

UDC 548.73:541.49:546.75

CRYSTAL AND MOLECULAR STRUCTURE OF CICESIUM  
BIS(MALONATO)-DI- $\mu$ -SULPHIDO-BIS[OXOMOLYBDATE(V)] DIHYDRATE:  
 $\text{Cs}_2[\text{Mo}_2\text{O}_2\text{S}_2(\text{MALONATE})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

M. Abou Fadel<sup>1</sup>, N. Watfa<sup>1,2</sup>, S. Floquet<sup>1</sup>, J. Marrot<sup>1</sup>, M. Awada<sup>1</sup>, A. Hijazi<sup>2</sup>, D. Naoufal<sup>2</sup>, E. Cadot<sup>1</sup>

<sup>1</sup>*Institut Lavoisier de Versailles, UMR 8180, University of Versailles Saint-Quentin en Yvelines, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France*

E-mail: sebastien.floquet@uvsq.fr

<sup>2</sup>*Lebanese University, Faculty of Sciences, Laboratory of Organometallic and Inorganic Coordination Chemistry, Hadath, Beirut, Lebanon*

Received February, 18, 2014

The compound  $\text{Cs}_2[\text{Mo}_2\text{O}_2\text{S}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  has been synthesized and isolated as single crystals. It crystallizes in the *Pnma* space group and the structural analysis reveals that all the components are held together to build a 3D compact layered network, evidencing that  $\{\text{Mo}_2\text{O}_2\text{S}_2\}$ -based molecular complexes can be used as building units for the elaboration of metal organic frameworks materials.

**Key words:** cluster, chalcogenide, thiometalate, polyoxometalate, molybdenum, sulfur.

#### INTRODUCTION

Due their capability to engage in facile electron and proton transfer processes, transition metal-sulphide systems, especially Mo—S clusters, are important components in many enzymes such as nitrogenases [ 1, 2 ]. Among the Mo—S clusters, the dinuclear oxothiocation  $[\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{O})_6]^{2+}$  received a great attention in many domains. This dinuclear complex can be combined with inorganic ligands such as vacant polyoxometalates for giving dynamic supramolecular assemblies [ 3 ] or with various organic ligands to lead to either models mimicking the active site of enzymes [ 4—8 ] or a wide family of cyclic host-guest systems when polycarboxylate or polyphosphate ligands are used [ 9, 10 ]. These  $\text{Mo}_2\text{O}_2\text{S}_2$ -based compounds revealed catalytic activity for the reduction alkenes [ 11 ], or efficient electro-catalytic activity for protons reduction into hydrogen either in organic or in aqueous media [ 12, 13 ]. For the latter application, the design of robust  $\text{Mo}_2\text{O}_2\text{S}_2$ -based materials is therefore needed. In order to elaborate viable and efficient materials for electro-catalytic hydrogen evolution reaction, a possible way is the use of metal organic frameworks (MOFs) built on  $\text{Mo}_2\text{O}_2\text{S}_2$ -based complexes. Following this idea, the  $\{\text{Mo}_2\text{O}_2\text{S}_2\}$  building unit possesses several coordination sites on each molybdenum atom which are easily accessible to ditopic ligands. In the present contribution, we report the synthesis and the structural characterization of the cesium salt of the complex  $[\text{Mo}_2\text{O}_2\text{S}_2(\text{malonate})_2(\text{H}_2\text{O})_2]^{2-}$  which exhibits 3D connections ensuring through the coordination of the cesium cation by the carboxylato groups.

#### EXPERIMENTAL SECTION

**Syntheses.** The precursor  $\text{K}_{2-x}(\text{NMe}_4)_x[\text{I}_2\text{Mo}_{10}\text{O}_{10}\text{S}_{10}(\text{OH})_{10}(\text{H}_2\text{O})_5] \cdot 20\text{H}_2\text{O}$  ( $0 < x < 0.5$ ) was prepared as described in literature [ 14 ] and characterized by usual routine methods. Chemicals were purchased from Aldrich Chemicals or Acros Chemicals and used without further purification.

