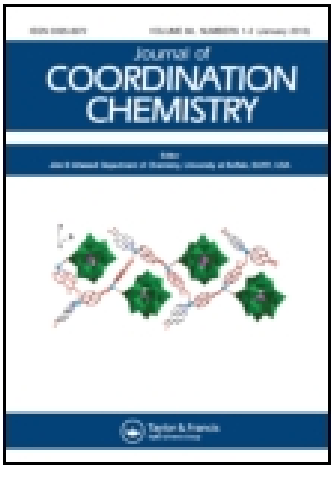

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

N-Hydroxyhomoazaadamantanone and its complexes with dioxo-molybdenum(VI) and copper(II): synthesis and structure

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Accepted author version posted online: 02 Apr 2014.Published online: 22 Apr 2014.

Journal of Coordination Chemistry, 2014
Vol. 67, No. 8, 1437–1448, http://dx.doi.org/10.1080/00958972.2014.910598

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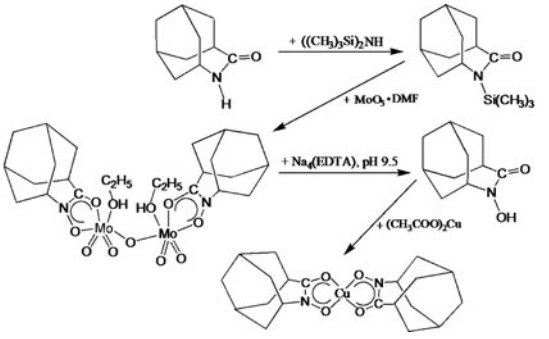
(*Received 14 November 2013; accepted 11 March 2014*)



A hydroxamic acid of a new type, N-hydroxyhomoazaadamantanone (HL), has been synthesized, combining several structure peculiarities: cage skeleton, heterocyclicity, and rigidly fixed *cis*-orientation of the oxygens of the hydroxamate fragment of the molecule. Complexes of HL with dioxo-molybdenum (VI) ($(MoO_2LC_2H_5OH)_2O$) and copper(II) (CuL_2) have been synthesized. All compounds were characterized by IR and ^1H NMR spectroscopy. X-ray structural analyses of N-hydroxyhomoazaadamantanone hydrochloride and the coordination compounds have been carried out.

Keywords: Hydroxamic acid; Tricyclic skeleton; Heterocyclic cage; Binuclear molybdenyl complex; Copper complex; X-ray structure

1. Introduction

A number of adamantane-containing compounds possess pronounced antiviral and antibacterial properties and are widely used in chemotherapy [1]. The incorporation of adamantyl

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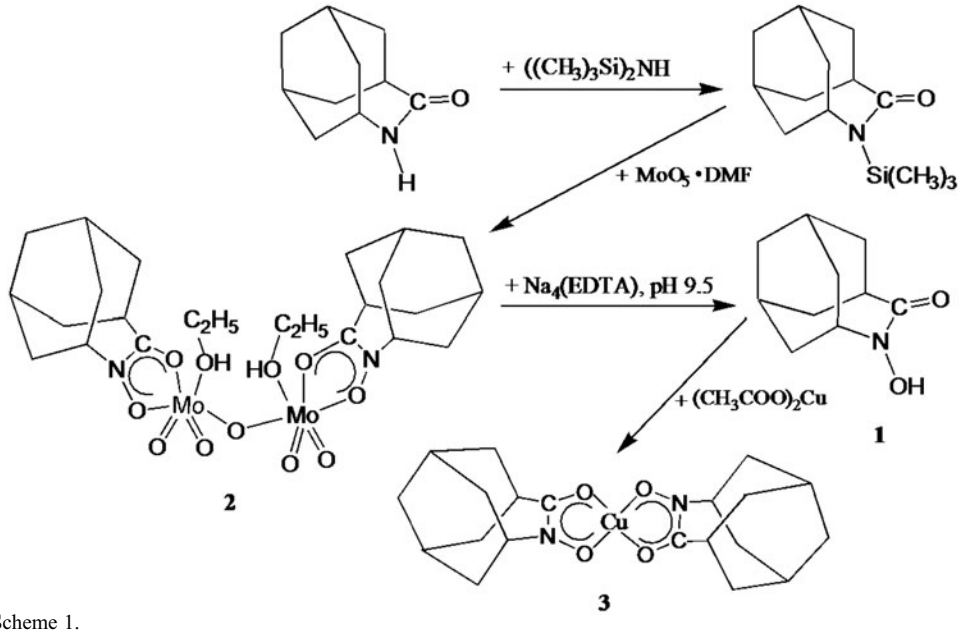

