metal-organic papers

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Key indicators

Single-crystal X-ray study
$T = 213$ K
Mean σ(C–C) = 0.010 Å
H-atom completeness 78%
Disorder in solvent or counterion
R factor = 0.057
wR factor = 0.166
Data-to-parameter ratio = 14.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

A molecular pair having two quadruply bonded dimolybdenum units linked by a terephthalate dianion

The title compound, μ-terephthalate-bis[tris(μ-N,N'-di-p-anisylformamidinate)dimolybdenum(II)] hexane disolvate, [{Mo$_2$(DAniF)$_3$}$_2$(μ-O$_2$CC$_6$H$_4$CO$_2$)] (DAniF is N,N'-di-p-anisylformamidinate, C$_{15}$H$_{15}$N$_2$O$_2$) crystallizes as the bis(-hexane) solvate, in the form of large red needles, in space group $P2_1/c$. The molecule sits on an inversion center, and the bridging aryl ring displays a twist angle of 8.6 (10)° with respect to the plane defined by the two Mo$_2$ axes.

## Comment

We have been interested in the preparation, structural characterization, and electrochemical study of compounds having metal–metal bonded units linked by a variety of groups, such as dicarboxylates (Cotton, Lin & Murillo, 2001*a*, 2002), XO_4^{2-} (for X = S, Mo, and W) (Cotton, Donahue & Murillo, 2001), CO_3^{2-} (Cotton, Lin & Murillo, 2001*b*), and diamidates (Cotton, Daniels *et al.*, 2002). These give rise to a number of molecular architectures such as pairs, triangles, squares, cages, one- and two-dimensional arrays, and more complex structures.

(*A*)

= dianion of a dicarboxylic acid

N,N'-di(p-anisyl)formamidinate = (DAniF)
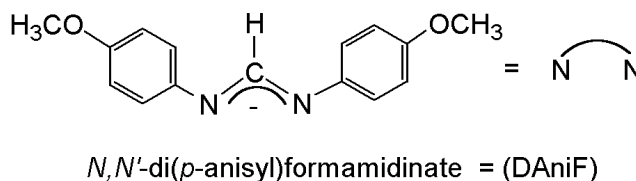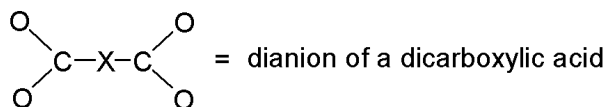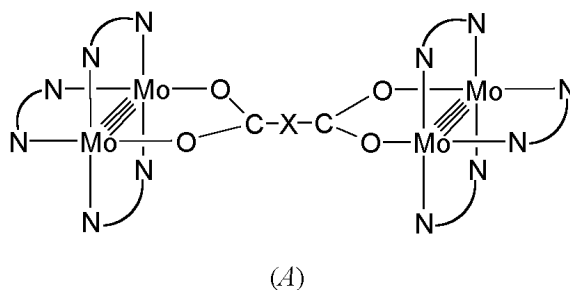
Figure 1
Generic structure type for dicarboxylate bridged pairs of Mo$_2$(DAniF)$_3^+$ units.

·2C₆H₁₄

(I)
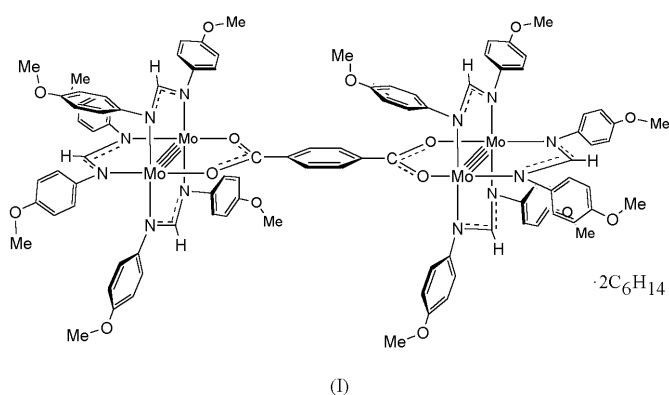
The simplest members of the family are pairs with two quadruply bonded $Mo_2(DAniF)_3^+$ units linked by dicarboxylate anions (A in Fig. 1). Here DAniF represents the anion of N,N'-di-p-anisylformamidine. For dicarboxylate linkers, we have reported 14 structures ranging from oxalate, the simplest of the family, to units of various lengths and degrees of conjugation (Cotton, Donahue, Lin & Murillo, 2001), with some also having chiral linkages (Cotton, Donahue & Murillo, 2002). Compounds of this type generally display two reversible oxidations, one corresponding to each Mo_2^{4+} unit, the separation between which is determined by the length and nature of the dicarboxylate bridge. To provide a structural benchmark and a more complete context for discussion of the properties of bridged compounds with aryl linkers, we now present the structure of [{$Mo_2(DAniF)_3$}$_2$-(μ-$O_2CC_6H_4CO_2$)]·2C₆H₁₄, (I).