**Synthesis of  $\text{Cs}_2[\text{Mo}_2\text{O}_2\text{S}_2(\text{malonate})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , **Cs1**.**  $\text{K}_{2-x}(\text{NMe}_4)_x[\text{I}_2\text{Mo}_{10}\text{O}_{10}\text{S}_{10}(\text{OH})_{10} \cdot (\text{H}_2\text{O})_5] \cdot 20 \text{H}_2\text{O}$  (500 mg, 1.04 mmol of  $\text{Mo}_2\text{O}_2\text{S}_2$ ) was solubilized and hydrolyzed in HCl 1M (10 ml). Malonic acid (in excess: 1.6 g, 15.2 mmol) suspended in 15 ml of water was added (initial pH was 0.6). The pH was adjusted to 3 by KOH 1M. The resulting solution was stirred for 30 min at 50 °C. Then, CsCl (350 mg, 2.08 mmol) was added, thus provoking the formation of a yellow powder which was removed by filtration after cooling at room temperature. The resulting solution was kept in air for slow evaporation and gave parallelepiped red-orange crystals after three days which were collected by filtration, washed with cold water and dried in air (365 mg, yield 44 %). IR (ATR Diamond after ATR correction):  $\nu$  ( $\text{cm}^{-1}$ ) = 1664 (m), 1597 (ms, sh), 1563 (s), 1437 (m), 1360 (m), 1283 (mw), 1193 (w), 985 (w), 937 (m), 784 (w), 723 (mw), 580 (mw, br.) 514 (w), 461 (w), 416 (w), 338 (w). Anal. calc. for  $\text{Cs}_2[\text{Mo}_2\text{O}_2\text{S}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (M = 830.0 g/mol) (found): C 8.68 (8.70); H 1.46 (1.52); S 7.73 (7.97). EDX ratios found (expected): Mo/S = 1.05 (1.00); Mo/Cs = 1.10 (1.00). TGA: weight loss of 8.8 % between 20 °C and 160 °C corresponding to the 4 water molecules (calculated 8.7 %).

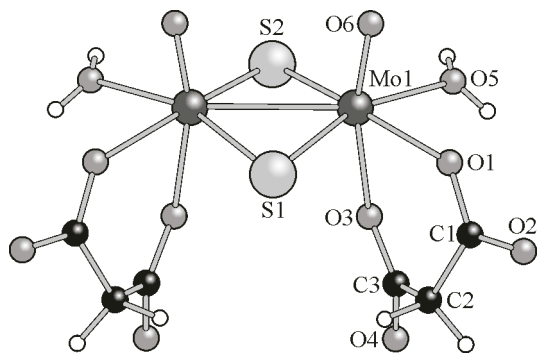
**Physical methods. Infrared spectra** were recorded on a 6700 FT-IR Nicolet spectrophotometer, using diamond ATR technique. ATR correction was applied on the IR spectra. **Elemental analyses** were performed by the "service d'analyses du CNRS", ICSN, Gif sur Yvette, France. **EDX** measurements were performed on a JEOL JSM 5800LV apparatus.

**X-ray crystallography.** Data collection was carried out for **Cs1** by using a Bruker Nonius X8 APEX 2 diffractometer equipped with a CCD bi-dimensional detector using the monochromatized wavelength  $\lambda(\text{MoK}_\alpha) = 0.71073 \text{ \AA}$ . As the crystals loose rapidly their crystallinity upon dehydration, they were mounted in paratone oil and data collections were performed at 200 K. Absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program [ 15 ] based on the method of Blessing [ 16 ]. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package [ 17 ]. Heavier atoms (Mo) for each structure were initially located by direct methods. The remaining non-hydrogen atoms were located from Fourier differences and were refined with anisotropic thermal parameters. Further details about of the crystal structure determinations may be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) on quoting the depository number CCDC-969253.

## RESULTS AND DISCUSSION

**Synthesis.** Considering the propensity of the thioanion  $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$  to give cyclic compounds in presence of dicarboxylate ligands in water in the 3–5 pH range, the synthesis of **Cs1** was carried out in the presence of a large excess of malonic acid. In these conditions, any self-condensation process of the thioanions is avoided and the formation of the discrete molecular complex  $[\text{Mo}_2\text{O}_2\text{S}_2(\text{malonato})_2]^{2-}$  is favored. The compound **1** was isolated as a cesium salt after slow evaporation of the solution.