Scheme 1.

into compounds that are active substances of drugs increases substantially the therapeutic index of derivative compounds in comparison with parent compounds [2]. In the overwhelming majority of such structures, the alicycle is bound in the molecule through the nodal position of the hydrocarbon skeleton (1-adamantyl), as is shown [3]. The structures where the adamantyl substituent is bound in the molecule through the bridge position of a tricyclic skeleton (2-adamantyl) are much less observed [4]. Improvement of the medicinal properties of known compounds is the main incentive to prepare adamantane-substituted compounds, e.g. modification of bioligands, such as hydroxamic acids, with adamantane [5]. In this context, compounds with hydroxamate incorporated into a rigid tricyclic skeleton could be of special interest. This article describes the synthesis and structural characteristics of heterocyclic cage hydroxamic acid: 4-azatricyclo[4.3.1.$1^{3,8}$]undecan-5-on-4-ol (N-hydroxyhomoazaadamantanone) (**1**) and its chelate complexes with dioxo-molybdenum (VI) (**2**) and copper(II) (**3**) (scheme 1).

2. Experimental

2.1. *General*

All chemicals were of reagent grade. Solvents were purified by distillation. Dimethylformamide (DMF) of MERCK was purified as described earlier [6]. Silica gel TLC plates of MERCK were used for qualitative analysis. IR spectra were recorded in KBr pellets from 4000 to 400 cm^{-1} on a SPECORD M 80 spectrophotometer equipped with an IBM-compatible operating computing system. Elemental analyses have been carried out on a CARLO ERBA 1106 analyzer. ^{1}H NMR spectra were recorded on a VARIAN VXR-300 spectrometer in $CDCl_3$ solutions with an internal TMS standard.

2.2. *Synthesis of μ-oxo-bis[(4-azatricyclo[4.3.1.1^{3,8}]undecan-5-on-4-ato)-dioxo-molybdenum(VI)-ethanol(1/1)]*

Complex **2**, μ-oxo-bis[(N-oxyhomoazaadamantanonato)-dioxo-molybdenum(VI)-ethanol(1/1)], has been synthesized by a procedure analogous to that for bis(N-oxycaprolactamato)-dioxo-molybdenum(VI) [7]. 2.00 g (12.1 mM) of homoazaadamantanone and several drops of trimethylchlorosilane were refluxed with protection against moisture in 60 mL of hexamethyldisilazane for 7 h. The excess silylating agent was distilled off. After cooling in an argon stream to room temperature, the residue was dissolved in 30 mL of dry methylene chloride and mixed with a solution of 1.51 g (6.05 mM) of (N,N-dimethylformamido)-oxo-diperoxo-molybdenum(VI) in 50 mL of dry methylene chloride. The orange homogeneous reaction mixture was stirred for 30 h with a magnetic stirrer with protection against moisture, and then the solvent was evaporated to dryness. The light brown nonvolatile residue was crystallized twice from ethanol to obtain pale yellow, plate-like crystals suitable for X-ray structural analysis. Yield: 1.22 g, 28%. Anal. Calcd for $C_{24}H_{40}N_2O_{11}Mo_2$ (MW 724.46): C, 39.79; H, 5.57; N, 3.87. Found: C, 40.12; H, 5.51; N, 3.75%. IR (KBr, cm^{-1}): 3371, 2970, 2917, 2867, 2846, 1598, 1472, 1432, 1392, 1369, 1351, 1320, 1313, 1295, 1244, 1221, 1184, 1173, 1094, 1070, 1041, 999, 930, 896, 876, 866, 789, 759, 649, 584, 538, 494, 415. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 4.10–4.05 (m, 1H (cage, N–O)), 3.72 (q, $^3J_{H\text{-}H} = 6.9$ Hz, 2H, CH_2), 2.92–2.84 (m, 1H (cage, C=O)), 2.19–2.12 (m, 2H (cage)), 2.10–1.82 (m, 8H (cage)), 1.78–1.72 (m, 2H (cage)), 1.25 (t, $^3J_{H\text{-}H} = 6.9$ Hz, 3H, CH_3).

