, and after 3 weeks >95% 3 was present. Heating to 35 °C for a further week revealed further increase in 3, while type 4, the bis(S-bonded sulfoxide) made *in situ* independently from Ru(TMP)(MeCN)₂, was never detected (Table 2); about one equiv. of free CEESO (based on [Ru]) was also observed at this stage. The thioether complex Ru(TMP)(CEES)₂ (Table 2), similarly made *in situ*, was unreactive toward 1 atm O₂ at r.t. over 3 weeks; addition of benzoic acid to this system also did not produce detectable amounts of CEESO, implying no reactivity via the 'outer sphere' mechanism evident in the corresponding Et₂S system (see Introduction).

The reaction of BCES with **1a** was also studied. After ~50 h at r.t., NMR data revealed a composition mixture of 25% **1a**, 35% **2**, and 40% **3**; after ~4 days, **1a** was no longer present and **2** and **3** were seen in a 2:3 ratio, the isomerization of **2** to **3** then continuing slowly to a 3:5 ratio over 20 days. As in the CEES system, Ru(TMP)(BCES)₂ and Ru(TMP)(BCESO)₂ species (Table 2) were not observed, as proven by their *in situ* syntheses from Ru(TMP)(MeCN)₂. Ru(TMP)(BCES)₂ was also unreactive toward 1 atm O₂.

Addition of BCESO to a C_6D_6 solution of $Ru(TMP)(BCES)_2$ did establish the equilibria shown in Eqs. (2) and (3), with ¹H NMR integration intensities allowing for calculation of K₂ as 0.34 (at 20 °C). This equilibrium is readily shifted in either direction by changing the [BCES]/[BCESO] ratio; K₁ is too large (> 10) to calculate a more precise value.

$$Ru(TMP)(BCES)_{2} + BCESO \stackrel{K_{1}}{\longleftarrow} Ru(TMP)(BCES)(BCESO) + BCES$$
(2)
$$Ru(TMP)(BCES)(BCESO) + BCESO \stackrel{K_{2}}{\longleftarrow} Ru(TMP)(BCESO)_{2} + BCES$$
(3)

The Ru(OCP)(O)₂ complex (**1b** in Scheme 1) also reacts with CEES and BECS, but under the same r.t. conditions used for **1a**, only the bis(*O*-bonded-sulfoxide) complexes (type **2**) were detected after 3h (Table 3). The only change on heating the CEES reaction to 50 °C for 48 h was formation of a trace amount of free CEESO. With the BCES system, **1b** was completely consumed after ~12 h at r.t., and no further changes were observed after heating to 50 °C. The presence of chlorine in BCES and CEES clearly decreases the nucleophilicity of the S-atom to the extent that no O-atom transfer occurs from the *trans*-Ru-dioxo species to these thioethers.

Acknowledgements

We thank the Natural Sciences and Engineering Council of Canada for funding, and the Department of National Defence, Canada, for a contract grant (W7702-9-R152/01-XSG) in 1990-1992; the manuscript is the responsibility of the authors and does not reflect an official position of the Department of National Defence. We also thank Johnson, Matthey Ltd for the loan of RuCl₃•3H₂O.

Appendix A. Supplementary material

SI-1 presents an X-ray Structure Report for *trans*-Ru(TMP)(BECS)₂, and all the crystallographic data are available free of charge as the CCDC number 1585855 from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>. Supplementary data associated with this article can be found, in the online version, at http:...

References

- [1] B.R. James, A Pacheco, S.J. Rettig, I.S. Thorburn, R.G. Ball, J.A. Ibers, J. Mol. Catal. 41(1987) 147.
- [2] B.R. James, A. Pacheco, S.J. Rettig, J.A. Ibers, Inorg. Chem. 27 (1988) 2414.
- [3] (a) F. Liu, Z. Fu, Y. Liu, C. Lu, Y. Wu, F. Xie, Z. Ye, X. Zhou, D. Yin, Ind. Eng. Chem. Res. 49 (2010) 2533;
 (b) D.P. Riley, M.R. Smith, P.E. Correa, J. Am. Chem. Soc. 110 (1988) 177;
 - (c) L. Roecker, J.C. Dobson, W.J. Vining, T.J. Meyer, Inorg. Chem. 26 (1987) 779.
- [4] (a) N. Rajapaske, B.R. James, D. Dolphin, Catal. Lett. 2 (1989) 219;
 (b) N, Rajapaske, B.R. James, D. Dolphin, Stud. Surf. Sci.Catal. 55 (1990) 109, and refs.

therein;

(c) B.R.James, Chem. Ind. 47 (1992) 245.