**Structure of Cs1.** The compound  $\text{Cs}_2[\text{Mo}_2\text{O}_2\text{S}_2(\text{malonato})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , **Cs1**, crystallize in the *Pnma* space group. The labeled molecular structure of the complex  $[\text{Mo}_2\text{O}_2\text{S}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$  is depicted in the Fig. 1. It contains the  $[\text{Mo}_2\text{O}_2\text{S}_2]^{2+}$  core



which is connected to two malonato ligands acting as a bis-chelate and to two aquo ligands. The two equivalent molybdenum atoms are octahedrally coordinated and are related through a mirror plan cutting the bridging sulphur atoms S1 and S2. Each molybdenum atom is bound to a terminal oxo ligand (O6, Mo—O = 1.683 Å), two bridging sulfido ligands S1 and S2 (Mo—S =

Fig. 1. Labeled molecular structure of the complex  $[\text{Mo}_2\text{O}_2\text{S}_2(\text{malonato})_2(\text{H}_2\text{O})_2]^{2-}$ , **1**

Table 1

*Structural parameters for compounds Cs1*

Compound	<b>Cs1</b>
Empirical formula	C <sub>6</sub> H <sub>12</sub> Cs <sub>2</sub> Mo <sub>2</sub> O <sub>14</sub> S <sub>2</sub>
Formula weight	829.98
Temperature, K	200(2)
Crystal size, mm	0.26×0.12×0.04
Crystal shape	Parallelepiped
Crystal colour	Red
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å	10.4907(3), 14.3470(5), 12.8047(4)
$\alpha$ , $\beta$ , $\gamma$ , deg.	90, 90, 90
<i>V</i> , Å <sup>3</sup>	1927.24(11)
<i>Z</i>	4
<i>D</i> <sub>c</sub> , g·cm <sup>-3</sup>	2.860
$\mu$ , mm <sup>-1</sup>	5.304
Data / restraints / parameters	2908 / 0 / 140
<i>R</i> <sub>int</sub>	0.0301
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0323, <i>wR</i> <sub>2</sub> = 0.0902
Final <i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0329, <i>wR</i> <sub>2</sub> = 0.0906
Goodness of fit	1.108
Residual extrema	+2.684 / -2.664

Table 2

*Selected distances (d, Å) in compound Cs1*

Compound	<i>d</i>	Compound	<i>d</i>	Compound	<i>d</i>
Mo1—O6	1.683(3)	Cs1—O3	3.122(3)	Cs2—O1w	2.995(5)
Mo1—O5(w)	2.170(3)	Cs1—O2	3.249(3)	Cs2—O4	3.166(3)
Mo1—O1	2.122(3)	Cs1—O4	3.341(3)	Cs2—O6	3.065(3)
Mo1—O3	2.198(3)	Cs1—O1w	3.151(5)	Cs2—S1	3.672(2)
Mo1—S1	2.317(2)	Cs1—S2	3.664(2)	Cs2—S2	3.798(2)
Mo1—S2	2.328(1)		and 3.711(2)		
Mo1—Mo1'	2.829(2)				

= 2.317—2.328 Å), two oxygen atoms of a malonato ligand coordinated in equatorial (O1, Mo—O = 2.122 Å) and in axial positions (O3, Mo—O = 2.198 Å) and a terminal aquo ligand (O5, Mo—O = 2.170 Å). The connectivity of the Mo atoms is achieved with a Mo—Mo bond (Mo—Mo = 2.829 Å). These interatomic distances are summarized in the Table 2 and are in agreement with the literature data reported for similar molecular complexes based on the [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>]<sup>2+</sup> core [5—8, 11, 18, 19].

The analysis of the structure of **Cs1** reveals that the cesium cations cannot be considered as separated from the molecular complex [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>. Two different cesium cations, labelled Cs1 and Cs2, are found in the solid state structure of **Cs1**. As depicted in Fig. 2, the Cs1 cation is surrounded by eight oxygen atoms belonging to the malonato ligands of the complex **1** (O2, O3 and O4 atoms), and to two hydration water molecules (O1w). Furthermore, Cs1 interacts with two sulphur atoms (S2) belonging to two different complexes **1**. As depicted in the Fig. 3, the environment of the Cs2 cations appears quite different. Cs2 cation is surrounded by six oxygen atoms belonging to