2.3. *Synthesis of 4-azatricyclo[4.3.1.1^{3,8}]undecan-5-on-4-ol*

N-Hydroxyhomoazaadamantanone (**1**) has been synthesized by a procedure analogous to that for N-hydroxy-ε-caprolactam [7]. About 1.2 g (1.66 mM) of **2** was vigorously stirred with 100 mL of 1 M Na_4(EDTA) solution (pH 9.5) at 60 °C for 2 h until almost complete dissolution of the complex had occurred. The aqueous phase was cooled to room temperature, filtered, acidified with hydrochloric acid to pH 7.5, and then extracted with five 25 mL portions of chloroform. The combined chloroform extracts were dried over Na_2SO_4, the solvent was removed on a rotary evaporator, and the yellowish solid residue was purified by sublimation (bath temperature 80 °C, 13 hPa). Yield: 572 mg, 95%. Anal. Calcd for $C_{10}H_{15}NO_2$ (MW 181.24): C, 66.27; H, 8.34; N, 7.73. Found: C, 66.12; H, 8.47; N, 7.91%. M.p. 177–182 °C. IR (KBr, cm^{-1}): 3103, 2922, 2846, 1632, 1440, 1367, 1353, 1332, 1295, 1254, 1235, 1218, 1180, 1148, 1116, 1087, 1066, 1025, 993, 966, 936, 915, 877, 863, 763, 746, 727, 625, 561, 540, 461, 443, 421, 409. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 8.09 (br.s, 1H, OH), 3.95–3.90 (m, 1H (cage, N–O)), 2.90–2.86 (m, 1H (cage, C=O)), 2.14–2.08 (m, 2H (cage)), 2.00–1.82 (m, 8H (cage)), 1.78–1.72 (m, 2H (cage)).

2.4. *Synthesis of bis(4-azatricyclo [4.3.1.1^{3,8}]undecan-5-on-4-ato)copper(II)*

To a solution of 450 mg (0.248 mM) of N-hydroxyhomoazaadamantanone in 30 mL of ethanol a solution of 204 mg (0.248 mM) of sodium acetate in 10 mL of water was added. To the resulting homogeneous reaction a solution of 211 mg (0.124 mM) of copper(II) chloride dihydrate in 10 mL of water was added dropwise under vigorous stirring with a magnetic stirrer. The blue–green reaction mixture was further stirred for 1 h; precipitated crystals were filtered and then washed in a filter with three 10 mL portions of water. The solid precipitate was purified by recrystallization from an ethanol/water mixture (1/1) to obtain

blue-gray needle crystals suitable for X-ray analysis, which were dried in air to constant mass. Yield of **3** (bis(N-oxyhomoazaadamantanonato)copper(II)): 500 mg, 95%. Anal. Calcd for $C_{20}H_{28}N_2O_4Cu$ (MW 423.99): C, 55.66; H, 6.65; N, 6.61. Found: C, 56.32; H, 6.49; N, 6.72%. M.p. 279–281 °C. IR (KBr, cm^{-1}): 2911, 2854, 1598, 1465, 1434, 1368, 1353, 1319, 1293, 1239, 1220, 1172, 1090, 1072, 1038, 998, 967, 940, 915, 881, 869, 840, 764, 747, 711, 644, 597, 543, 512, 415.

