

Synthesis and X-ray diffraction data for dibromo-dioxo-(1,10-phenanthroline-N,N')-molybdenum(VI) ($C_{12}H_8N_2MoBr_2O_2$)

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The dibromo-dioxo-(1,10-phenanthroline-N,N')-molybdenum(VI) complex ($C_{12}H_8N_2MoBr_2O_2$) was prepared from molybdic acid and 1,10-phenanthroline using hydrobromic acid as solvent. The molybdenum complex solid was separated by filtration and washed with ethyl ether. The X-ray powder diffraction pattern for the title compound was analyzed and found to crystallize in monoclinic system, space group $P2_1/c$ (No14) with refined unit-cell parameters $a = 12.036$ (1), $b = 9.819$ (1), $c = 12.671$ (2) Å, and $\beta = 110.44^\circ$ (1). The volume of the unit cell is $V = 1403.2$ (3) Å³. © 2016 International Centre for Diffraction Data. [doi:10.1017/S0885715615000949]

Key words: dioxomolybdenum complex, X-ray powder diffraction, oxygen atom transfer

I. INTRODUCTION

1,10-Phenanthroline represents one of the most representative bidentate chelating ligands in coordination chemistry (Accorsi *et al.*, 2009). Its versatility, manifested in the ability to be functionalized in different positions has expanded its coordination compounds in new applications in areas such as medicine (Ganeshpandian *et al.*, 2014; Inci *et al.*, 2015), electronics devices (Kurtz *et al.*, 2015), sensors (Kaur and Alreja, 2015), and new materials to oxidation (Yang *et al.*, 2015) or degradation of organic compounds (Abolhosseini *et al.*, 2014). Structurally, the main difference with the common 2,2'-bipyridine ligand is imposed by the rigid center ring in which the two nitrogen atoms are always held in juxtaposition, increasing the formation rates of bidentate coordination complex (Sammes and Yahioglu, 1994). Among the innumerable metal complexes with 1,10-phenanthroline ligand and phenanthroline derivatives ligand, ruthenium (II) (Heidary *et al.*, 2014), copper (II) (Liu *et al.*, 2014), nickel (Cai *et al.*, 2013), and iridium (Kwon *et al.*, 2015) metals are certainly the most widely used. We have reported, over the years, the synthesis of several molybdenum complexes with bidentate chelating ligands such as bipyridyl (Páez *et al.*, 2008, 2009) and bis-pyrazolyl (Castellanos *et al.*, 2012) ligands and studied, under homogeneous and heterogeneous conditions, their properties as oxygen atom transfer agents (Arzoumanian *et al.*, 2010). In a previous work, we have reported the powder diffraction data of a related molybdenum complex (Camargo *et al.*, 2014). Currently, our interest focuses on the study of the electron density effect of different bidentate ligands in oxygen atom transfer processes catalyzed by dioxo-molybdenum entity. In this work, we report the synthesis, molecular

characterization [Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR)], and X-ray powder diffraction (XRPD) data for the compound dibromo-dioxo-(1,10-phenanthroline-N,N')-molybdenum(VI) newly synthesized (Figure 1).

II. EXPERIMENTAL

A. Synthesis

All materials were commercial and were used without further purification unless otherwise noted. All solvents were thoroughly degassed prior to use. Acetonitrile was distilled and kept under argon. Molybdic acid ($H_2MoO_4 \cdot H_2O$, 5 g) was dissolved in the minimum volume (ca. 25 ml) of warm concentrated (46%) hydrobromic acid and the mixture was slowly stirred at 25 °C for 1 h. 1,10-Phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$, 5, 50 g) was added in the solution to obtain a yellow solid. The product was separated by filtration, washed with diethyl ether (3 × 100 ml) and recrystallized from acetone (yield 82%). The molecular characterization was carried out with ultraviolet–visible (UV–Vis) spectroscopy which showed two absorption bands at 270 and 350 nm. Infrared spectrometry showed stretching vibrations; ν : 1650 (C=N); 1434 (C=C); 940, 895 (Mo=O); and NMR on protons (¹H NMR, 400 MHz, dimethyl sulfoxide (DMSO)) showed δ (ppm) = 8.15 (d-d, 2H), 7.51 (d-d, 2H), 7.02 (s, 2H), 6.82 (d-d, 2H).