- [5] (a) J.T. Groves, R. Quinn, Inorg. Chem. 23 (1984) 3844;
 (b) J.T. Groves, R. Quinn, J.Am.Chem.Soc. 107 (1985) 5790;
 (c) M.J. Camenzind, B.R. James, D. Dolphin, J. Chem. Soc. Chem. Commun. 1137 (1986).
- [6] All Ru(porp)L₂ complexes in this paper, where porp is a porphyrin dianion, and L is any ligand, are trans species.
- [7] (a) T. Mlodnicka, B.R. James. Oxidations Catalyzed by Ruthenium Porphyrins. In Metalloporphyrin-Catalyzed Oxidations, E. Montanari, L. Casella (Eds.) Kluwer, Dordrecht, 121(1994).
 - (b) J.T. Groves, K. Shalyaev, J. Lee. *In* The Porphyrin Handbook, K.M. Kadish, K.M. Smith and R. Guilard (eds.), Academic Press, Sn Diego, CA, 2000, Vol.4, Ch.26;
 - (c) M.B. Ezhova, B.R. James. Catalytic Oxidations using Ruthenium Porphyrins. *In* Catalyzed O₂-Oxidations. L.Simandi (ed.), 1-77, Kluwer, Dordrecht, 1 (2003).
- [8] (a) Y-C.Yang, L.L. Szafraniec, W.T. Beaudry, F.A. Davis, J. Org. Chem. 55 (1990) 3664;
 (b) F.L. Hsu, L.L. Szafraniec, W.T.Beaudry, Y.C. Yang, J. Org. Chem. 55 (1990) 4153;
 (c) E.E. Reid, ed. Organic Chemistry of Bivalent Sulfur, Vol 2, Chemical Pub. Co., New York, 1960, Ch.5.
- [9] Q-Q. Wang, R.A. Begum, V.W. Day, K. Bowman-James, Org. Biomol. Chem. 10 (2012) 8786, and refs. therein.
- [10] (a) C. Montoro, F. Linares, E. Quartapelle Procopio, I. Senkovska, S. Kaskel, S. Galli, N. Masciocchi, E. Barea, J.A.R. Navarro, J. Am. Chem. Soc. 133 (2011) 11888;
 (b) Y. Liu, C.T. Buru, A.J. Howarth, J.J. Mahle, J.H. Buchanan, J.B. DeCoste, J.T. Hupp, O.K. Farha, J. Materials Chem. A, 4 (2016) 13809, and refs. therein;
 (c) S. Popiel, J. Nawala, D. Dziedzic, D. Gordon, B. Dawidziuk, Int. J. Chem. Kinet. 50 (2018) 75-89, and refs. therein.
- [11] W. Steinkopf, J. Herold, J.Stohr, Ber. 53 (1920) 1007.
- [12] S. Mehraban, B.Sc. thesis, University of British Columbia, Canada, 1992.
- [13] M.J. Camenzind, B.R. James, D.Dolphin, J.W. Sparany, J.A. Ibers, Inorg. Chem. 27 (1988) 3054.
- [14] <u>PHASE</u> (Patterson Heavy Atom Solution Extractor). J.C. Calbrese, Univ. of Wisconsin-Madison, Ph.D. Thesis (1972).
- [15] <u>DIRDIF</u> (Direct Methods for Difference Structures). P.T. Beurskens, Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.
- [16] teXsan TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985).
- [17] Y-C.Yang, L.L. Szafraniec, W.T. Beaudry, J.R. Ward, J. Org. Chem. 53 (1988) 3293.
- [18] S.Y.S. Cheng, N. Rajapaske, S.J. Rettig, B.R.James, J. Chem. Soc. Chem. Commun. 2669 (1994).
- [19] A. Pacheco, B.R. James, S.J. Rettig, Inorg.Chem. 38 (1999) 5579.
- [20] A. Pacheco, B.R. James, S.J. Rettig, Inorg.Chem. 34 (1995) 3477.
- [21] P. Spica, Gaz.Chim.Ital., 49(II) (1919) 299.
- [22] P.S. Bailey, A-I.Y. Khashab, J. Org. Chem. 43 (1978) 675, and refs. therein.
- [23] (a) E. Bullock, E.E. Burnell, B. Gregory, Chem. Commun.193 (1967);
 (b) W. Kitching, C. J. Moore, D. Doddrell, Aust. J. Chem. 22 (1969) 1149.