2.5. *X-ray crystallography*

Suitable colorless needles of **1** hydrochloride have been obtained by acidification of a saturated alcoholic solution of N-hydroxyhomoazaadamantanone with a double excess of 10% hydrochloric acid at room temperature and subsequent cooling of the mixture to 5 °C. The structures of **1** hydrochloride, **2,** and **3** were determined by X-ray crystallography. The intensity data were collected at 100 K on a Smart Bruker APEX(II) CCD area detector diffractometer with graphite-monochromated Mo Kα radiation (50 kV, 25 mA) with φ and ω scans at 1.0° width. Integration of raw intensities and LP-correction were performed with SAINT+ [8]. Absorption correction was done semi-empirically from equivalent reflections with SADABS [9]. Additional scaling, averaging, and statistical

Table 1. Crystal data and structure refinements for **1–3**.

Compound no.	**1**	**2**	**3**
Empirical formula	$C_{10}H_{16}NO_2$, Cl	$C_{24}H_{40}Mo_2N_2O_{11}$	$C_{20}H_{28}CuN_2O_4$
Formula weight	217.69	724.46	423.98
Crystal system, space group	Monoclinic, *P21/c*	Monoclinic, *C2/c*	Orthorhombic, *Pbca*
Unit cell dimensions (Å, °)	$a = 9.8791(2)$	$a = 21.1410(5)$	$a = 11.5849(2)$
	$b = 6.5192(2)$	$b = 9.7305(2)$	$b = 11.8977(2)$
	$c = 15.4695(3)$	$c = 14.1859(3)$	$c = 13.4623(2)$
	$\alpha = 90$	$\alpha = 90$	
	$\beta = 91.938(1)$	$\beta = 110.626(1)$	
	$\gamma = 90$	$\gamma = 90$	
Volume ($Å^3$)	995.73(4)	2731.16(10)	1855.56(5)
Z	4		
Calcd density ($g\,cm^{-3}$)	1.452	1.762	1.518
μ (mm^{-1})	0.357	0.981	1.206
F (0 0 0)	464	1480	892
Crystal size (mm)	0.10 × 0.15 × 0.55	0.11 × 0.21 × 0.56	0.10 × 0.10 × 0.50
θ Range (°)	2.1–30.7	2.1–33.2	2.9–33.2
Limiting indices	$-14 \le h \le 14$	$-32 \le h \le 32$	$-17 \le h \le 17$
	$-9 \le k \le 9$	$-14 \le k \le 14$	$-18 \le k \le 18$
	$-22 \le l \le 22$	$-21 \le l \le 21$	$-20 \le l \le 19$
Total number of collected reflections	13,485	17,103	30,525
Number of unique reflections	3078	5187	3564
R_{int}	0.024	0.016	0.027
Observed data [$I > 2\,\sigma(I)$]	2716	4741	2770
No. of reflections used in refinement	3078	5193	3564
No. of parameters	135	181	124
R_1[a]	0.039	0.0220	0.0279
wR_2[b]	0.0874	0.0597	0.0806
S	1.09	1.04	1.012
Max. and Av. shift/error	0.00/0.00		
Largest diff. peak/hole (e $Å^{-3}$)	0.44/−0.23	1.29/−0.811	0.39/−0.43

[a] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$.
[b] $wR_2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2$; for **1**: $w = 1/[\sigma^2(F_o^2) + (0.0283P)^2 + 0.8695P]$; for **2**: $w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 5.8592P]$; for **3**: $w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 0.6682P]$, where $P = (F_o^2 + 2F_c^2)/3$.