B. Powder data collection

A small portion of the title compound was gently ground in an agata mortar and sieved to a grain size <38 µm. The specimen was mounted on a polymethyl methacrylate specimen holder. The XRPD pattern was recorded with a D8 ADVANCE BRUKER diffractometer operating in DaVinci

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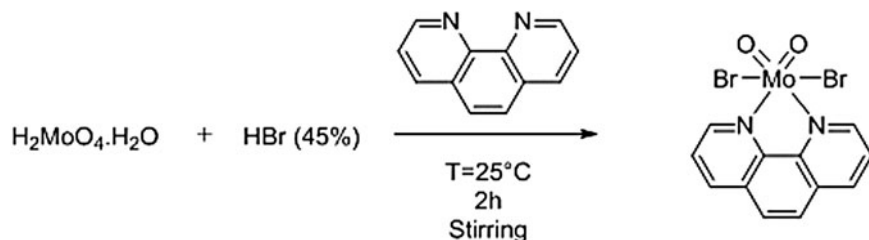


Figure 1. Synthesis of dibromo-dioxo-(1,10-phenanthroline-N,N')-molybdenum(VI).

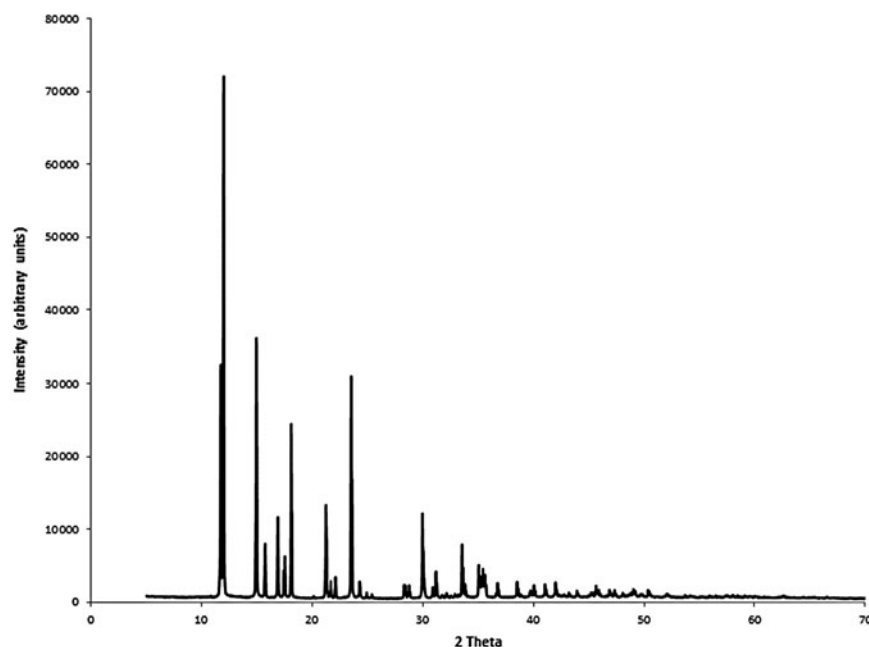


Figure 2. Powder X-ray diffraction pattern of dibromo-dioxo-(1,10-phenanthroline-N,N')-molybdenum(VI).

TABLE I. X-ray Powder Diffraction data of dibromo-dioxo-(1,10-phenanthroline-N,N')-molybdenum(VI).

