C.B.Ü. Fen Bilimleri Dergisi ISSN 1305-1385 C.B.U. Journal of Science
1.1 (2005) 1 – 5 1.1 (2005) 1 – 5

RESULTS of the CHEMICAL REDUCTION STUDIES of $Cp_2^{*}Mo_2O_5$ BY Zn at LOW pH in AQUEOUS MEDIA

Funda DEMIRHAN

Celal Bayar University, Faculty of Sciences & Liberal Arts, Department of Chemistry 45140, Muradiye-Manisa, TURKEY.

Abstract: The zinc reduction of $Cp_2*Mo_2O_5$ (Cp*:pentamethylcylopentadienyl) in a MeOH-H_2O mixture in the presence of acetic acid affords the diamagnetic dinuclear compound $[Cp*MoO(O_2CCH_3)]_2$. The analogous reduction at lower pH (trifluoroaceticacid) leads to the crystallization of different trinuclear complexes depending on conditions. From THF-heptane a compound that can be formulated as $[Mo_3(Cp*)_3(\mu\text{-}O)_{6-n}(\mu\text{-}OH)_n]^{2+}$ x $2CF_3COO^-$was obtained. Crystallization from THF/diethyl ether, on the other hand, yielded a different compound, $[Cp*_3Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(\mu\text{-}O_2CCF_3)_3]_2[Zn_2(O_2CCF_3)_6]$.

Keywords: *Aqueous organometallic chemistry; Molybdenum;Oxo ligands; Half-sandwich complexes;*

$Cp_2^{*}Mo_2O_5$ BİLEŞİĞİNİN SULU ORTAMDA ve DÜŞÜK pH'da Zn ile KİMYASAL İNDİRGENME ÇALIŞMALARININ SONUÇLARI

Özet: MeOH-H_2O ortamında, asetik asit varlığında Zn ile indirgenen $Cp_2*Mo_2O_5$ dimeri diyamanyetik, çift çekirdekli $[Cp*MoO(O_2CCH_3)]_2$ bileşiğini verir. $Cp_2*Mo_2O_5$ dimerinin benzer koşullarda trifloroasetikasit varlığında çinko ile indirgenmesi sonucunda üç çekirdekli iki farklı kompleks elde edilir. THF-Heptan'dan kristallendirilen bileşik $[Mo_3(Cp*)_3(\mu\text{-}O)_{6-n}(\mu\text{-}OH)_n]^{2+}$ $.2CF_3COO^-$ formülüne sahipken, THF-dietileterden kristallendirilen bileşik $[Cp*_3Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(\mu\text{-}O_2CCF_3)_3]_2[Zn_2(O_2CCF_3)_6]$ yapısındadır.

Anahtar Kelimeler: *Sulu orgonametallik kimya; Molibden; Okso Ligandlar; Yarım Sandaviç Kompleksler*

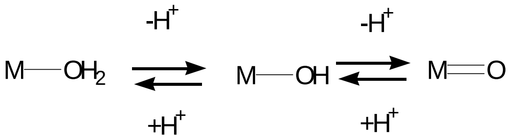
Corresponding author.

funda.demirhan@bayar.edu.tr

1. INTRODUCTION

The investigation of organometallic compounds in aqueous media has attracted great interest for a variety of reasons. The use of water as a solvent is attractive for homogeneous catalytic applications [1,2]. Separation and recycling of water-soluble transition metal catalysts is easier under aqueous biphasic conditions. Water is also more attractive from the economic and environmental issues (it is readily available, inexpensive and non toxic liquid) and it is better than most solvents for heat exchange purposes.

Most of the aqueous organometallic chemistry investigation carried out so far involve low to middle-valent transition metal complexes. High oxidation state orgonometallic chemistry has been intensively development in the last 20 years but most of this research work has been confined to non aqueous media. The greater metal electronegativity in the higher oxidation states confers a greater degree of covalency to the resulting metal–carbon bonds, which consequently may become quite resistance to hydrolytic conditions. It is therefore somewhat surprising that the physical behavior and chemical reactivity of high oxidation state organometallics is not systematically investigated in water, although aqueous reagents are sometimes used for their syntheses. Indeed, high oxidation state complexes are often stabilized by the highly π-donating and electronegative oxo ligand, which is nothing more than a doubly deprotonated water molecule. The relationship between the aqua, hydroxo, and oxo ligands is shown in Scheme 1 and it is obvious that an increase of the metal oxidation state increases the acidity of the oxygen-bound protons, stabilizing the oxo form. Aqua-complexes will be more favored, on the other hand, in the lower oxidation states.