treatment of reflections were carried out by Blessing algorithms implemented in SORTAV [10] to reject systematic absence violations, inconsistent equivalents, and beam-stop affected reflections by statistical evaluation of the initial data-set. The crystal structure was solved by direct methods using SIR-92 [11]. Nonhydrogen atoms were first refined by full-matrix least squares based on F^2 using SHELX-97 [12]. All hydrogens bonded to carbon were positioned geometrically and refined using a riding model with C–H = 0.99 Å for CH_2, C–H = 1.00 Å for CH with Uiso(H) = 1.2Ueq(C), and C–H = 0.98 Å for CH_3 with Uiso(H) = 1.5Ueq(C). The hydrogens bonded to oxygen were located in a difference Fourier map with their positions and thermal parameters refined freely. The structure of **3** is affected by positional disorder of hydroxamate, resulting in equal contribution (presumably) of *cis*- and *trans*-isomers. Positions of C1/N1 and C2/N2 were treated with equal contribution of carbon and nitrogen with restrained positional and atomic displacement parameters. Final model was checked with Hirshfeld rigid body test [13] suggesting correct structural hypothesis. Experimental data are given in table 1.

3. Results and discussion

Maltin and Sammes discovered a method for oxidation of silylated secondary amides to hydroxamate complexes of molybdenum with subsequent isolation of N-hydroxy derivatives [14]. The use of aprotic oxidants based on molybdenum peroxides allows synthesizing alicyclic hydroxamic acids, such as N-hydroxy-ε-caprolactam, in moderate yield. When 1,1,1,3,3,3-hexamethyldisilazane is used as silylating reagent, after removing excess reagent, the intermediate silylamide may be used without isolation. In contrast to the binuclear molybdenyl complex synthesized by us, a mononuclear complex, bis(N-oxycaprolactamato)-dioxo-molybdenum(VI), has been isolated in a similar oxidation of silylated caprolactam. Trimethylsilyl derivatives are very sensitive to water and protic solvents, being solvolyzed to the parent amide [7]. Therefore, methylene chloride, which is used as solvent, was thoroughly dried over 0.4 nm molecular sieves by a procedure analogous to that described earlier for DMF [6]. The experimental technique, which is employed in the syntheses of organolithium compounds, is well suited for chelating oxidation of silylated lactams [15]. Silylated homoazaadamantanone was oxidized with (N,N-dimethylformamido)-oxo-diperoxo-molybdenum(VI) (scheme 1); the resulting reaction product was purified via twice-repeated recrystallization from ethanol to isolate crystals of **2** suitable for X-ray diffraction analysis.

Compound **2** is fairly stable in saturated ethanol solution, but decomposes quickly in air, probably losing coordinated alcohol. IR spectra of the complex contain strong absorptions at 930 and 896 cm^{-1}, assigned to symmetrical and asymmetrical (Mo=O) vibrations for *cis*-[MoO_2], and a strong absorption at 759 cm^{-1}, which relates to μ-oxo vibrations. The above values are in agreement with those found for dioxo-μ-oxo compounds of molybdenum with monodentate [16], bidentate [17], and tridentate [18] ligands. The spectrum contains a strong absorption at 789 cm^{-1}, which may be assigned to Mo–O vibrations of coordinated ethanol. The characteristic vibrations of C–O bonded to the metal (1598 cm^{-1}) are noticeably shifted to higher frequencies in comparison with those found for molybdenyl bis-hydroxamates (~1580 cm^{-1}) [19]. The strong broadened absorption at 3371 cm^{-1} confirms the presence of coordinated ethanol in binuclear molybdenum(VI) complex. The ^1H NMR spectrum of the solution of **2** in $CDCl_3$ contains a narrow poorly resolved

multiplet at 4.10–4.05 ppm, assigned to the proton at a tertiary carbon adjacent to nitrogen; at 3.72 ppm, a characteristic quartet ($^3J_{H\text{-}H} = 6.9$ Hz) from the methylene protons of coordinated ethanol is observed; at 2.92–2.84 ppm there is a relatively narrow poorly resolved multiplet of the proton on a tertiary carbon adjacent to the carbonyl carbon; the three groups of poorly resolved multiplets from two protons at 2.19–2.12 ppm, from eight protons at 2.10–1.82 ppm, and from two protons at 1.78–1.72 ppm were assigned to signals of the hydrocarbon skeleton; at 1.25 ppm, a triplet ($^3J_{H\text{-}H} = 6.9$ Hz) of the methyl protons of coordinated alcohol is observed. IR and NMR spectroscopic data corroborate the chemical structure of **2** shown in scheme 1.

