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Crystal structure of bis(tetra-*n*-butylammonium) tris(2-sulfidopropionato)sulfidodioxodimolybdate(V) monohydrate, $[(NC_4H_9)_4]_2Mo_2O_2S(C_2H_4SCOO)_3 \cdot H_2O$

M. Liu-González[I], F. Sanz-Ruíz[I], P. Palanca[II], V. Sanz[II], M. Pérez-Priede[III], S. García-Granda*[,III] and E. García-Rodríguez[III]

[I] Universidad de Valencia, Facultad de Física, Departamento de Termodinámica, Avenida Dr. Moliner 50, 46100 Burjassot-Valencia, Spain
[II] Universidad de Valencia, Facultad de Química, Departamento de Química Orgánica, Avenida Dr. Moliner 50, 46100 Burjassot-Valencia, Spain
[III] Universidad de Oviedo, Facultad de Química, Departamento de Química Física y Analítica, 33006 Oviedo, Asturias, Spain

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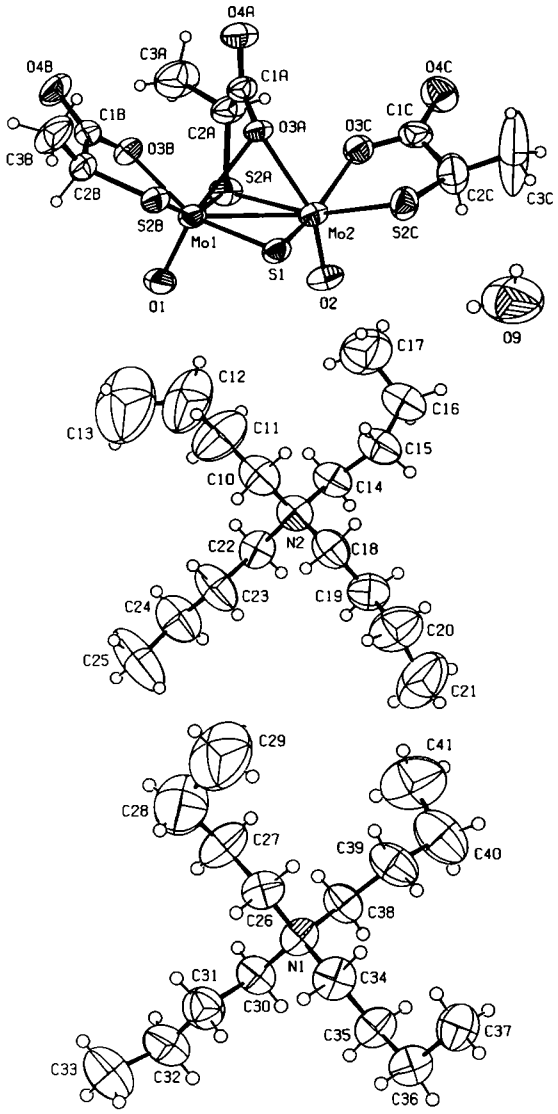

Abstract

$C_{41}H_{86}Mo_2N_2O_9S_4$, triclinic, $P\bar{1}$ (no. 2), $a = 10.498(9)$ Å, $b = 14.555(3)$ Å, $c = 18.546(8)$ Å, $\alpha = 96.61(4)°$, $\beta = 101.64(6)°$, $\gamma = 97.86(6)°$, $V = 2719.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.077$, $wR_{ref}(F^2) = 0.214$, $T = 293$ K.

