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Reaction of Oxomolybdenum Complexes with Amidoximes. Synthesis and Structure of a Nitrosylacetamidoximato(1–) Complex with a N,O-side-on Bonded Acetamidoximate(1–) Ligand: $[Mo(acac)_2\{CH_3C(NH_2)NO\}(NO)]$

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Oxo-group reactivity in high-valent oxomolybdenum species such as $Mo^{VI}O_2^{2+}$ or $Mo^{V}O^{3+}$ has attracted considerable attention [1]. Well-documented examples are the reactions of *cis*-dioxo chelate complexes and molybdate(VI) with substituted hydrazines, hydroxylamine, or N-substituted hydroxylamines to produce diazenido- or hydrazido-type compounds [1, 2] and nitrosyl or hydroxylaminate complexes [3, 4, 5]. We recently described the reaction of $[MoO_2(acac)_2]$ with phenylhydrazine [6]. Looking for other small organic molecules which might similarly react with oxomolybdenum compounds, we are now exploring the reactivity of amidoximes which are formed by addition of hydroxylamine to nitriles [7]. We report here the reaction of acetamidoxime with $[MoO_2(acac)_2]$.

A mixture of $[MoO_2(acac)_2]$ (1.63 g) and acetamidoxime (0.74 g) in methanol (25 ml) was stirred for 1 h and allowed to stand at room temperature. Large orange crystals of $[Mo(acac)_2\{CH_3C(NH_2)NO\}(NO)]$ (**1**) grew and were filtered off after three days. Yield: 0.6 g, 30%. Another batch of crystals could be obtained from the filtrate upon standing; yet white crystals of a compound (**2**) precipitated along with crystals of **1**; they were separated mechanically. **2** appeared to be a tetranuclear complex $[CH_3C(NH_2)NHOH]_2[Mo_4O_{12}\{CH_3C(NH_2)NO\}_2]$ [8]. **1** has been characterized by elemental analysis, IR spectroscopy, and X-ray diffraction. *Anal.* Calc. for $C_{12}H_{19}N_3O_6Mo$: C, 36.28; H, 4.82; N, 10.58; Mo, 24.15. Found: C, 36.25; H, 4.88; N, 10.43; Mo, 23.52%.

IR (KBr pellet). The IR spectrum showed the absence of Mo=O bands and the occurrence of a band at 1675 cm^{-1} which might be attributed to a $[MoNO]^{3+}$ unit [9]; it also showed the bands characteristic of chelated acetylacetonate and of acetamidoximate ($\nu_{(N-H)}$ at 3320 and 3470 cm^{-1}). If the NO ligand does occur, its origin is not clear so an X-ray study was undertaken.

Crystal data. $M = 397.24$; monoclinic; space group $P2_1/n$; $a = 8.276(2)$, $b = 8.038(2)$, $c = 24.872(3)$ Å, $\beta = 98.370(5)°$, $V = 1635$ Å^3, $Z = 4$, 2910 reflections with $I \geqslant 3\sigma(I)$ recorded at room temperature, final $R = 0.021$ ($R_w = 0.023$).

This Mo^{II} 18-electron complex has a pentagonal–bipyramid surrounding (Fig. 1); NO is in apical position; both N and O oxime ligated atoms are in equatorial positions; each acetylacetonate is chelated. The nitrosyl and acetamidoximate coordination sites are reminiscent of the terminal oxygen positions in the starting compound. To the best of our knowledge, **1** is the first example of a side-on-ligated acetamidoximate ligand. Amidoximes have been otherwise found to ligate either through the nitrogen atom of the monodentate neutral amidoxime as in $[PdCl_2\{CH_3C(NH_2)NOH\}_2]\cdot 2H_2O$ [10], or chelated through the oxygen atom and the imine nitrogen atom of the hydroxyamidinate tautomer as in $[Ni\{C_6H_5C(NH)NHO\}\{C_6H_5C(NH)NNO\}]$ [11]. However side-on (N,O) coordination is known for some oximes [5] such as in $[Mo\{(CH_3)_2CNO\}(C_5H_5)(CO)_2]$ [12].

