

Chemistry of dimolybdenum complexes containing bridging anions of *N,N'*-di(3-methoxyphenyl)formamidine

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Dedicated to the memory of Professor F.A. Cotton, a great mentor and friend.

Abstract

Reaction of $\text{Mo}(\text{CO})_6$ with excess *N,N'*-di(3-methoxyphenyl)formamidine (HDmAniF) in *o*-dichlorobenzene afforded the yellow complex $\text{Mo}_2(\text{DmAniF})_4$, **1**. The structure of **1** reveals that the ligands bridge the two metal centers through the two nitrogen atoms, forming two *s-cis*, *s-trans* and two *s-trans*, *s-trans* conformations. Reaction of **1** with Me_3OBF_4 in CH_3CN gave *cis*- $[\text{Mo}_2(\text{DmAniF})_2(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$, **2**, which crystallized in two different forms. The first form, $2 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{CH}_3\text{CN}$, **2a**, showing one BF_4^- anion coordinating to the axial positions of the Mo–Mo bond [$\text{Mo} \cdots \text{F} = 2.685(4) \text{ \AA}$], contains two *cis* DmAniF[−] ligands which adopt the same *s-cis*, *s-trans* conformation. The other form, $2 \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{CH}_3\text{CN}$, **2b**, involves two independent molecules. While one [$\text{Mo} \cdots \text{N} = 2.692(8) \text{ \AA}$] of the two molecules shows axial interaction by CH_3CN [$\text{Mo} \cdots \text{N} = 2.692(8) \text{ \AA}$] and the two *cis* DmAniF[−] ligands adopt the same *s-cis*, *s-trans* conformation, the other one [$\text{Mo} \cdots \text{N} = 2.1317(9) \text{ \AA}$] shows no axial interaction and the two *cis* DmAniF[−] ligands adopt different conformations, which are *s-cis*, *s-trans* and *s-cis*, *s-cis*, respectively. The Mo–Mo distance of **2a**, 2.1281(6) Å, is the shortest among the compounds having $\text{Mo}_2(\mu_2\text{-L})_2(\text{CH}_3\text{CN})_4$ core, where L is the anionic, cationic or neutral form of a formamidine ligand. Reaction of **2** with NaOCH_3 in CH_3OH produced the tetranuclear complex *cis*- $[\text{Mo}_2(\text{DmAniF})_2]_2(\mu\text{-OCH}_3)_4$, **3**. The molecule of **3** bears four bridging CH_3O^- groups that link two quadruply bonded moieties and the ligands adopts the *s-trans*, *s-trans* conformation.

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1. Introduction

The coordination chemistry of formamidinate compounds has been investigated extensively during recent years [1–5]. Many efforts have been concentrated in their ability to form bridges between metal atoms. Preparations, structures and spectroscopic properties of tetrakis(μ -diarylformamidinato)dimolybdenum complexes of the type $\text{Mo}_2(\text{form})_4$, where form is the generic formamidinate, were the subjects of several studies [6]. Crystalline $\text{Mo}_2(\text{form})_4$ can be pre-

pared by stoichiometric ligand metathesis between the dimolybdenum tetraacetate $\text{Mo}_2(\text{O}_2\text{CR})_4$ and the lithiated formamidinate. A conformational descriptor for diarylformamidinate bearing an *m*-alkoxy substituent has been proposed by Ren and co-authors [5b]. Based on their proposition, three stable conformations exist for diarylformamidinate which are defined as (a) *s-cis*, *s-cis*- (*s-cis*/*s-trans*- are defined between the N–C (methine) bond and the ring C–C bond prioritized by the OR group), (b) *s-cis*, *s-trans*-, and (c) *s-trans*, *s-trans*- [5b].

Although dimolybdenum complexes containing *N,N'*-di(4-methoxyphenyl)formamidinate (HDpAniF) [4] and *N,N'*-di(2-methoxyphenyl)formamidinate (HDoAniF) [5g,5h]

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have been subjected to several studies, dimolybdenum complex containing their isomeric ligand *N,N'*-di(3-methoxyphenyl)formamidine (HDmAniF) has not been structurally characterized. We report herein several dimolybdenum complexes of the types $\text{Mo}_2(\text{DmAniF})_4$ and *cis*- $[\text{Mo}_2(\text{DmAniF})_2(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$, and a tetranuclear complex *cis*- $[\text{Mo}_2(\text{DmAniF})_2]_2(\mu\text{-OCH}_3)_4$. The syntheses, structures and ligand conformations of these complexes form the subject of this report.

2. Experimental section

2.1. General procedures

All manipulations were carried out under dry, oxygen-free nitrogen by using Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. Hexanes, THF and diethyl ether were purified by distillation from sodium/benzophenone, acetonitrile from CaH_2 , methanol from Mg/I_2 and dichloromethane from P_2O_5 . The visible absorption spectra were recorded on a Hitachi U-2000 spectrophotometer. NMR spectra were measured on a Bruker Avance 300 MHz spectrometer. IR spectra were obtained with the use of a Jasco FT/IR-460 plus spectrometer. Elemental analyses were obtained from a PE 2400 series II CHNS/O analyzer.