* Correspondence author (e-mail: sgg@fq.uniovi.es)

Source of material

$[Mo^{VI}O_2(OCOCH(S)CH_3)_2]$ is reduced by $CH_3CH(SH)CO_2H$ to the stable dimeric molybdenum(V) complexes $[Mo_2{}^{V}O_2S(OCOCH(S)CH_3)_3]$ and $[Mo_2{}^{V}O_2S_2(OCOCH(S)CH_3)]_2$, and the thiolactic acid is oxidized to disulfide as shown by ^{1}H and ^{13}C NMR spectroscopy. The ESR spectrum of this reaction shows the presence of a monomeric molybdenum(V) species, with an isotropic g-value of $\langle g \rangle = 1.976$ and an isotropic 95.97 Mo hyperfine parameter $\langle A \rangle = 36 \times 10^{-4}$ cm^{-1}, respectively, which rapidly dimerizes forming an ESR-silent molybdenum(V) complex. In a reaction vessel previously deoxygenated, 50 mmol thiolactic acid ($CH_3CH(SH)CO_2H$), 6 mmol (n-$C_4H_9)_4NBr$ and 2 mmol $Na_2[MoO_4] \cdot 2H_2O$ were placed. Over these 20 ml of methanol (previously deoxygenated by bubbling argon 30 min in an ultrasonic bath) was added under argon stream, which was maintained for an additional 15 min, and then the vessel was flame-sealed. By cooling the resulting solution to 5 °C overnight, clear orange and yellow prismatic crystals were obtained.

Elemental analysis: found – C, 46.75 %; H, 8.04 %; N, 2.67 %; S, 12.20 %; calc. for $Mo_2O_8S_4C_{41}H_{84}N_2$ – C, 46.76 %; H, 8.04 %; N, 2.66 %; S, 12.18 %. ^{1}H, ^{13}C NMR, IR and UV/VIS data are available in the CIF.

Experimental details

Due to the low crystal quality the number of observed reflections was small, the crystal decay hight and geometrical restraints were used when needed. Distance restraints were applied to the N–C–C–C chains on both tetrabutylammonium moieties to keep all distances close to 1.50 Å. The $OCOCH(S)CH_3$ ligands were refined keeping similar bond lengths and angles using soft restraints. H atoms were geometrically fixed to their parent ones and their displacement parameters calculated as $1.2U_{eq}$(C) or $1.5U_{eq}$(C). At the end of the refinement the highest peak in the electron density was of 0.68 eÅ^{-3} and the deepest hole of –0.57 eÅ^{-3}, near Mo1 and Mo2 respectively.

Discussion

Thiols may be considered physiological reductants acting as endogenous electron donors in reductase reactions of molybdenum hydroxylases [1] in animals and microorganisms. Previous studies showed [2-5] that reduction of aqueous molybdate by 2-mercapto-acetic acid (thioglycolic acid) yields solutions exhibiting ESR signals which account for about 1 % of the available molybdenum with parameters similar to those for xanthine oxidase. Thereafter these authors demonstrated the capacity of molybdate

ions to oxidize thioglycolic acid, cysteine and glutathione giving disulfide derivatives. The proposed mechanism involves the formation of the $[Mo^{VI}O_2(OCOCH_2(S))_2]$ complex which is subsequently reduced by excess of thioglycolic acid to give an ESR-active monomeric molybdenum(V) species which rapidly dimerizes forming an ESR-silent-oxo complex and disulfide. Our investigations [6,7] have demonstrated that the Mo(VI) complexes containing sterically hindered ligands can be quantitatively reduced by the free acid yielding the monomeric molybdenum(V) complexes, the structure of which has been determined by X-ray crystallography. All these features have encouraged us to carry out a more detailed examination of the reaction products of the molybdenum-thioglycolic acid derivative systems in order to obtain more detailed information on its reaction mechanism.

The crystal structure of the title compound consist of a dimeric molybdenum(V) complex anion with tetrabutylammonium as the counter ions and one water molecule linked by an H bond to one of the carboxylic oxygen atoms (O4A) of the complex. The binuclear complex anion exhibits a cofacial bi-octahedral geometry which appears to be quite common in molybdenum(V) chemistry. Each molybdenum is bonded to one fully deprotonated terminal thioglycolate dianion acting as a bidentate ligand through the thiolic sulfur and carboxylic oxygen atoms. It was observed a sulfur atom bonded to each molybdenum in a *syn* conformation. The distorted-octahedral geometry of each molybdenum is completed by a brinding sulfur group and one dianionic thioglycate ligand doubly brinding through its thiolic sulfur and carboxylic oxygen atoms.