$2\theta_{\text{obs}} (^{\circ})$	$d_{\text{obs}} (\text{\AA})$	$(I/I_0)_{\text{obs}}$	H	k	l	$2\theta_{\text{cal}} (^{\circ})$	$d_{\text{cal}} (\text{\AA})$	$\Delta 2\theta (^{\circ})$
11.682	7.5692	46	0	1	1	11.686	7.5668	0.004
11.942	7.4049	100	-1	1	0	11.941	7.4055	-0.001
14.906	5.9385	56	0	0	2	14.910	5.9368	0.004
15.696	5.6413	12	2	0	0	15.703	5.6390	0.007
16.850	5.2575	17	-1	1	2	16.849	5.2577	-0.001
17.385	5.0969	6	-2	1	1	17.382	5.0977	-0.003
			0	1	2	17.442	5.0804	
17.487	5.0674	9	-2	0	2	17.490	5.0665	0.003
18.053	4.9098	36	0	2	0	18.054	4.9095	0.001
21.197	4.1881	22	1	1	2	21.202	4.1872	0.005
21.629	4.1054	4	2	1	1	21.632	4.1049	0.003
22.058	4.0265	4	1	2	1	22.055	4.0272	-0.003
23.492	3.7839	51	0	2	2	23.495	3.7834	0.003
23.670	3.7558	1	3	0	0	23.648	3.7593	-0.022
24.240	3.6688	4	-2	1	3	24.251	3.6671	0.011
24.876	3.5764	1	-3	1	2	24.880	3.5758	0.004
25.345	3.5113	1	3	1	0	25.349	3.5108	0.004
28.263	3.1551	3	0	3	1	28.261	3.1553	-0.002
			-1	0	4	28.267	3.1546	
28.371	3.1433	3	1	3	0	28.371	3.1433	0.000
28.719	3.106	3	-3	2	1	28.724	3.1055	0.005
			3	1	1	28.749	3.1028	
			-3	2	0	29.912	2.9848	
29.934	2.9826	20	-4	0	2	29.938	2.9822	0.004
30.059	2.9705	4	0	0	4	30.081	2.9684	0.022
			1	3	1	30.085	2.9680	
			-2	1	4	30.093	2.9672	

Continued

TABLE I. Continued

$2\theta_{\text{obs}} (^{\circ})$	$d_{\text{obs}} (\text{\AA})$	$(I/I_0)_{\text{obs}}$	H	k	l	$2\theta_{\text{cal}} (^{\circ})$	$d_{\text{cal}} (\text{\AA})$	$\Delta 2\theta (^{\circ})$
30.847	2.8964	3	-1	3	2	30.840	2.8970	-0.007
31.149	2.869	7	-2	3	1	31.145	2.8694	-0.004
			-3	0	4	31.171	2.8670	
			0	3	2	31.179	2.8663	
31.701	2.8203	1	4	0	0	31.710	2.8195	0.009
32.102	2.786	1	1	2	3	32.101	2.7860	-0.001
			-3	2	3	32.141	2.7827	
32.875	2.7222	1	3	2	1	32.880	2.7218	0.005
33.177	2.6981	1	-4	1	3	33.183	2.6976	0.006
33.509	2.6721	13	1	3	2	33.505	2.6725	-0.004
33.617	2.6638	2	3	1	2	33.601	2.6650	-0.016
33.791	2.6505	3	2	3	1	33.788	2.6507	-0.003
35.021	2.5602	8	1	1	4	35.023	2.5600	0.002
			-4	2	1	35.133	2.5523	
35.178	2.5491	4	-4	2	2	35.182	2.5488	0.004
			0	2	4	35.305	2.5402	
35.295	2.5409	5	-3	3	1	35.373	2.5355	0.010
			-4	0	4	35.405	2.5332	
			0	3	3	35.564	2.5223	
35.577	2.5214	6	-2	3	3	35.582	2.5210	0.005
36.728	2.4450	3	4	2	0	36.728	2.4450	0.000
38.492	2.3369	4	-5	1	2	38.495	2.3367	0.003
38.819	2.318	1	1	4	1	38.820	2.3179	0.001
			-1	3	4	39.649	2.2713	
			-2	4	1	39.673	2.2700	
39.690	2.2691	2	0	4	2	39.701	2.2685	0.011
			2	1	4	39.988	2.2528	
40.018	2.2512	3	-4	2	4	40.018	2.2512	0.000
			-2	4	0	40.027	2.2507	
			0	3	4	41.015	2.1988	
41.020	2.1985	3	-5	1	0	41.024	2.1983	0.004
41.962	2.1513	4	-5	1	4	41.965	2.1512	0.003
			0	2	5	42.241	2.1378	
42.268	2.1365	1	-5	2	1	42.265	2.1366	-0.003
			-4	3	0	42.274	2.1362	
			-5	2	3	42.727	2.1146	
42.734	2.1142	1	3	3	2	42.740	2.1139	0.006
			-2	0	6	42.783	2.1119	
43.180	2.0934	1	-3	4	1	43.177	2.0935	-0.003
43.905	2.0605	2	1	3	4	43.908	2.0604	0.003
45.194	2.0047	1	-6	0	2	45.193	2.0047	-0.001
			-4	3	4	45.228	2.0033	
45.619	1.9870	3	1	4	3	45.621	1.9869	0.002
			-3	4	3	45.650	1.9857	
45.885	1.9761	2	-4	0	6	45.874	1.9766	-0.011
			-5	3	2	46.828	1.9385	
46.842	1.9379	2	-4	1	6	46.848	1.9377	0.006
			0	5	1	46.854	1.9375	
			-1	4	4	46.858	1.9373	
			-5	3	1	47.274	1.9212	
47.303	1.9201	2	5	2	1	47.301	1.9202	-0.002
			2	1	5	47.309	1.9199	
			-6	0	4	47.313	1.9197	
48.056	1.8918	1	0	4	4	48.058	1.8917	0.002
			1	5	1	48.061	1.8916	
			-5	2	5	48.561	1.8733	
48.572	1.8729	1	-1	5	2	48.574	1.8728	0.002
48.778	1.8655	1	-2	5	1	48.783	1.8653	0.005
			5	1	2	48.786	1.8652	
			-3	4	4	48.800	1.8646	
			0	5	2	48.806	1.8644	
49.012	1.8571	2	-5	3	0	49.007	1.8573	-0.005
49.182	1.8511	1	-4	4	0	49.173	1.8514	-0.009
			-4	3	5	49.210	1.8501	
49.668	1.8341	1	0	2	6	49.629	1.8354	0.016
			-4	2	6	49.684	1.8335	

