Crystal structure of bisacetonitrile-tetracarbonylmolybdenum — acetonitrile solvate, $\text{Mo}(\text{CO})_4(\text{NCCH}_3)_2 \cdot \text{CH}_3\text{CN}$

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Abstract

$\text{C}_{10}\text{H}_9\text{MoN}_3\text{O}_4$, monoclinic, $C12/c1$ (No. 15), $a = 12.904(2)$ Å, $b = 12.771(2)$ Å, $c = 9.211(1)$ Å, $\beta = 116.16(2)^\circ$, $V = 1362.5$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.064$, $wR_{\text{ref}}(F^2) = 0.156$, $T = 193$ K.

Source of material

Molybdenum hexacarbonyl was suspended in dry acetonitrile and dissolved by heating to 353 K (8 h). Upon cooling to 253 K a mixture of $\text{Mo}(\text{CO})_6$ and $\text{Mo}(\text{CO})_4(\text{NCCH}_3)_2 \cdot \text{CH}_3\text{CN}$ crystallized. 0.30 g of this mixture were redissolved in 12 mL of acetonitrile. After 20 hours at 253 K a first fraction of $\text{Mo}(\text{CO})_6$ crystallized. Its filtrate was evaporated to 8 mL and at 243 K $\text{Mo}(\text{CO})_4(\text{NCCH}_3)_2 \cdot \text{CH}_3\text{CN}$ was obtained.

Experimental details

The H atoms of the non-coordinated acetonitrile molecule (N2–C5–C6) were not taken into account. Additionally, the positions of the H atoms of coordinated acetonitrile (N1–C3–C4) are not reliable.

Discussion

The molecular structure agrees with results by spectroscopic studies [1]. The arrangement of the four carbonyl groups is comparable to that in $[\text{Mo}(\text{CO})_4\text{I}]_2$ [2]. The site symmetry of the $\text{Mo}(\text{CO})_4(\text{NCCH}_3)_2$ molecule is 2. The additional acetonitrile molecule is situated on the two-fold rotation axis. Therefore, the methyl group must be disordered. Its H atoms were not localized. Due to the mutual *trans* influence, the Mo–C(1) bond is longer than Mo–C(2), which is *trans* to a weakly bonded acetonitrile ligand.

Table 1. Data collection and handling.

Crystal:	yellow fragment, size $0.10 \times 0.20 \times 0.30$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	9.57 cm^{-1}
Diffractionmeter, scan mode:	Stoe IPDS, φ
$2\theta_{\text{max}}$:	51.82°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4583, 1287
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 878
$N(\text{param})_{\text{refined}}$:	96
Program:	SHELX-97 [3]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(4A)	8 <i>f</i>	0.373(8)	−0.041(8)	−0.17(1)	0.06(3)
H(4B)	8 <i>f</i>	0.26(1)	−0.032(9)	−0.13(2)	0.07(4)
H(4C)	8 <i>f</i>	0.36(1)	−0.04(1)	−0.07(2)	0.09(6)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Mo	4 <i>e</i>	1/2	0.27495(9)	1/4	0.0307(4)	0.0350(5)	0.0278(5)	0	0.0056(3)	0
C(1)	8 <i>f</i>	0.3657(6)	0.2805(7)	0.3098(9)	0.041(3)	0.034(4)	0.033(4)	0.002(4)	0.005(3)	0.003(4)
O(1)	8 <i>f</i>	0.2901(5)	0.2895(6)	0.3442(9)	0.052(3)	0.085(6)	0.072(5)	0.008(3)	0.037(3)	0.014(4)
C(2)	8 <i>f</i>	0.4236(6)	0.3840(8)	0.092(1)	0.033(3)	0.052(6)	0.035(5)	−0.009(4)	0.010(3)	−0.007(4)
O(2)	8 <i>f</i>	0.3789(5)	0.4529(6)	−0.0028(8)	0.058(3)	0.056(4)	0.047(4)	0.018(3)	0.018(3)	0.022(3)
N(1)	8 <i>f</i>	0.4151(5)	0.1451(6)	0.0786(8)	0.038(3)	0.036(4)	0.032(4)	−0.006(3)	0.007(3)	−0.006(3)
C(3)	8 <i>f</i>	0.3740(6)	0.0767(7)	−0.006(1)	0.035(3)	0.040(5)	0.038(5)	0.007(4)	0.012(3)	0.004(4)
C(4)	8 <i>f</i>	0.320(1)	−0.0111(9)	−0.118(2)	0.041(5)	0.045(6)	0.049(6)	−0.005(5)	0.006(5)	−0.013(5)
N(2)	4 <i>e</i>	0	0.373(1)	1/4	0.068(7)	0.07(1)	0.063(9)	0	0.018(6)	0
C(5)	4 <i>e</i>	0	0.286(2)	1/4	0.045(6)	0.08(1)	0.041(7)	0	0.019(5)	0
C(6)	4 <i>e</i>	0	0.172(1)	1/4	0.09(1)	0.044(9)	0.06(1)	0	0.037(8)	0

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