- [24] E.E. Reid, Ed. Chemistry of Bivalent Sulfur; Chemical Publishing Co.: New York.1960, Ch.5.
- [25] O.B. Helfrich, E.E. Reid, J. Am. Chem. Soc. 42 (1920) 1208. Accepter

10

Graphical Abstract



Highlights : Crystal Structure of Ru-Mustard Gas complex Acceleration

Table 1

¹H NMR data (δ , ppm) at r.t. (~20 °C) for some organo-sulfur compounds: (ClCH₂CH₂)₂S (BCES), ClCH₂CH₂SCH₂CH₃ (CEES), (CH₃CH₂)₂S and their sulfoxides and sulfones. ¹H signals are assigned in the order shown in the formulae (i.e. from left to right).

Compound	in C ₆ D ₆	in (CD ₃) ₂ CO
(ClCH ₂ CH ₂) ₂ S	3.00 t, 2.20 t	3.75 t, 2.98 t
(ClCH ₂ CH ₂) ₂ SO	3.45 m, 2.15m	4.00 m, 3.26 m
	3.20 m, 2.05 m	
(ClCH ₂ CH ₂) ₂ SO ₂		4.05 t, 3.71 t

Compound	in C ₆ D ₆	in (CD ₃) ₂ CO
ClCH ₂ CH ₂ SCH ₂ CH ₃	3.22 t, 2.48 t, 2.05 q, 0.95 t	3.70 t, 2.87 t, 2.62 q, 1.24 t
ClCH ₂ CH ₂ S(O)CH ₂ CH ₃	3.70 m, 2.40 m, 2.00 m, 0.85 t	3.98 m, 3.10 m, 2.75 m, 1.28 t
	3.40 m, 2.20m	
ClCH ₂ CH ₂ S(O) ₂ CH ₂ CH ₃		3.95 t, 3.55 t, 3.18 q, 1.34 t

Compound in ($CD_3)_2CO$
$(CH_3CH_2)_2S$	1.20 t, 2.52 q
(CH ₃ CH ₂) ₂ SO	1.23 t, 2.72 m and 2.60 m
$(CH_3CH_2)_2SO_2$	1.30 t, 3.02 q

Table 2

¹H NMR data in C₆D₆ at r.t. (~20 °C) for axial ligands of Ru(TMP)L₂.^{*a*}

L ₂	$ClCH_2$	$ClCH_2CH_2$	CH ₂ CH ₃	CH ₃
$(CEESO)_2$	0.82 t	−1.44 t	−1.90 q	-0.96 t
(CEESO)(CEESO)			−1.76 m	-1.08 t
			-2.16 m	-1.12 t
$(CEESO)_2$	0.90 t	−1.05 m, −1.58 m	−1.75 m, −2.05 m	-1.00 t
$(CEES)_2$	1.22 t	-1.40 t	−1.88 q	-0.96 t
$(BCESO)_2$	1.13 t	−1.68 t		
(BCESO)(BCESO)	1.24 t, 1.04 t	−1.99 t, −0.97 m,		
		−1.42 m		
$(BCESO)_2$	1.15 t	−1.20 m, −1.65 m		
(BCES) ₂	1.08 t	-1.62 t		

^{*a*} δ ranges of ¹H singlets for the TMP are: pyrrole-H (8.43-8.60); *m*-H, 7.2-7.3; *p*-Me, 2.43-2.60; *o*-Me, 1.95-2.20.

Table 3

¹H NMR data in C₆D₆ at r.t. (~20 °C) for the L ligands of Ru(OCP)L₂.^{*a*}

	$ClCH_2$	$ClCH_2CH_2$	CH_2CH_3	CH ₃
CEESO	1.25 t	-1.18 t	-1.66 q	-0.90 t
BCESO	1.14 t	-1.40 t		
δ ¹ H sig 5.92/6.90	nals for the (t, <i>p</i> -Me)	e OCP are: δ8 for CEESO/BO	3.32 (s, pyrr CESO speci	ole), 7.36 ies.
	6	2		