As is usual for oxomolybdenum complexes, the Mo atom is not a centre of the coordination octahedron but is shifted toward the terminal unshared oxygen atom. Distortion from a regular octahedral coordination is evident in the values of the axial angles which range from 149.5(2)° to 162.0(1)°. Alternatively, the complex may also be viewed in terms of two squared-pyramidal coordination polyhedra sharing an edge, with a sixth more distant ligand (carboxylate (O3A)) *trans* to both Mo=O bonds. The bond lengths Mo=O of 1.682(6) Å and 1.671(6) Å are according with other reported values for Mo^{V}=O bonds. The Mo—Mo distance of 2.781(2) Å, indicative of a direct single metal-metal bond, as well as the pattern of angles for the triply bridged unit are consistent with those found for similar triply bridged molybdenum(V) complexes. The doubly brinding thioglycate ligand is contained on a LSQ-plane nearly perpendicular (89.9(2)°) to the LSQ-plane built for Mo1-Mo2-S1-S2A. In the same way, the LSQ-planes containing the other thioglycate form dihedral angles of 18.6(3)° and 14.9(3)° with the LSQ-plane built for Mo1-Mo2-S1-S2A.

Table 1. Data collection and handling.

Crystal:	red, prismatic, size 0.16 × 0.20 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.61 cm^{-1}
Diffractometer, scan mode:	Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9897, 9571
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4380
$N(param)_{refined}$:	529
Programs:	DIRDIF [8], SHELX-97 [9], PLATON [10], WinGX [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.5093	0.4092	0.2825	0.105
H(3A)	2*i*	0.5644	0.5108	0.2046	0.219
H(3B)	2*i*	0.5125	0.5597	0.2702	0.219
H(3C)	2*i*	0.4209	0.5343	0.1903	0.219
H(5)	2*i*	−0.0451	0.4149	0.0255	0.112
H(6A)	2*i*	−0.2316	0.4404	0.0631	0.198
H(6B)	2*i*	−0.1421	0.5351	0.0612	0.198
H(6C)	2*i*	−0.1472	0.4998	0.1374	0.198
H(8)	2*i*	0.4388	0.0767	0.3530	0.150
H(9A)	2*i*	0.3287	0.0283	0.4404	0.607
H(9B)	2*i*	0.3670	0.1311	0.4828	0.607
H(9C)	2*i*	0.4775	0.0726	0.4705	0.607
H(26A)	2*i*	0.7124	0.1008	0.7680	0.107
H(26B)	2*i*	0.5885	0.1223	0.7974	0.107
H(35A)	2*i*	0.7953	0.1273	1.0160	0.105
H(35B)	2*i*	0.9217	0.1064	0.9886	0.105
H(14A)	2*i*	0.9564	0.2703	0.2697	0.103
H(14B)	2*i*	0.9195	0.1831	0.3078	0.103
H(38A)	2*i*	0.7675	0.2591	0.9690	0.097
H(38B)	2*i*	0.7103	0.2988	0.8965	0.097
H(18A)	2*i*	0.8113	0.3932	0.3590	0.118
H(18B)	2*i*	0.9324	0.4375	0.4234	0.118
H(23A)	2*i*	1.1236	0.3502	0.5122	0.149
H(23B)	2*i*	1.1478	0.4378	0.4717	0.149
H(34A)	2*i*	0.6643	0.0505	0.9011	0.104
H(34B)	2*i*	0.7922	0.0341	0.8739	0.104