According to X-ray structural analysis, **2** is binuclear, in which two symmetrically equivalent molybdenum-containing fragments ($C_{10}H_{15}NO_2MoO_2C_2H_5OH$) are bonded by a bridging oxygen (μ-oxo) (figure 1); the Mo…Mo separation is 3.7427(9) Å. The chemical environment of each molybdenum contains, besides μ-oxo group, a pair of *cis* terminal oxo ligands, a deprotonated hydroxamic acid fragment, and an ethyl alcohol. The coordination polyhedron [MoO_6] of each fragment has a distorted octahedral geometry like the structure of bis-hydroxamates and other dioxo-molybdenum(VI) complexes. The values of the valence angles are: O2–Mo1–O1 (in the chelate ring) – 73.23(4)°, O5–Mo1–O3 – 79.73(4)°, and O6–Mo1–O4 – 104.28(5)° (table 2). The Mo1–O4 and Mo1–O6 bond lengths are 1.70 Å, which corresponds to the Mo=O double bond. The O1–C1 and N1–C1 bond lengths indicate delocalization of electron density between C1, O1, and N1 [20]. The Mo–O bond lengths in the chelate ring are nonequivalent, as in related bis-hydroxamate structures [21], because of the strong *trans* effect of Mo=O. The Mo1–O5 bond is very short in comparison with Mo1–O3, which may also be due to the *trans* effect of oxo groups. The Mo1–O5 bond length is 1.8867(2) Å, which agrees with data for other μ-oxo-bridged molybdenum(VI) complexes. The Mo1–O5–Mo1^{i} angle is 165.33(9)°. According to literature data, bridge bond angle values for binuclear complexes of dioxo-molybdenum(VI) vary over a wide range: 143.5° for Mo_2O_4(μ-O)Cl_2(di-t-Bu-bipy)$_2$ (where di-t-Bu-bipy is 4,4′-di-tert-butyl-2,2′-bipyridine) [22],

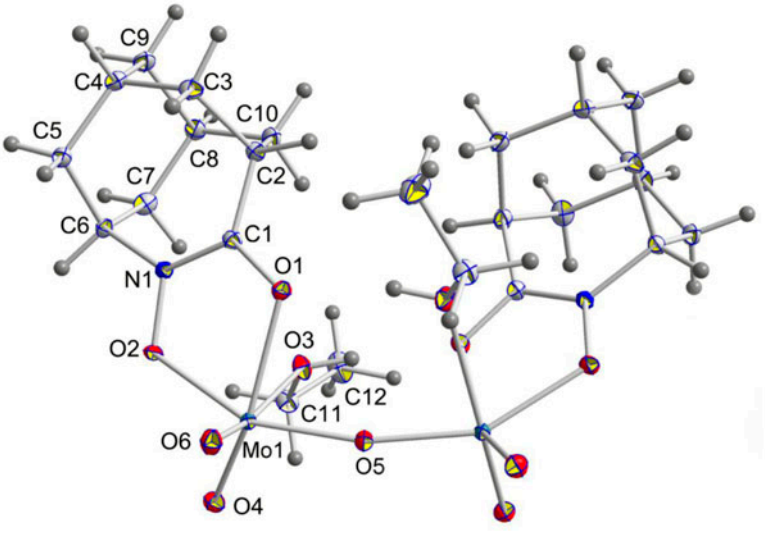

Figure 1. Molecular structure of **2**.

Table 2. Selected bond lengths (Å) and angles (°) for **1–3**.