2.2. Materials

The complexes $\text{Mo}_2(\text{DmAniF})_4$ [2b], $[\text{Mo}_2(\text{CH}_3\text{CN})_{10}][\text{BF}_4]_4$ [7], and the ligand *N,N'*-di(3-methoxyphenyl)formamidine (HDmAniF) [5a,8] were prepared according to previously reported procedures. The reagents $\text{Mo}(\text{CO})_6$, Me_3OBF_4 and MeONa were purchased from Strem Chemical Co.

2.3. Preparation of $\text{Mo}_2(\text{DmAniF})_4$ (1)

$\text{Mo}(\text{CO})_6$ (1.0 g, 3.79 mmol) and HDmAniF (2.43 g, 9.47 mmol) were placed in a flask containing 10 mL *o*-dichlorobenzene. The mixture was then refluxed for 20 h to yield a brown solution. After the mixture was cooled to room temperature, 80 mL MeOH was then added to give a yellow precipitate. The precipitate was filtered, washed by diethyl ether and then dried under reduced pressure to give the yellow product. Yield: 1.72 g (75%). UV-vis: 443 nm (CH_2Cl_2 , $\epsilon = 2636 \text{ M}^{-1} \text{ cm}^{-1}$). ^1H NMR (CDCl_3 , ppm): 8.54 (s, 4H, CH), 6.85 (t, 8H, H^{meta}), 6.44 (d, 8H, H^{para}), 6.03 (d, 8H, H^{ortho}), 5.80 (s, 8H, H^{ortho}), 3.26 (s, 24H, OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): 160.45 (C), 157.68 (CH), 152.02 (C), 129.73 (CH), 115.19 (CH), 110.16 (CH), 108.01 (CH), 54.92 (CH_3). Calc. for $\text{C}_{60}\text{H}_{60}\text{Mo}_2\text{N}_8\text{O}_8$ ($MW = 1213.04$): C, 59.40; H, 4.98; N, 9.24%;

Table 1
Crystal data for compounds 1–3

Compound	1	2a	2b	3
Formula	$\text{C}_{60}\text{H}_{60}\text{Mo}_2\text{N}_8\text{O}_8$	$\text{C}_{41}\text{H}_{47}\text{B}_2\text{Cl}_2\text{F}_8\text{Mo}_2\text{N}_9\text{O}_4$	$\text{C}_{39.5}\text{H}_{44.5}\text{B}_2\text{ClF}_8\text{Mo}_2\text{N}_{8.5}$	$\text{C}_{64}\text{H}_{72}\text{Mo}_4\text{N}_8\text{O}_{12}$
Fw	1213.04	1166.28	1103.29	1529.06
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
A, Å	15.9394(8)	11.6403(9)	13.0132(7)	8.7284(8)
B, Å	9.8710(5)	12.3965(10)	19.5509(10)	12.5187(11)
C, Å	18.2809(10)	18.9062(13)	22.4735(12)	15.325(4)
α , °	90	103.426(5)	96.721(1)	103.059(12)
β , °	106.415(1)	103.615(5)	106.810(1)	100.854(12)
γ , °	90	97.719(7)	107.319(1)	96.747(7)
V, Å ³	2759.0(2)	2527.0(3)	5094.5(5)	1579.5(4)
Z	2	2	4	1
$d_{\text{calc.}}$, g/cm ³	1.460	1.533	1.438	1.608
F(000)	1248	1176	2224	776
Cryst. size, mm	0.44 × 0.48 × 0.74	0.2 × 0.6 × 0.8	0.3 × 0.4 × 0.4	0.1 × 0.4 × 0.4
$\mu(\text{Mo K}\alpha)$, mm ⁻¹	0.518	0.680	0.619	0.844
reflections collected	10605	10104	24790	6637
Independent reflections	4774 [$R(\text{int}) = 0.0288$]	8734 [$R(\text{int}) = 0.0246$]	16984 [$R(\text{int}) = 0.0362$]	5487 [$R(\text{int}) = 0.0316$]
Data/restraints/parameters	4774/0/472	8734/0/613	16984/6/1183	5487/0/474
Quality-of-fit indicator ^c	1.091	1.046	1.024	1.039
final R indices [$I > 2\sigma(I)$] ^{a,b}	$R_1 = 0.0278$ $wR_2 = 0.0749$	$R_1 = 0.0615$ $wR_2 = 0.1670$	$R_1 = 0.0694$ $wR_2 = 0.1526$	$R_1 = 0.0529$ $wR_2 = 0.1231$
R indices (all data)	$R_1 = 0.0293$ $wR_2 = 0.0767$	$R_1 = 0.0725$ $wR_2 = 0.1785$	$R_1 = 0.0819$ $wR_2 = 0.1616$	$R_1 = 0.0821$ $wR_2 = 0.1388$
Largest diff. peak and hole, e/Å ³	0.319 and -0.495	1.118 and -1.344	1.464 and -0.646	1.001 and -0.838

^a $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

^b $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + (bp)]$, $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. $a = 0.0369$, $b = 1.4931$, **1**; $a = 0.1022$, $b = 5.5102$, **2a**; $a = 0.0315$, $b = 26.2974$, **2b**; $a = 0.0566$, $b = 5.0489$, **3**.

^c Quality-of-fit = $[\Sigma w(|F_o^2| - |F_c^2|)^2/N_{\text{observed}} - N_{\text{parameters}}]^{1/2}$.

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