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(15A)	2*i*	0.7467	0.2981	0.2453	0.137
H(15B)	2*i*	0.7055	0.2327	0.3012	0.137
H(19A)	2*i*	0.9282	0.4291	0.2704	0.134
H(19B)	2*i*	1.0584	0.4632	0.3319	0.134
H(16A)	2*i*	0.6324	0.1676	0.1700	0.138
H(16B)	2*i*	0.7797	0.1579	0.1714	0.138
H(10A)	2*i*	0.9125	0.3065	0.4820	0.129
H(10B)	2*i*	0.7887	0.2608	0.4198	0.129
H(36A)	2*i*	0.8443	−0.0568	0.9792	0.108
H(36B)	2*i*	0.8729	−0.0056	1.0614	0.108
H(39A)	2*i*	0.5654	0.1548	0.9501	0.139
H(39B)	2*i*	0.5093	0.2043	0.8827	0.139
H(22A)	2*i*	1.1319	0.3406	0.3608	0.102
H(22B)	2*i*	1.1166	0.2519	0.4005	0.102
H(30A)	2*i*	0.9011	0.2731	0.8611	0.093
H(30B)	2*i*	0.9512	0.2200	0.9272	0.093
H(41A)	2*i*	0.4686	0.4123	0.9814	0.287
H(41B)	2*i*	0.4202	0.3469	0.9046	0.287
H(41C)	2*i*	0.5678	0.3960	0.9301	0.287
H(27A)	2*i*	0.7618	0.2627	0.7579	0.156
H(27B)	2*i*	0.6265	0.2753	0.7777	0.156
H(31A)	2*i*	0.9249	0.1485	0.7761	0.128
H(31B)	2*i*	0.9723	0.0933	0.8420	0.128
H(37A)	2*i*	0.6728	−0.1061	1.0341	0.175
H(37B)	2*i*	0.6202	−0.0529	0.9682	0.175
H(37C)	2*i*	0.6491	−0.0024	1.0506	0.175
H(24A)	2*i*	1.3217	0.3064	0.4933	0.162
H(24B)	2*i*	1.3450	0.3904	0.4493	0.162
H(40A)	2*i*	0.4504	0.2558	0.9991	0.187
H(40B)	2*i*	0.5970	0.3066	1.0272	0.187
H(11A)	2*i*	1.0058	0.1703	0.4657	0.209
H(11B)	2*i*	0.8813	0.1244	0.4031	0.209
H(9I)	2*i*	0.7490	0.4147	0.5945	0.297
H(9J)	2*i*	0.6873	0.4133	0.5216	0.297
H(20A)	2*i*	0.8347	0.5536	0.3099	0.200
H(20B)	2*i*	0.9439	0.5805	0.3837	0.200
H(28A)	2*i*	0.6237	0.2574	0.6457	0.235
H(28B)	2*i*	0.6359	0.1516	0.6504	0.235
H(17A)	2*i*	0.6673	0.0162	0.1860	0.279
H(17B)	2*i*	0.6242	0.0636	0.2554	0.279
H(17C)	2*i*	0.7729	0.0556	0.2596	0.279
H(25A)	2*i*	1.4759	0.4257	0.5680	0.357

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(25B)	2*i*	1.3510	0.4111	0.6021	0.357
H(25C)	2*i*	1.3742	0.4952	0.5581	0.357
H(32A)	2*i*	1.1072	0.2720	0.8313	0.165
H(32B)	2*i*	1.1579	0.2072	0.8889	0.165
H(33A)	2*i*	1.2705	0.2009	0.7933	0.325
H(33B)	2*i*	1.1372	0.1644	0.7352	0.325
H(33C)	2*i*	1.1912	0.1016	0.7937	0.325
H(21A)	2*i*	0.9818	0.6834	0.3011	0.367
H(21B)	2*i*	0.9899	0.5995	0.2420	0.367

