

## Synthesis and X-ray diffraction data of dichlorodioxido (4,4-dimethoxycarbonyl-2,2'-bipyridyl) molybdenum(VI)

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The dichlorodioxido(4,4'-dimethoxycarbonyl-2,2'-bipyridyl)molybdenum(VI) complex was prepared from molybdenum(VI) dichloride dioxide and 4,4-dimethoxycarbonyl-2,2'-bipyridyl in CH<sub>2</sub>Cl<sub>2</sub> obtaining a clear green solution. The molybdenum complex was separated by precipitation with ethyl ether. The XRPD pattern for the new compound showed that the crystalline compound belongs to the monoclinic space group *P2<sub>1</sub>/c* (No 14) with refined unit-cell parameters *a* = 12.104(1) Å, *b* = 14.933 (2) Å, *c* = 11.010 (2) Å and  $\beta$  = 115.409° (9). The volume of the unit cell is *V* = 1797.6 (3) Å<sup>3</sup>.

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### I. INTRODUCTION

Oxygen atom transfer to or from a substrate, is a very delicate operation that is performed in nature by enzymes such as oxotransferases or hidrosilasas, which mostly have molybdenum-oxygen entity (Mo=O) as the active site (Enemark *et al.*, 2004; Holm *et al.*, 2011). Numerous bio-inspired dioxo-Mo complexes have been synthesized and it has been observed that the transfer of oxygen and the stability of these complexes is directly related to the chemical environment (metal-ligand interaction) surrounding its active site (Arzoumanian, 1998; Amini *et al.*, 2013). Among the innumerable bidentate chelating ligands used to obtain complexes with transition metals, the 2,2'-bipyridine is certainly one of the most widely used because of its ability of introducing different substituents and modify its physical and chemical properties (Constable and Steel, 1989; Ittel *et al.*, 2000). This property has allowed us to study the coordination sphere effect in the reactivity of the Mo=O entity (Kühn *et al.*, 2000; Günyar *et al.*, 2009). We have reported, over the years, the synthesis of several complexes with bipyridil ligands and studied, under homogeneous and heterogeneous conditions, their properties as oxygen atom transfer agents (Paez *et al.*, 2008; Arzoumanian *et al.*, 2010; Castellanos *et al.*, 2012). Their ability to participate in catalytic oxidation has been reported in the selective oxidation of phosphines, arylalkanes and the photochemical oxidative decomposition of persistent organic pollutants (POPs) specifically using molecular O<sub>2</sub> as oxygen atom donor under visible light irradiation (Paez *et al.*, 2009; Bakhtchadjian *et al.*, 2011; Castellanos *et al.*, 2013). In this work we report the synthesis and results on the molecular characterization (FTIR, NMR) and X-ray powder diffraction data for the compound dichlorodioxido (4,4-dimethoxycarbonyl-2,2'-bipyridyl) molybdenum(VI).

### II. EXPERIMENTAL

#### A. Synthesis

The ligand 4,4'-dimethoxycarbonyl-2,2'-bipyridyl was previously synthesized according to the literature procedure (Arzoumanian and Bakhtchadjian, 2006). CH<sub>2</sub>Cl<sub>2</sub> solution containing 2.57 mmol of 4,4'-dimethoxycarbonyl-2,2'-bipyridyl (0.7 g) was added over a slenckh containing 3 mmol of solid MoO<sub>2</sub>Cl<sub>2</sub>. We observed the gradual disappearance of the solid and change in coloration of the solution (light green) after 3 h of reaction. The solution was filtered and the product was precipitated with ethyl ether to give a light green solid with yield of 85%. Its synthesis is shown in the Figure 1. The density of 1.604 g cm<sup>-3</sup> was measured by the flotation method in an aqueous solution of potassium iodine.

The molecular characterization which was carried out with ultraviolet-visible (UV-Vis) spectroscopy showed two absorption bands in the regions 230–300 and 310–379 nm. Infrared (IR) spectrometry showed stretching vibrations;  $\nu$ : 1727 (C=O); 1434 (C=C); 944, 911 (Mo=O); and nuclear magnetic resonance on protons (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>) showed  $\delta$  (ppm) = 9.73 (d, 2H), 8.92 (s, 2H), 8.30 (d, 2H), 4.16 (t, 6H).