1			
O1–C1	1.3005(15)	N1–C1	1.2993(16)
O2–N1	1.3907 (14)	N1–C6	1.4909(16)
2			
Mo1–O4	1.7036(10)	O1–C1	1.2890(16)
Mo1–O6	1.6977(10)	N1–C1	1.3061(16)
Mo1–O5	1.8867(2)	O2–N1	1.3663(15)
Mo1–O2	2.0322(10)	O3–C11	1.4444(16)
Mo1–O1	2.1904(10)	N1–C6	1.4782(17)
Mo1–O3	2.3973(10)		
3			
Cu1–O1^{ii}	1.9151(8)	O1–C1A	1.3275(12)
Cu1–O1	1.9151(8)	O2–N1A	1.3386(12)
Cu1–O2^{ii}	1.9038(8)	C1A–N1A	1.3022(14)
Cu1–O2	1.9038(8)	N1A–C6	1.4823(14)
1			
C1–N1–O2	116.95(10)	N1–C1–C2	121.44(11)
C1–N1–C6	126.93(11)	O1–C1–C2	121.27(11)
O2–N1–C6	115.77(10)	N1–C6–C7	111.36(11)
N1–C1–O1	117.29(11)	N1–C6–C5	111.15(11)
2			
O6–Mo1–O4	104.28(5)	O2–Mo1–O1	73.23(4)
O4–Mo1–O5	105.45(5)	C1–O1–Mo1	114.10(8)
O6–Mo1–O5	99.30(4)	Mo1–O5–Mo1^{i}	165.33(9)
O6–Mo1–O2	99.70(5)	C11–O3–Mo1	124.32(9)
O6–Mo1–O1	96.12(5)	N1–O2–Mo1	117.17(7)
O5–Mo1–O2	151.86(5)	N1–C6–C7	111.78(10)
O5–Mo1–O1	84.27(5)	N1–C6–C5	109.70(10)
O4–Mo1–O1	155.41(4)	C1–N1–O2	117.00(11)
O4–Mo1–O2	89.70(4)	C1–N1–C6	127.87(12)
O4–Mo1–O3	87.31(4)	O2–N1–C6	114.53(10)
O6–Mo1–O3	168.12(5)	O1–C1–N1	117.36(12)
O5–Mo1–O3	79.73(4)	O1–C1–C2	121.18(11)
O2–Mo1–O3	77.41(4)	N1–C1–C2	121.36(12)
O1–Mo1–O3	72.00(4)		
3			
O2^{ii}–Cu1–O2	180.0	C1A–N1A–O2	118.73(9)
O2–Cu1–O1	84.95(3)	C1A–N1A–C6	124.55(9)
O2^{ii}–Cu1–O1	95.05(3)	O2–N1A–C6	116.68(9)
O2–Cu1–O1^{ii}	95.05(3)	N1A–C1A–O1	118.49(9)
O2^{ii}–Cu1–O1^{ii}	84.95(3)	N1A–C1A–C2	123.77(9)
O1^{ii}–Cu1–O1	180.00(5)	O1–C1A–C2	117.74(9)
N1A–O2–Cu1	108.81(7)	N1A–C6–C5	112.23(10)
C1A–O1–Cu1	108.99(6)	N1A–C6–C7	111.82(10)

Note: Symmetry codes: (i) $1-x, y, 1/2-z$; (ii) $-x, -y, 1-z$.

151° for $Mo_2O_4(\mu\text{-}O)Cl_2$ (pyrazole)$_4$ [16], 175° for $Mo_2O_4(\mu\text{-}O)Cl_2$-(DMF)$_2$ [23], and 156° and 180° for $Mo_2O_4(\mu\text{-}O)Cl_2(PzPy)_2$ conformers, where PzPy stands for 2-(3-pyrazolyl) pyridine [24]. This spread of values is caused by intramolecular contacts, such as π–π interaction between aromatic ligands [17] and the spatial characteristics of ligands. Ethanol within **2** are positioned *trans* to each other relative to the Mo–O–Mo bond. This stabilizes the binuclear structure through a strong intramolecular hydrogen bond to the carbonyl

oxygen (table 3). The packing of the single crystal (figure 2) is supported with very weak C–H…O interactions, which are similar to those described earlier [25].