Scheme 1

The systematic investigation of high oxidation state organometallic complexes in water can open new perspectives for aqueous catalysis and, if a highly redox-active metal is selected, also for electrocatalysis. For instance, one can envisage the combined reduction and protonation of oxo complexes to yield labile aqua ligands, making coordination sites available for substrate coordination. The activated substrate may then be capable of accepting electrons from the metal and protons from the medium, yielding a hydrogenated product by use of proton and electrons (instead of molecular hydrogen), while regenerating the high oxidation state oxo complex [3,4].

One of the oldest high oxidation state organometallic complexes is $Cp_2Mo_2O_5$, first reported by Malcolm Green in 1964 [5]. The Cp* analogue was first described by Herberhold in 1985 [6] and structurally characterized later in several different polymorphs [7,8], always showing a symmetric Mo-O-Mo bridge. Some aspects of the synthetic procedures leading to these complexes involve water as a solvent and/or as a reagent. For instance, $CpMoCl_4$ is hydrolyzed in air-free water leading to $[CpMoO_2]_n$ [9]. Subsequent aerial oxidation and/or basic hydrolysis leads to the dinuclear Mo(VI) products [10].

2. METHODS and RESULTS

2.1 Chemical Reduction Study at Low pH

The zinc reduction of compound $Cp_2{}^*Mo_2O_5$ in an aceticacid 1:1(v/v) MeOH-H_2O mixture (pH ca 4) takes place extremely slowly. During several days of stirring at room temperature, the mixture undergoes several color changes through orange, red, and brown to finally yielded a blue-green suspension.

The final precipitate was blue, but in all cases the pure product was recovered in small yields by recrystallization of the final blue or blue-green solid from hot heptane. In a separate experiment, an intermediate red reduction product was isolated and shown to correspond to the already known $Cp^{*}_{2}Mo_{2}O_{4}$, confirming by NMR.

The X-ray structure of the isolated blue product indicates that is a dinuclear compound of Mo(IV) with formula $[Cp^{*}MoO(O_{2}CCH_{3})]_{2}$. Therefore, the redox process corresponds to the stochiometry of Eq(1).

$$Cp^{*}_{2}Mo_{2}O_{5} + 2Zn + 6CH_{3}COOH \longrightarrow [Cp^{*}MoO(O_{2}CCH_{3})]_{2} + 2Zn(O_{2}CCH_{3})_{2} + 3H_{2}O \quad (1)$$

The product is diamagnetic, as indicated by the ^{1}HNMR spectrum which shows two resonances in the expected ratio and with the expected chemical shifts for the Cp* and $CH_{3}CO_{2}$ protons. An independent cyclic voltammetric study of the isolated compound in $CH_{2}Cl_{2}$ shows that it undergoes a reversible one-electron oxidation process at $E_{1/2} = -0.50$ V, confirming the existence and stability of the cationic species. A view of the molecular structere as determined by the single crystal X-ray analysis is shown in Fig 1.

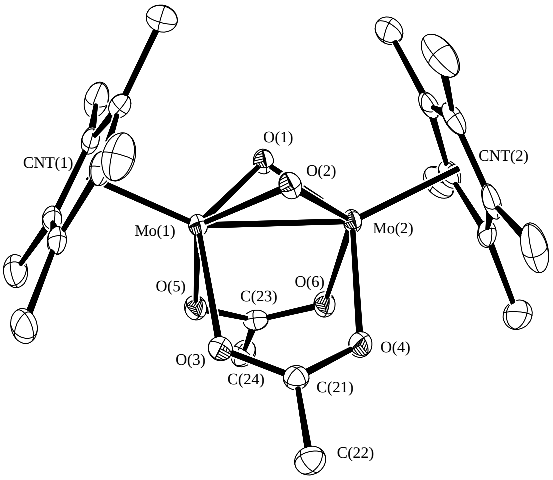


Figure 1. An ORTEP view of the $Cp^{*}_{2}Mo_{2}O_{2}(O_{2}CCH_{3})_{2}$ molecule.

The structure shows two oxo and two acetato groups bridging the two metal atoms that are, in addition, held together by a direct metal-metal interaction (Mo-Mo: 2.5524(3) Å) [11]. This structure is based on the four-legged piano stool ligand arrangement which is typical of $Cp^{*}Mo^{IV}$ dinuclear species, as seen for instance in $[Cp^{*}Mo(S)(SMe)]_{2}$ and in other similar derivatives [12], but it is the first example of a dinuclear $Cp^{*}Mo^{IV}$ compound which is fully supported by O-donor ligands. It can be considered as an example of a stabilized aqueous $Cp^{*}_{2}Mo_{2}O_{2}^{2+}$ species.