Compound (I) was prepared in 57% yield by method B of a literature procedure (Cotton, Donahue, Lin & Murillo, 2001) and crystallized as large red needles. The bridging aryl ring displays a twist angle of 8.6 (10)° with respect to the plane defined by the two Mo_2 axes (Fig. 2). This value is relatively modest compared to the corresponding angles of 30.6, 34.2, and 32.9° observed, respectively, in the structures of [{$Mo_2(DAniF)_3$}$_2$(μ-$O_2CC_6F_4CO_2$)] (Cotton, Donahue, Lin & Murillo, 2001), [{$Mo_2(DAniF)_3$}$_2$$\{\mu$-OCN(Ph)C₆H₄CON(Ph)}] (Cotton, Daniels et al., 2002), and [{$Mo_2(DAniF)_3$}$_2$$\{\mu$-OCN($m$-CF₃Ph)C₆H₄CON($m$-CF₃Ph)}] (Cotton, Daniels et al., 2002). One effect of this out-of-plane twist is that the $\Delta E_{1/2}$ between successive Mo_2^{4+}/Mo_2^{5+} oxidations is small (100 mV) and of a value consistent with through-space interaction rather than effective communication through the aryl π system. The distance between the centers of the Mo_2 units is 11.236 Å; all other metric parameters (Table 1), including the Mo—Mo distance of 2.0904 (7) Å, are unexceptional.

Future work will describe the preparations, crystal structures, electrochemistry, absorption spectra, and electronic structures, as revealed by both static and time-dependent DFT (density functional theory) calculations of a new series of [{$Mo_2(DAniF)_3$}$_2$(μ-O_2CXCO_2)] compounds, where the bridging species are highly unsaturated dicarboxylate dianions.

Experimental

The title compound was prepared according to method B in the published procedure of Cotton et al. (2001) and crystallized as the bis(hexane) solvate by diffusion of hexanes into a dichloromethane solution under an N₂ atmosphere.

Crystal data

[Mo₄(C₁₅H₁₅N₂O₂)₆-(C₈H₄O₄)]·2C₆H₁₄	$D_x = 1.463$ Mg m⁻³
$M_r = 2251.96$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5933
$a = 14.6579$ (15) Å	reflections
$b = 18.1630$ (19) Å	$\theta = 2.2$–24.8°
$c = 19.268$ (2) Å	$\mu = 0.55$ mm⁻¹
$\beta = 94.621$ (2)°	$T = 213$ (2) K
$V = 5113.2$ (9) Å³	Needle, red
$Z = 2$	$0.46 \times 0.15 \times 0.08$ mm

Data collection

Bruker SMART 1000 area-detector diffractometer	9046 independent reflections
ω scans	5610 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Blessing, 1995)	$R_{int} = 0.069$
	$\theta_{max} = 25.1°$
$T_{min} = 0.788$, $T_{max} = 0.958$	$h = -10 \rightarrow 17$
29479 measured reflections	$k = -21 \rightarrow 21$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$+ 6.2815P]$
$wR(F^2) = 0.166$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.029$
9046 reflections	$\Delta\rho_{max} = 1.11$ e Å⁻³
626 parameters	$\Delta\rho_{min} = -0.63$ e Å⁻³
H-atom parameters constrained	
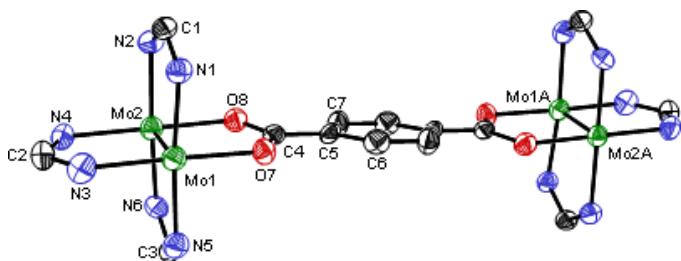
Figure 2

The core structure of [{$Mo_2(DAniF)_3$}$_2$(μ-$O_2C_6H_4CO_2$)], showing 50% probability displacement ellipsoids. For clarity, the p-anisyl groups and all H atoms have been omitted.