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(21C)	2*i*	1.0987	0.6266	0.3158	0.367
H(29A)	2*i*	0.4149	0.1652	0.6153	0.400
H(29B)	2*i*	0.4285	0.2370	0.6874	0.400
H(29C)	2*i*	0.4411	0.1319	0.6937	0.400
H(13A)	2*i*	0.8934	0.0992	0.6100	0.549
H(13B)	2*i*	1.0118	0.1549	0.5851	0.549
H(13C)	2*i*	0.9603	0.0493	0.5517	0.549
H(12A)	2*i*	0.8008	0.1866	0.5275	0.295
H(12B)	2*i*	0.7715	0.0835	0.4852	0.295

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	2*i*	0.17253(9)	0.29426(6)	0.12378(5)	0.0797(7)	0.0439(5)	0.0586(6)	0.0019(4)	0.0219(5)	0.0020(4)
Mo(2)	2*i*	0.31241(9)	0.19768(6)	0.22530(5)	0.0656(6)	0.0457(5)	0.0680(6)	0.0053(4)	0.0191(5)	−0.0004(4)
S(1)	2*i*	0.0903(3)	0.1592(2)	0.1670(1)	0.068(2)	0.044(1)	0.071(2)	−0.001(1)	0.013(1)	0.003(1)
O(1)	2*i*	0.1859(7)	0.2517(5)	0.0379(4)	0.120(6)	0.069(5)	0.062(4)	0.006(4)	0.028(4)	−0.002(4)
O(2)	2*i*	0.3814(7)	0.1220(4)	0.1770(4)	0.078(5)	0.061(4)	0.099(5)	0.014(4)	0.027(4)	−0.013(4)
O(3A)	2*i*	0.2330(5)	0.3381(3)	0.2553(3)	0.064(4)	0.041(3)	0.060(4)	−0.001(3)	0.021(3)	−0.006(3)
C(1A)	2*i*	0.3179(8)	0.4148(5)	0.2765(5)	0.074(7)	0.049(6)	0.072(7)	−0.003(5)	0.020(6)	0.002(5)
C(2A)	2*i*	0.4387(9)	0.4218(5)	0.2433(5)	0.12(1)	0.054(7)	0.094(9)	−0.015(6)	0.048(8)	0.002(6)
S(2A)	2*i*	0.4170(3)	0.3256(2)	0.1682(2)	0.085(2)	0.069(2)	0.081(2)	−0.004(2)	0.038(2)	0.003(2)
O(4A)	2*i*	0.3069(7)	0.4787(4)	0.3223(4)	0.106(6)	0.070(5)	0.088(5)	−0.002(4)	0.033(5)	−0.016(4)
C(3A)	2*i*	0.489(1)	0.5149(6)	0.2255(7)	0.18(2)	0.10(1)	0.16(1)	−0.03(1)	0.07(1)	0.01(1)
O(3B)	2*i*	0.1920(6)	0.4359(4)	0.1267(4)	0.105(6)	0.044(4)	0.082(5)	0.003(4)	0.019(5)	0.010(4)
C(1B)	2*i*	0.0986(9)	0.4844(5)	0.1103(5)	0.12(1)	0.055(7)	0.058(7)	0.001(7)	0.012(7)	0.007(6)
C(2B)	2*i*	−0.0389(8)	0.4298(5)	0.0791(5)	0.13(1)	0.052(6)	0.077(8)	0.009(7)	−0.016(7)	0.007(6)
S(2B)	2*i*	−0.0514(3)	0.3174(2)	0.1128(2)	0.081(2)	0.053(2)	0.071(2)	0.009(1)	0.006(2)	0.003(1)
O(4B)	2*i*	0.1165(8)	0.5698(4)	0.1207(5)	0.156(8)	0.041(4)	0.126(7)	−0.003(5)	−0.014(6)	0.011(4)