#### B. Powder data collection

A small portion of the title compound was gently ground in an agate mortar and sieved to a grain size less than 38  $\mu$ m. The specimen was mounted on a polymethyl methacrylate (PMMA) specimen holder. The XRPD pattern was recorded with a D8 ADVANCE BRUKER diffractometer operating in DaVinci geometry equipped with a Cu-target X-ray tube (40 kV and 30 mA), a nickel filter and a 1-dimensional LynxEye detector. A receiving slit (RS) of 0.6 mm and primary and secondary soller slits (SS) of 2.5° were used. The scan range was 2–70° 2 $\theta$  with a step size of 0.015 2 $\theta$ ° and a

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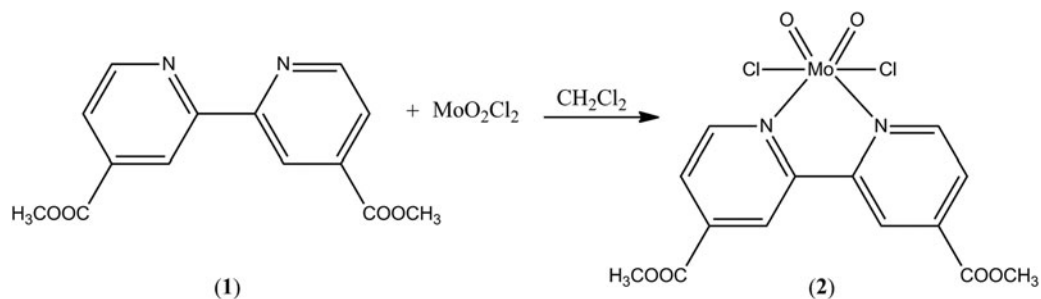


Figure 1. Synthesis of 1-[N-(methyl)-(3,5-dimethylphenylamino)]methylphthalene.

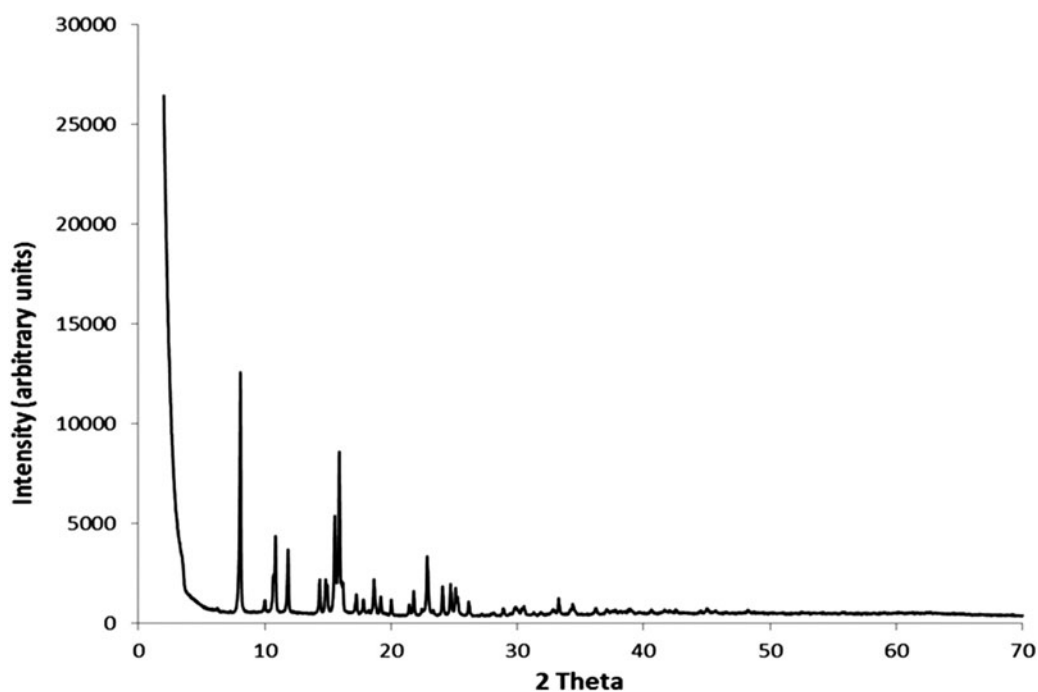


Figure 2. Powder X-ray diffraction pattern of 1-[N-(methyl)-(3,5-dimethylphenylamino)]methylphthalene.