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Table 1
Selected geometric parameters (Å, °).

Mo1—Mo2	2.0904 (7)	N2—C13	1.425 (7)
Mo1—N3	2.123 (5)	N3—C20	1.333 (8)
Mo1—O1	2.144 (4)	N3—C21	1.415 (8)
Mo1—N5	2.152 (5)	N4—C20	1.324 (8)
Mo1—N1	2.155 (5)	N4—C28	1.439 (7)
Mo2—N4	2.119 (5)	N5—C35	1.317 (8)
Mo2—O2	2.122 (4)	N5—C36	1.433 (7)
Mo2—N6	2.137 (5)	N6—C35	1.326 (7)
Mo2—N2	2.137 (5)	N6—C43	1.408 (8)
O1—C1	1.266 (7)	C1—C2	1.473 (8)
O2—C1	1.279 (6)	C2—C4	1.395 (8)
N1—C5	1.327 (7)	C2—C3	1.398 (8)
N1—C6	1.413 (8)	C3—C4^i	1.364 (9)
N2—C5	1.322 (8)	C4—C3^i	1.364 (9)
Mo2—Mo1—N3	92.69 (14)	C5—N2—Mo2	116.6 (4)
Mo2—Mo1—O1	91.33 (11)	C13—N2—Mo2	122.9 (4)
N3—Mo1—O1	175.97 (18)	C20—N3—C21	118.8 (5)
Mo2—Mo1—N5	93.70 (13)	C20—N3—Mo1	117.3 (4)
N3—Mo1—N5	91.8 (2)	C21—N3—Mo1	122.7 (4)
O1—Mo1—N5	88.23 (17)	C20—N4—C28	120.2 (5)
Mo2—Mo1—N1	92.10 (14)	C20—N4—Mo2	117.7 (4)
N3—Mo1—N1	91.6 (2)	C28—N4—Mo2	120.6 (4)
O1—Mo1—N1	87.95 (17)	C35—N5—C36	117.4 (5)
N5—Mo1—N1	173.13 (18)	C35—N5—Mo1	115.4 (4)
Mo1—Mo2—N4	92.81 (14)	C36—N5—Mo1	127.1 (4)
Mo1—Mo2—O2	92.45 (11)	C35—N6—C43	117.8 (5)
N4—Mo2—O2	174.51 (17)	C35—N6—Mo2	117.5 (4)
Mo1—Mo2—N6	91.96 (13)	C43—N6—Mo2	124.3 (4)
N4—Mo2—N6	91.58 (19)	O1—C1—O2	122.5 (5)
O2—Mo2—N6	89.82 (17)	O1—C1—C2	120.1 (5)
Mo1—Mo2—N2	93.49 (13)	O2—C1—C2	117.3 (5)
N4—Mo2—N2	92.7 (2)	C4—C2—C3	117.6 (6)
O2—Mo2—N2	85.39 (17)	C4—C2—C1	121.6 (5)
N6—Mo2—N2	172.9 (2)	C3—C2—C1	120.9 (5)
C1—O1—Mo1	116.9 (4)	C4^i—C3—C2	121.7 (6)
C1—O2—Mo2	116.7 (4)	C3^i—C4—C2	120.8 (6)
C5—N1—C6	118.8 (5)	N2—C5—N1	120.7 (6)
C5—N1—Mo1	116.7 (4)	N4—C20—N3	119.5 (6)
C6—N1—Mo1	124.5 (4)	N5—C35—N6	121.3 (6)
C5—N2—C13	118.6 (5)		

Symmetry code: (i) $2 - x, 2 - y, -z$.

All H atoms were refined as riding atoms with isotropic displacement parameters. The molecules of interstitial hexanes were highly disordered and were refined with fixed partial site-occupancy factors. Disorder in a *p*-methoxy group of one of the *N,N'*-di-*p*-anisylformamidinate ligands caused slight oscillation of its H atoms; this gradually diminished as the structure was subjected to extended refinement cycles.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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