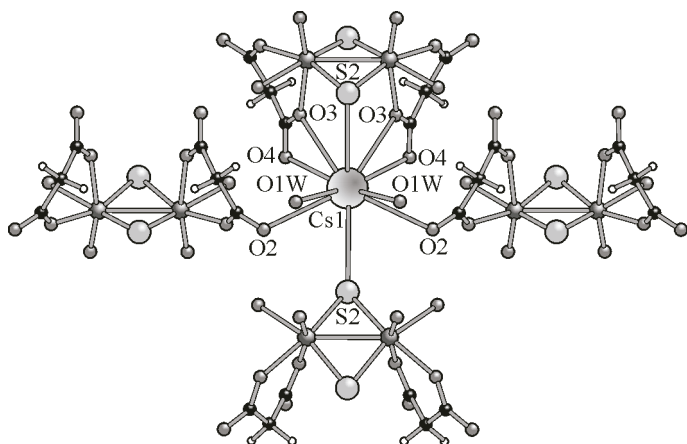


Fig. 2. Representation of the coordination sphere of the Cs1 cation

malonato ligands of two complexes **1** (namely O4 and O6) and to the two hydration water molecules (O1w). The coordination of Cs2 cations is achieved through interactions with two sulphur atoms (namely S1 and S2) belonging to two complexes **1**. The Cs—O distances (see Table 2) are found in the 2.995–3.341 Å range, whereas the Cs—S distances are longer (3.664–3.798 Å). These distances are in agreement with those of the literature data [5, 18, 20].

Interestingly, the coordination sphere of the two cesium cations Cs1 and Cs2 contains common coordinating centres, namely S2, O4 and O1w which bridges these two Cs<sup>+</sup> cations as depicted in the Fig. 4.

**3D network.** As described, the Cs1 cations are linked to four different complexes **1**, the Cs2 cations are linked to three complexes **1** and the Cs1 and Cs2 cations are bridged together by three different atoms. Logically, such a connectivity scheme should give a 3D network built from all these connections between the complexes, the cations and the hydration water molecules. Simply considering the Cs1 cations, a 3D network arises from connection between the molecular complexes **1** as depicted in the Fig. 5. The Cs2 cations fill this network for giving a complicated 3D network closely connecting all the constituting elements of the compound Cs<sub>2</sub>[Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>(malonate)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O as seen in the projection along the *b* axis given in the Fig. 6. Unfortunately, this network appears quite compact and no porosity can be evidenced by X-ray structure analysis. Finally, interestingly, the projection along the *a* axis depicted in the Fig. 7 evidences that the cesium cations Cs1 and Cs2 and the bridging sulfur atoms are located in the same plane perpendicular to the *b* axis. These planes are stacked with an interplane distance of 7.17 Å, giving a 3D layered solid. In the same way, the dinuclear cores {Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>} are oriented perpendicularly to the {Cs,S} planes, leading to intercalated double-sheet of molybdenum. It is interesting to note that the organic part, composed by the malonate ligands appear closely sandwiched between the inorganic layers.