The formation of **1** from $[MoO_2(acac)_2]$ and from $CH_3C(NH_2)NOH$ is also the first example of an amidoxime acting as a source of NO. We have as yet no detail about the reaction mechanism. The nitrosylating agent actually might well be free hydroxylamine arising from acetamidoxime i.e. the reverse reaction of its synthesis; this assumption is supported by Malatesta and coworkers who observed the stoichiometric liberation of benzonitrile from benzamidoxime [11].

Some important structural features follow: Mo–N(21) = 1.758(2) Å, N(21)–O(22) = 1.200(3) Å, Mo–N(21)–O(22) = 175.9(2)°, Mo–O(7) = 2.077(2)

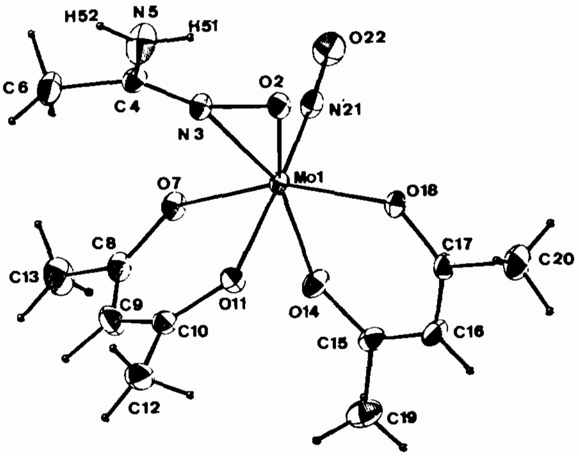

Fig. 1. ORTEP drawing of $[Mo(acac)_2\{CH_3C(NH_2)NO\}(NO)]$ showing 20% probability thermal ellisoids with hydrogen thermal parameters constrained to isotropic $B = 0.3$ Å^2.

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Å, Mo–O(14) = 2.069(2) Å, Mo–O(18) = 2.073(2) Å, Mo–O(11) = 2.143(2) Å (the latter is lengthened by nitrosyl ***trans*** influence), Mo–O(2) = 2.074(2) Å, Mo–N(3) = 2.057(2) Å, O(2)–Mo–N(3) = 39.04(7)° (this bite angle does not noticeably differ from the values observed in side-on-coordinated hydroxylaminate(1–) [3, 4] and in side-on monooximate [5, 12] ligands), C(4)–C(6) = 1.483(4) Å, C(4)–N(3) = 1.276(3) Å, C(4)–N(5) = 1.321(4) Å (these two values suggest some π-delocalisation within the ligand).

The overall geometry of **1** is similar to that of (hydroxylaminato-*O,N*)nitrosylmolybdenum complexes [3, 4] and of (oximato-*O,N*)nitrosylmolybdenum complexes [5]. Nevertheless these compounds may be divided into two classes according to the nitrogen stereochemistry of the Mo–O–N ring; it is sp^3 in hydroxylaminate(1–) complexes but sp^2 in the title complex and in $[Mo\{(CH_3)_2CNO\}(NCS)_4(NO)]^{2-}$ [5]. The group Mo–O(2)–N(3)–C(4)–N(5)–C(6) is planar within experimental error. The NH_2 hydrogen atoms also lie in this plane and build up hydrogen bonds. H(52) is connected to the O(2) oxime atom of another complex molecule (H(52)–O(2′) = 2.20(4) Å, N(5)–H(52)–O(2) = 161(2)°). H(51) is in bifurcated interaction with an intramolecular contact with O(2) (H(51)–O(2) = 2.39(3) Å, N(5)–H(51)–O(2) = 100(3)°), and with an intermolecular contact with the O(11) acetylacetonate atom of the second complex molecule cited above (H(51)–O(11′) = 2.40(3) Å, N(5)–H(51)–O(11′) = 120(3)°). This results in infinite chains stretching along the *b* axis.

The reactivity of other amidoximes towards oxomolybdenum complexes is currently under investigation.

Supplementary Material

Tables giving data on atomic positional parameters, bond lengths, bond angles and temperature factors can be obtained from the authors.

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