C(3B)	2*i*	−0.1497(9)	0.4808(7)	0.0858(8)	0.11(1)	0.078(9)	0.19(2)	0.045(8)	−0.03(1)	0.009(9)
O(3C)	2*i*	0.4547(6)	0.2502(4)	0.3184(4)	0.077(5)	0.066(4)	0.075(5)	0.010(4)	0.020(4)	0.009(4)
C(1C)	2*i*	0.4760(9)	0.2148(6)	0.3798(5)	0.078(8)	0.076(8)	0.079(9)	0.014(6)	−0.012(7)	−0.013(7)
C(2C)	2*i*	0.3938(9)	0.1207(7)	0.3785(6)	0.13(1)	0.11(1)	0.11(1)	−0.020(9)	−0.020(9)	0.039(9)
S(2C)	2*i*	0.2356(3)	0.1104(2)	0.3145(2)	0.088(2)	0.071(2)	0.088(2)	0.001(2)	0.013(2)	0.027(2)
O(4C)	2*i*	0.5623(7)	0.2507(5)	0.4339(4)	0.087(6)	0.118(7)	0.099(6)	0.003(5)	−0.002(5)	0.006(5)
C(3C)	2*i*	0.392(2)	0.085(1)	0.4491(8)	0.36(4)	0.29(3)	0.41(4)	−0.18(3)	−0.25(3)	0.28(3)
N(2)	2*i*	0.9471(8)	0.3064(6)	0.3778(4)	0.072(6)	0.099(7)	0.080(7)	0.020(5)	0.032(5)	0.004(6)
C(26)	2*i*	0.678(1)	0.1484(7)	0.7958(5)	0.091(9)	0.076(8)	0.087(9)	0.005(7)	0.001(7)	0.000(7)
C(35)	2*i*	0.829(1)	0.0830(6)	0.9846(5)	0.11(1)	0.052(6)	0.092(9)	0.007(6)	0.016(8)	0.009(6)
N(1)	2*i*	0.7603(7)	0.1694(4)	0.8746(4)	0.089(7)	0.046(5)	0.076(6)	−0.001(4)	0.011(5)	0.006(4)
C(14)	2*i*	0.903(1)	0.2461(8)	0.3023(5)	0.079(8)	0.095(9)	0.080(8)	0.011(7)	0.027(7)	−0.012(7)
C(38)	2*i*	0.708(1)	0.2428(6)	0.9203(6)	0.086(8)	0.057(6)	0.099(9)	0.013(6)	0.029(7)	−0.007(6)
C(18)	2*i*	0.907(1)	0.4017(7)	0.3738(6)	0.095(9)	0.11(1)	0.080(9)	0.020(8)	0.019(7)	−0.009(8)
C(23)	2*i*	1.162(1)	0.374(1)	0.4731(6)	0.079(9)	0.21(2)	0.075(9)	0.01(1)	0.022(7)	−0.02(1)
C(34)	2*i*	0.756(1)	0.0770(5)	0.9050(5)	0.11(1)	0.033(5)	0.103(9)	−0.006(6)	0.020(8)	−0.006(6)
C(15)	2*i*	0.759(1)	0.2401(9)	0.2647(7)	0.10(1)	0.12(1)	0.11(1)	−0.008(8)	0.020(9)	−0.014(9)
C(19)	2*i*	0.963(1)	0.4591(9)	0.3214(7)	0.11(1)	0.10(1)	0.12(1)	0.013(8)	0.032(9)	0.004(9)
C(16)	2*i*	0.714(1)	0.1583(9)	0.2015(7)	0.09(1)	0.12(1)	0.12(1)	0.001(9)	0.022(8)	−0.02(1)
C(10)	2*i*	0.883(1)	0.2643(9)	0.4353(6)	0.086(9)	0.15(1)	0.083(9)	0.005(9)	0.038(8)	−0.001(9)
C(36)	2*i*	0.816(1)	−0.0114(6)	1.0124(7)	0.11(1)	0.047(6)	0.11(1)	0.002(6)	0.015(8)	0.011(6)