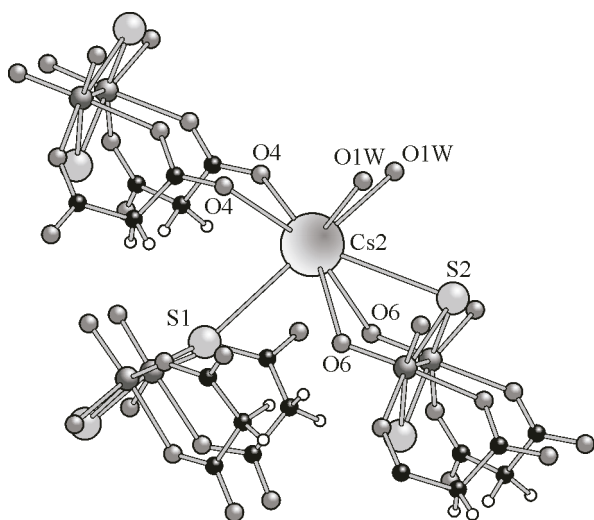


Fig. 3. Representation of the coordination sphere of the Cs2 cation

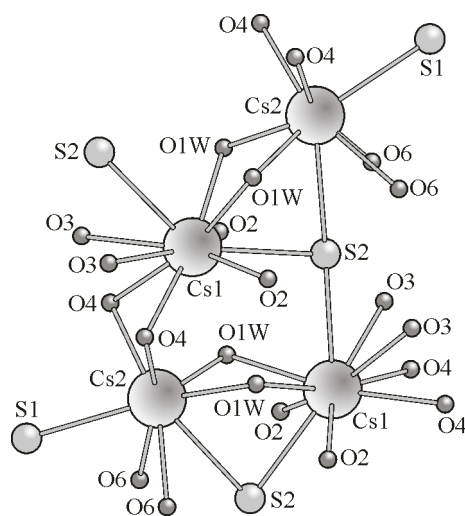
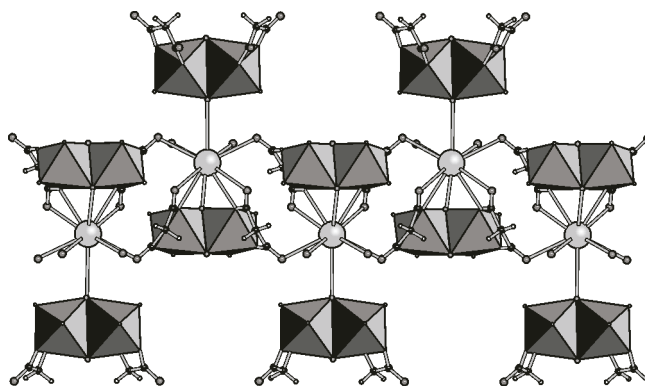


Fig. 4. Connectivity between Cs<sup>+</sup> cations

Fig. 5. Partial representation of the connections between Cs<sup>+</sup> cations and complexes [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>(malonato)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>



### CONCLUSIONS

A new complex of the thioation [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>]<sup>2+</sup> has been synthesized with malonato ligands and isolated as a cesium salt. The analysis of the X-Ray structure reveals number of connections between the anionic complexes [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>(malonato)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> and the counter cations, thus building a compact 3D layered network. This result demonstrates the possibility to build easily MOF materials based on [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>]<sup>2+</sup> complexes. In this way, the use of dications instead of the Cs<sup>+</sup> cations or rigid and larger ligands as linker could induce some porosity. This work is under progress.

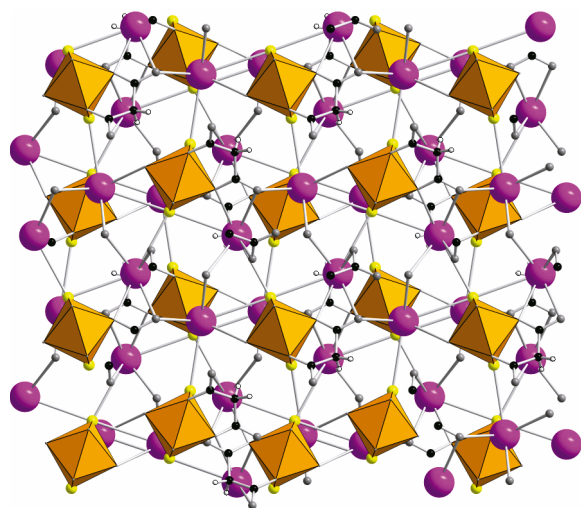


Fig. 6. Representation along the *b* axis of the 3D network built from the connections of Cs<sup>+</sup> cations, hydration water molecules and complexes [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>(malonato)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>. The [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>O<sub>6</sub>] cores are depicted in orange polyhedra, the sulphur atoms are in yellow and the cesium cations are given in pink

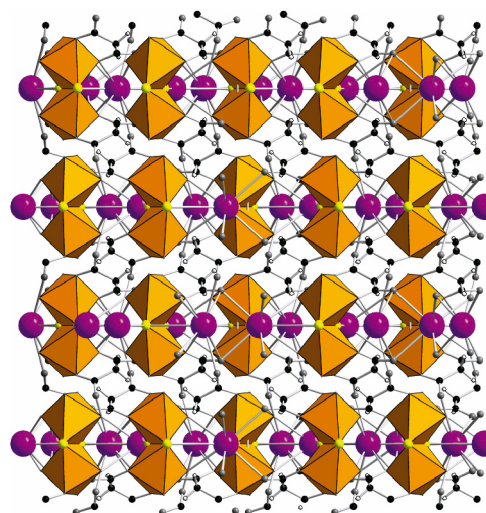


Fig. 7. Representation along the *a* axis of the 3D network built from the connections of Cs<sup>+</sup> cations, hydration water molecules and complexes [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>(malonato)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>. The [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>O<sub>6</sub>] cores are depicted in orange polyhedra, the sulphur atoms are in yellow and the cesium cations are given in pink

**Acknowledgements.** We gratefully acknowledge the Centre National de la Recherche Scientifique (CNRS) and the Ministère de l'Enseignement Supérieur et de la Recherche (MESR) for their financial support. The University of Versailles is also acknowledged for financial support (BQI) accorded to M.A.F.