2.2 Chemical Reduction Study at Lower pH

The zinc reduction carried out at lower pH (trifluoroacetic acid) under otherwise identical conditions is accompanied by analogous color changes, yielding a green-blue precipitate. From this solid, however, only dark blue trinuclear reduction products could be crystallized. The nature of the isolated product delicately depends on the crystallization conditions. From THF-heptane, crystals that can be formulated as $[Cp^{*}_{3}Mo_{3}(\mu\text{-}O)_{6-n}(\mu\text{-}OH)_{n}]^{2+} \times 2CF_{3}COO^{-}$ were recovered. High disorder in the trifluoroacetate and Cp* fragments, confirmed on several crystals from different batches, hampered a satisfactory refinement of the X-ray data, thus the intimate structural details cannot be obtained. However, the basic equilateral triangular $Cp^{*}_{3}Mo_{3}(\mu\text{-}O)_{6}$ core (Mo-Mo: 2.79 Å) and the trifluoroacetate arrangement as depicted schematically in Figure 2 are unambiguously shown [13]. The two trifluoroacetates establish close contacts between *both* oxygen atoms and different μ-oxo ligands above and below the Mo_{3} triangle, as shown in the Figure, the O··O distance being typical of hydrogen bonds (2.6 Å). Therefore, the value of n in the chemical formula is most likely 4, corresponding to an average oxidation state of +4.33 for the metal atoms. It is relevant to note that a related structure, also characterized by severe disorder, has previously been reported for a compound formulated as $[Cp^{*}_{3}Mo_{3}(\mu\text{-}O)_{6-n}(\mu\text{-}$

$OH)_n]^{2+}$ x 2 Cl^-, this being obtained by a synthetic strategy similar to ours (zinc reduction of Cp^*MoO_2Cl in $CHCl_3$ in the presence of concentrated HCl) [14]. In that case, however, the most likely value of n was proposed as 5.

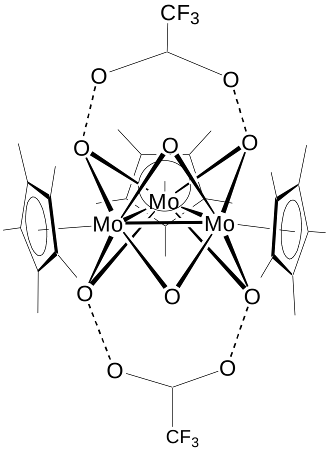


Figure 2 Structural arrangement of compound $[Cp^*_3Mo_3O_{6-n}(OH)_n][CF_3COO]_2$

When the crystallization was carried out from THF-diethyl ether, a different compound, identified as $[Cp^*_3Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(\mu\text{-}O_2CCF_3)_3]_2[Zn_2(O_2CCF_3)_6]$, was crystallized. The dianion $[Zn_2(O_2CCF_3)_6]^{2-}$ has a lantern type structure, similar to other previously reported neutral $Zn_2(O_2CCR)_4L_2$ complexes [15]. The structure of the unprecedented trinuclear monocation is shown in Figure 3. [16].

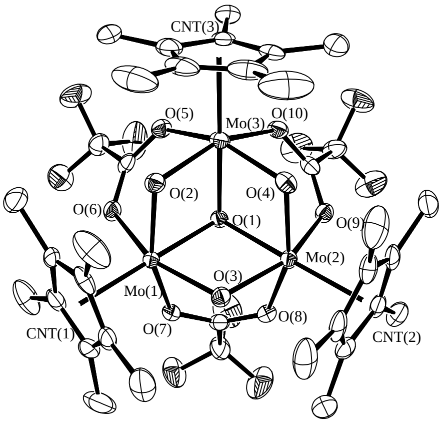


Figure 3. An ORTEP view of the $[Cp^*_3Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(\mu\text{-}O_2CCF_3)_3]^+$ cation.

The cation has a few novel and interesting features. No trinuclear Mo complex, either with or without Cp* ligands, in an oxidation state as high as +5 has been previously reported. The Mo_3O_4 core is typical of the oxidation state +4, and few examples in more reduced states are also known, but none in higher ones [17]. The metal atoms are not directly bonded to each other (average $Mo\cdots Mo$ = Mo-Mo, 3.129(2) Å).

This can be readily rationalized from simple considerations based on the coordination geometry and on the electronic structure [16].

3.CONCLUSION

The systematic study of high oxidation state organometallic compounds in water has not so far attracted a lot of attention. Some results of reductive chemistry of $Cp_2^*Mo_2O_5$ are summarized in this paper. As a final remark, we underline the robustness of the Cp*Mo bond, which remains intact upon long reaction times under strongly acidic aqueous conditions. This feature is encouraging for future development of catalytic and electrocatalytic process with Cp*Mo systems in an aqueous environment.

ACKNOWLEDGEMENT

I am very pleased to work with Prof. Rinaldo Poli (Toulouse-France) and Dr Philippe Richard (Dijon-France). Also I am grateful to the TUBİTAK-NATO for postdoctral fellowship.