TABLE I. X-ray powder diffraction data of 1-[N-(methyl)-(3,5-dimethylphenylamino)]methylphthalene. Cu- $K\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

$2\theta_{\text{obs}}$ (deg)	$d_{\text{obs}}$ ( $\text{\AA}$ )	$(III)_{\text{obs}}$	$h$	$k$	$l$	$2\theta_{\text{cal}}$ (deg)	$d_{\text{cal}}$ ( $\text{\AA}$ )	$\Delta 2\theta$ (deg)
8.081	10.9322	100	1	0	0	8.080	10.9330	-0.001
10.020	8.8206	6	1	1	0	10.019	8.8216	-0.001
10.692	8.2677	16	0	1	1	10.679	8.2775	-0.013
10.856	8.1432	33	-1	1	1	10.852	8.1465	-0.004
11.849	7.4629	28	0	2	0	11.843	7.4667	-0.006
14.360	6.1630	15	-1	2	0	14.353	6.1659	-0.007
14.833	5.9676	15	0	2	1	14.824	5.9711	-0.009
14.950	5.9211	13	-1	2	1	14.949	5.9213	-0.001
15.553	5.6929	42	1	1	1	15.552	5.6931	-0.001
15.914	5.5646	72	-2	1	1	15.909	5.5664	-0.005
16.192	5.4696	13	2	0	0	16.201	5.4665	0.009
17.258	5.1341	9	-2	1	0	17.260	5.1334	0.002
17.819	4.9737	7	0	0	2	17.823	4.9726	0.004
18.238	4.8604	2	-2	0	2	18.239	4.8601	0.001
18.664	4.7504	16	1	2	1	18.662	4.7508	-0.002
19.191	4.6211	8	-2	1	2	19.189	4.6215	-0.002
19.557	4.5355	1	-1	3	0	19.579	4.5303	0.022
20.026	4.4303	7	-1	3	1	20.024	4.4306	-0.002
			-1	2	2	20.028	4.4298	

Continued

TABLE I. Continued

$2\theta_{\text{obs}}$ (deg)	$d_{\text{obs}}$ (Å)	$(Hl)_{\text{obs}}$	$h$	$k$	$l$	$2\theta_{\text{cal}}$ (deg)	$d_{\text{cal}}$ (Å)	$\Delta 2\theta$ (deg)
21.451	4.1391	5	0	2	2	21.453	4.1388	0.002
21.805	4.0727	11	-2	2	2	21.802	4.0732	-0.003
22.448	3.9575	3	2	1	1	22.447	3.9577	-0.001
22.872	3.8850	28	-3	1	1	22.865	3.8863	-0.007
23.349	3.8067	3	1	1	2	23.361	3.8048	0.012
24.089	3.6915	14	-1	3	2	24.088	3.6915	-0.001
24.729	3.5973	14	2	2	1	24.733	3.5968	0.004
			-3	2	1	{ 25.115	3.5430	
25.126	3.5414	13	-3	1	0	{ 25.133	3.5404	0.007
25.288	3.5191	8	0	3	2	25.296	3.5180	0.008
26.161	3.4036	7	-3	2	2	{ 26.160	3.4037	-0.001
			-2	4	1	{ 28.130	3.1696	
28.156	3.1668	1	2	3	1	{ 28.156	3.1668	0.000
			-3	1	3	{ 28.160	3.1664	
28.884	3.0886	4	-1	4	2	{ 28.876	3.0894	-0.008
			1	3	2	{ 28.902	3.0868	
29.765	2.9992	3	-4	0	2	29.763	2.9994	-0.002
29.896	2.9863	4	0	4	2	{ 29.904	2.9855	0.008
30.046	2.9718	3	-3	2	3	{ 30.041	2.9723	-0.005
			3	1	1	{ 30.091	2.9674	
30.359	2.9418	4	-4	1	2	{ 30.372	2.9406	0.013
			3	3	0	{ 30.373	2.9405	
30.539	2.9249	4	-4	1	1	30.538	2.9250	-0.001
31.315	2.8542	1	-1	5	1	31.306	2.8549	-0.009
31.868	2.8059	2	3	2	1	31.868	2.8059	0.000
32.830	2.7258	3	-4	1	3	32.835	2.7254	0.005
33.640	2.6620	4	1	2	3	33.623	2.6633	-0.017
33.788	2.6507	8	-3	0	4	33.792	2.6504	0.004
34.187	2.6207	3	-2	5	0	{ 34.183	2.6210	-0.004
			2	3	2	{ 34.215	2.6186	
			-3	4	0	{ 34.360	2.6078	
34.394	2.6054	6	-1	4	3	{ 34.407	2.6044	0.013
36.203	2.4792	3	0	4	3	{ 36.209	2.4788	0.006
			3	0	2	{ 36.249	2.4762	
37.099	2.4214	3	-4	3	3	{ 37.092	2.4218	-0.007
			-5	0	2	{ 37.111	2.4206	
			-1	3	4	{ 38.032	2.3641	
38.087	2.3608	1	0	2	4	{ 38.118	2.3589	0.031
38.403	2.3421	1	-3	3	4	{ 38.448	2.3395	0.045
			-4	4	2	{ 38.469	2.3382	
38.833	2.3172	2	-5	1	3	38.832	2.3172	-0.001
			-4	2	4	{ 38.945	2.3107	
38.964	2.3097	2	-3	5	0	{ 38.958	2.3100	-0.006
			-1	5	3	{ 39.000	2.3076	
			1	6	1	{ 39.001	2.3076	
40.634	2.2185	2	0	5	3	{ 40.626	2.2189	-0.008
			3	3	2	{ 40.662	2.2170	
			-5	0	4	{ 41.656	2.1664	
41.698	2.1643	2	5	1	0	{ 41.714	2.1635	0.016
42.067	2.1462	1	-5	1	4	{ 42.113	2.1440	0.046
			2	5	2	{ 42.116	2.1438	
42.572	2.1219	2	-5	3	3	42.573	2.1218	0.001
			-4	4	4	44.448	2.0366	
44.485	2.0350	1	3	1	3	44.517	2.0336	0.032
			4	1	2	44.528	2.0331	
			-4	2	5	{ 44.990	2.0133	
45.022	2.0120	3	-6	0	2	{ 45.010	2.0125	-0.012
			4	4	1	{ 45.046	2.0110	
			-2	7	1	{ 45.068	2.0100	
45.722	1.9828	1	-3	5	4	{ 45.731	1.9824	0.009
			-6	1	3	{ 45.743	1.9819	
			-3	4	5	{ 48.238	1.8851	
			-4	5	4	{ 48.241	1.8849	
			-3	7	1	{ 48.241	1.8849	
48.262	1.8842	2	-6	2	1	{ 48.279	1.8835	0.017