### REFERENCES

1. Enemark J.H., Cooney J.J.A., Wang J.-J., Holm R.H. // Chem. Rev. – 2004. – **104**. – P. 1175.
2. Hille R. // Chem. Rev. – 1996. – **96**. – P. 2757.
3. Cadot E., Sokolov M.N., Fedin V.P., Simonnet-Jégat C., Floquet S., Secheresse F. // Chem. Soc. Rev. – 2012. – **41**. – P. 7335 – 7353.
4. Ott V.R., Swieter D.S., Schultz F.A. // Inorg. Chem. – 1977. – **16**. – P. 2538 – 2545.

5. Spivack B., Dori Z. // *J. Chem. Soc., Dalton Trans.* – 1973. – P. 1173 – 1177.
6. Li D.-M., Xing Y.-H., Li Z.-C., Xu J.-Q., Song W.-B., Wang T.-G., Yang G.-D., Hu N.-H., Jia H.-Q., Zhang H.-M. // *J. Inorg. Biochem.* – 2005. – **99**. – P. 1602 – 1610.
7. Shibahara T., Ogasahara O., Sakane G. // *Acta Crystallogr.* – 2008. – **E64**. – P. m605 – m606.
8. Yoshida R., Ogasahara S., Akashi H., Shibahara T. // *Inorg. Chim. Acta.* – 2012. – **383**. – P. 157 – 163.
9. Cadot E., Sécheresse F. // *Chem. Commun.* – 2002. – P. 2189 – 2197.
10. Lemonnier J.F., Duval S., Floquet S., Cadot E. // *Isr. J. Chem.* – 2011. – **51**. – P. 290 – 302.
11. Wu J.F., Li D.-M., Cui L.-F., Zhuang C.-F., Song S.-N., Wang T.-G., Xu J.-Q., Jia H.-Q., Hu N.-H. // *Appl. Organometal. Chem.* – 2007. – **21**. – P. 1033 – 1040.
12. Hijazi A., Kemmegne-Mbougouen J.C., Floquet S., Marrot J., Fize J., Artero V., David O., Magnier E., Pegot B., Cadot E. // *Dalton Trans.* – 2013. – **42**. – P. 4848 – 4858.
13. Keita B., Floquet S., Lemonnier J.F., Cadot E., Kachmar A., Bénard M., Rohmer M.M., Nadjou L. // *J. Phys. Chem. C.* – 2008. – **112**. – P. 1109 – 1114.
14. Cadot E., Salignac B., Marrot J., Dolbecq A., Sécheresse F. // *Chem. Commun.* – 2000. – P. 261 – 262.
15. Sheldrick G.M. SADABS. Program for scaling, correction of area detector data. – University of Göttingen, Germany, 1997.
16. Blessing R.H. // *Acta Crystallogr.* – 1995. – **A51**. – P. 33 – 38.
17. Sheldrick G.M. SHELX-TL version 5.03, Software Package for the Crystal Structure Determination, Siemens Analytical X-ray Instrument Division. – Madison, WI USA, 1994.
18. Dolbecq A., Salignac B., Cadot E., Sécheresse F. // *Bull. Pol. Acad. Sci. – Chem.* – 1998. – **46**. – P. 237 – 271.
19. Duval S., Floquet S., Simonnet-Jégat C., Marrot J., Biboum R.N., Keita B., Nadjou L., Haouas M., Taulelle F., Cadot E. // *J. Amer. Chem. Soc.* – 2010. – **132**. – P. 2069 – 2077.
20. Lemonnier J.F., Floquet S., Marrot J., Kachmar A., Bénard M., Rohmer M.M., Haouas M., Taulelle F., Henry M., Cadot E. // *Inorg. Chem.* – 2007. – **46**. – P. 9516 – 9518.