REFERENCES

1.Sinou, D., ‘‘ Metal Catalysis in Water’’, *Top. Curr. Chem.*, 206, 41-59, 1999.

2. Hanson, E. B., ‘‘ New Directions in Water Soluble Homogeneous Catalysis’’, *Coord. Chem. Rev.* 186, 795-807, 1999.

3. Collange, E., Demirhan, F., Gun, J., Lev, O., Modestov, A., Poli, R., Richard, P,Saurenz D., ‘‘Results of Perspectives of High Oxidation State Organomolybdenum Chemistry in Water’’ *Royal Society of Chemistry, Special Publication* No.287, Proceedings of the 20th International Conference on Organometallic Chemistry held in Corfu, Greece on 7-12 July 2002, 167-182, 2003.

4. Poli, R., ‘‘High Oxidation State Organometallic Chemistry in Aqueous Media: New Opportunities for Catalysis and Electrocatalysis’’, *Chem. Eur:J.*, 9, 1-11, 2003.

5. Cousins, M., Green, H. L. M., ‘‘Some Oxo- and Oxochloro-.cyclopentadienylmolybdenum Complexes’’, *J. Chem. Soc*., 1567-1573, 1964.

6. Herberhold, M., Kremnitz, W., Razavi, A., Schöllhorn, H., Thewalt, ‘‘$[(\mu^5\text{-}C_5H_5)CrO_2]_{2-}$A Dinuclear Oxo Complexes of Chromium (V)’’, *Angew. Chem*. 24, 601-602, 1985.

7. Faller, W. J., and Y. Ma, ‘‘High Oxidation State Organometallics pentamethylcyclopentadienyloxo-molybdenum (IV) and Tungsten (VI) complexes’’, *J. Organometal. Chem*, 340, 59-69,1988.

8. Rheingold, L. A., Harper, R. J., ‘‘A Comprison of the solid-state structures of four crystallographically independent molecules of bis $[Cp^*MoO_2]_2$’’, *J. Organometal. Chem*, 403, 335-344, 1991.

9. Bunker, J. M., Green L. H. M., ‘‘ Mono-μ-cyclopentadienylmolybdenum Chemistry. Some Oxo-, Oxohalogeno-, Halogeno-, Thio-μ-Disulphido-, and Thiohalogeno-derivates’’, J. Chem. Soc. Dalton, 847-851, 1981.

10. Saurenz, D., Demirhan, F., Richard, P., Poli, R.,Sitzmann, H., ‘‘Cyclopentadienylmolybdenum (VI) and Molybdenum(V) Oxo Chemistry: New Synthetic and Structural Features’’, *Eur. J. Inorg. Chem.* 1415-1424, 2002.

11. Demirhan , F., Richard, R. Poli, R, ‘‘High Oxidation State Aqueous Organometallics: Synthesis and Structure of a Dinuclear Oxo(pentamethylcyclopentadienyl)acetato complex of molybdenum(IV) $[Cp^*Mo(\mu\text{-}O)(\mu\text{-}O_2CCH_3)]_2$’’, *Inorg. Chim: Acta*., 347, 161-166, 2003.

12. DuBois, R. M., VanDerveer, C. M., DuBois L. D., Haltiwanger, C. R., Miller, K. W., ‘‘ Characterization of Reactions of Hydrogen with Coordination Sülfido Ligands’’, 102, (25), 7456-7461, 1980.

13. Demirhan, F., Richard, R. Poli, R, unpublished observation.

14. Bottomly, F., Chen, J., Preston, F., K., Thompson, C. R., ‘‘Organometallic Oxides : Preparation and Properties of Cluster $\{(\mu\text{-}C_5Me_5)_4Mo_5O_{11}$ and $[(\mu\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n((\mu\text{-}O)_{6-n}\}Cl_2$’’, *J. Am. Chem. Soc*:,116(18), 7989-7995, 1994.

15. Sing, B., Long, R. J., Biani, F.F., Gatteschi, D.,Stavropoulos, P., ‘‘Synthesis, Reactivity, and Catalytic Behavior of Iron/Zinc-Containing Species Involved in Oxidation of Hydrocarbons under Gif-Type Conditions’’ *J. Am. Chem. Soc*:, 119, 7030-7047, 1997.

16. Demirhan, F., Gun, J., Lev, O., Modestov, A., Poli, R., Richard, P.,‘‘High Oxidation State Aqueous Organometallics: Formation and Structure of an oxo-centered Cp^*Mo^v Trinuclear cation by Chemical reduction of $Cp_2^*Mo_2O_5$’’, *J. Am. Chem. Soc:, Dalton Trans*. 2109-2111, 2002.

17. Richens, T. D., ‘‘ The Chemistry of Aqua Ions’’ Wiley, Chichester, pp 259-336, 1997.