C(39)	2*i*	0.570(1)	0.2141(9)	0.9308(8)	0.09(1)	0.11(1)	0.14(1)	0.015(8)	0.022(9)	−0.027(9)
C(22)	2*i*	1.0951(9)	0.3146(8)	0.3994(5)	0.092(9)	0.096(9)	0.082(8)	0.033(7)	0.043(7)	0.014(7)
C(30)	2*i*	0.9010(8)	0.2115(6)	0.8762(6)	0.075(8)	0.051(6)	0.105(9)	−0.001(5)	0.024(7)	0.006(6)
C(41)	2*i*	0.493(2)	0.368(1)	0.947(1)	0.26(2)	0.11(1)	0.19(2)	0.08(2)	0.02(2)	−0.01(1)
C(27)	2*i*	0.673(2)	0.2313(9)	0.7541(7)	0.16(2)	0.13(1)	0.08(1)	0.02(1)	−0.01(1)	0.028(9)
C(31)	2*i*	0.971(1)	0.1553(8)	0.8278(7)	0.11(1)	0.10(1)	0.12(1)	0.024(9)	0.035(9)	0.015(8)
C(37)	2*i*	0.677(1)	−0.0463(9)	1.0167(8)	0.13(1)	0.10(1)	0.13(1)	0.000(9)	0.04(1)	0.032(9)
C(24)	2*i*	1.309(1)	0.371(1)	0.4902(8)	0.10(1)	0.19(2)	0.12(1)	0.03(1)	0.04(1)	−0.00(1)
C(40)	2*i*	0.527(2)	0.285(1)	0.9833(8)	0.13(1)	0.14(2)	0.20(2)	0.01(1)	0.05(1)	−0.03(1)
C(11)	2*i*	0.912(2)	0.168(1)	0.449(1)	0.20(2)	0.18(2)	0.21(2)	0.06(2)	0.14(2)	0.08(2)
O(9)	2*i*	0.744(1)	0.389(1)	0.550(1)	0.15(1)	0.20(1)	0.22(1)	0.029(9)	0.05(1)	−0.07(1)
C(20)	2*i*	0.928(2)	0.557(1)	0.331(1)	0.23(2)	0.11(1)	0.17(2)	0.03(1)	0.07(2)	0.00(1)
C(28)	2*i*	0.604(2)	0.205(2)	0.6723(8)	0.16(2)	0.24(2)	0.16(2)	−0.02(2)	0.02(2)	0.02(2)
C(17)	2*i*	0.693(2)	0.065(1)	0.2280(9)	0.26(2)	0.12(1)	0.17(2)	0.01(2)	0.03(2)	−0.00(1)
C(25)	2*i*	1.384(2)	0.431(2)	0.5610(9)	0.11(1)	0.43(4)	0.13(2)	−0.00(2)	−0.01(1)	−0.04(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(32)	2*i*	1.111(1)	0.207(1)	0.8383(8)	0.12(1)	0.17(2)	0.15(1)	0.06(1)	0.04(1)	0.03(1)
C(33)	2*i*	1.184(2)	0.165(2)	0.785(1)	0.19(2)	0.29(3)	0.22(2)	0.12(2)	0.11(2)	0.05(2)
C(21)	2*i*	1.007(2)	0.622(1)	0.294(1)	0.45(4)	0.13(2)	0.14(2)	0.04(2)	0.04(2)	0.02(1)
C(29)	2*i*	0.459(2)	0.183(2)	0.667(1)	0.26(3)	0.36(4)	0.14(2)	0.00(3)	−0.01(2)	0.01(2)
C(13)	2*i*	0.935(2)	0.107(3)	0.569(2)	0.31(4)	0.54(6)	0.32(4)	0.08(4)	0.14(3)	0.22(4)
C(12)	2*i*	0.841(2)	0.136(2)	0.508(1)	0.17(2)	0.37(4)	0.28(3)	0.08(2)	0.12(2)	0.21(3)

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