TABLE II. Parameters obtained by X-ray powder diffraction for the compound 1-[N-(methyl)-(3,5-dimethylphenylamino)]methyl-naphthalene.

1-[N-(methyl)-(3,5-dimethylphenylamino)]methyl-naphthalene	
$a$ (Å)	12.104 (1)
$b$ (Å)	14.933 (2)
$c$ (Å)	11.010 (2)
$\beta$ (°)	115.409 (9)
$V$ (Å <sup>3</sup> )	1797.6 (3)
$Z$	4
$M_{20}$	58.6
$F_{30}$	97.1 (0.0048, 66)
$D_m$ (g cm <sup>-3</sup> )	1.604

count time of 2 s per step. Powder data were collected at room temperature (298 K).

Powder analytical software was used to remove the background (Sonneveld and Visser, 1975), smoothing (Savitzky and Golay, 1964), to eliminate the  $K\alpha_2$  component (Rachinger, 1948) and the second derivative method was used to determine the position and intensities of the diffraction maxima from each reflection.

### III. RESULTS AND DISCUSSION

The X-ray powder pattern of the compound dichlorodioxido(4,4-dimethoxycarbonyl-2,2-bipyridyl)molybdenum(VI) (2) is shown in Figure 2. X-ray powder diffraction data for the compound (2) are given in the Table I. All reflections were indexed successfully using the DICVOL06 program (Boultif and Louër, 2004) on a monoclinic unit cell and the peak positions, each with an absolute error of 0.03° (2 $\theta$ ), were used in the calculations. The space group,  $P2_1/c$  (No. 14), estimated by the program CHEKCELL (Laugier and Bochu, 2002) was compatible with the systematic absences and with the crystal density. The unit-cell parameters of the compound (2) were refined with the program NBS\*AIDS83 software (Miguell *et al.*, 1981). Its crystal data, X-ray density and figures of merit  $M_{20}$  (de Wolff, 1968) and  $F_{20}$  (Smith and Snyder, 1979) are compiled in the Table II.

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