Continued

TABLE I. Continued

$2\theta_{\text{obs}}$ (°)	d_{obs} (Å)	$(I/I_0)_{\text{obs}}$	H	k	l	$2\theta_{\text{cal}}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
			1	3	5	50.320	1.8119	
50.337	1.8113	2	1	1	6	50.343	1.8111	0.006
52.067	1.7551	1	6	2	0	52.057	1.7554	−0.010
			−1	4	5	52.103	1.7539	
			0	4	5	53.657	1.7068	
53.703	1.7054	1	−5	4	1	53.677	1.7062	−0.026
			7	1	0	57.960	1.5899	
57.982	1.5893	1	5	4	1	57.965	1.5897	−0.017
			−6	3	5	58.090	1.4842	
			−7	2	1	58.096	1.4840	
62.572	1.4833	1	−4	2	8	62.559	1.4836	−0.013

TABLE II. Parameters obtained by XRPD for the compound dibromo-dioxo-(1,10-phenanthroline-N,N′)-molybdenum(VI).

Dibromo-dioxo-(1,10-phenanthroline-N,N′)-molybdenum(VI)	
a (Å)	12.036 (1)
b (Å)	9.819 (1)
c (Å)	12.671 (2)
β (°)	110.44 (1)
V (Å ³)	1403.2 (2)
Z	4
M_{20}	41.3
F_{30}	65.8 (0.0056, 82)
D_m (g cm ^{−3})	2.19

geometry equipped with an X-ray tube (CuK α radiation: $\lambda = 1.5406$ Å, 40 kV, and 30 mA) using a nickel filter and a one-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 5°–70° 2θ with a step size of 0.015 2° and a 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), to smooth the pattern (Savitzky and Golay, 1964), and to eliminate the $K\alpha_2$ component from each reflection (Rachinger, 1948). 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 dibromo-dioxo-(1,10-phenanthroline-N,N′)-molybdenum(VI) is shown in Figure 2. The XRPD data for the compound are given in Table I. All reflections were indexed successfully using the DICVOL06 program (Boulton and Louër, 2004) in a monoclinic unit cell. An absolute error of 0.03° (2θ), was assigned to all the peak positions used in the indexing of the pattern. 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 lattice 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) of the compound under study are compiled in Table II.

SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit <http://dx.doi.org/10.1017/S0885715615000949>.

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