The presence of coordinated ethanol in **2** does not hinder the isolation of hydroxamic acid **1** in high yield by exchange of complexation of molybdenum with the sodium salt of ethylenediaminetetraacetic acid at pH 7.5. The IR spectra of the sublimated crystalline compound contain a stretching vibration band (ν(C=O)) characteristic of hydroxamic acids, which is shifted by 34 cm^{-1} to higher frequencies as compared with that of the parent complex.

The ^1H NMR spectrum of solution of **1** in $CDCl_3$ contains a signal, broadened due to exchange, of one proton of OH at 8.09 ppm; a narrow poorly resolved multiplet at 3.95–3.90 ppm, assigned to proton on a tertiary carbon adjacent to nitrogen of the heterocycle; a relatively narrow poorly resolved multiplet of the proton at a tertiary carbon adjacent to carbonyl carbon is at 2.90–2.86 ppm; and three groups of poorly resolved multiplets at 2.14–2.08 ppm from two protons, at 2.00–1.82 ppm from eight protons and at 1.78–1.72 ppm from two protons, which are assigned to absorptions of the hydrocarbon skeleton. Thus, IR and NMR spectroscopic data corroborate the chemical structure of **1** shown in scheme 1.

Unfortunately, we failed to grow N-hydroxyhomoazaadamantanone crystals suitable for X-ray structural analysis. This hydroxamic acid decomposes gradually during room temperature storage (by about 10% per month according to our estimates). The hydrochloride of **1**

Table 3. Selected hydrogen bond parameters.

D–H···*A*	*D*–H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A* (°)
1				
O2–H1N···Cl1^{i}	0.88(2)	2.10(3)	2.9732(12)	175(2)
O1–H1O···Cl1	0.83(3)	2.07(3)	2.8917(10)	171(2)
2				
O3–H3O···O1^{ii}	0.84(3)	1.92(3)	2.7426(16)	165(2)

Note: Symmetry codes: (i) $1-x, -1/2+y, 1/2-z$; (ii) $1-x, y, 1/2-z$.

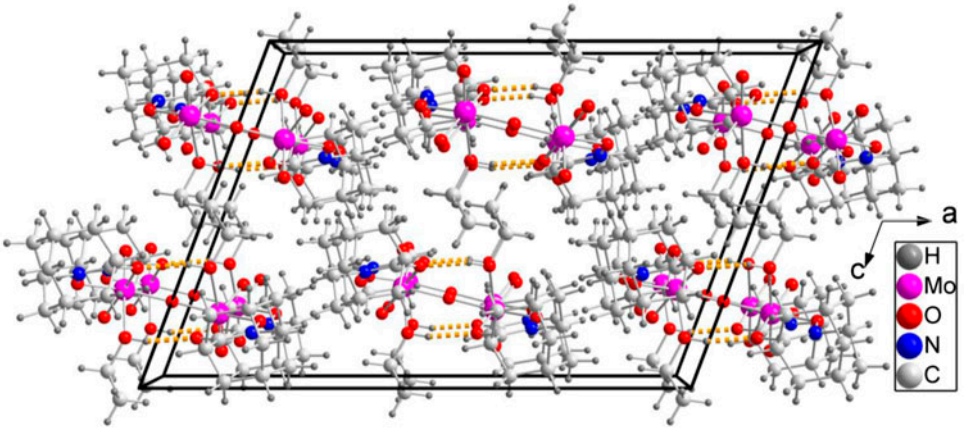

Figure 2. Crystal packing projection for **2**. The dashed lines indicate intramolecular H-bonds.

forms suitable single crystals, which are extremely unstable outside saturated acidified alcoholic solution. However, at 100 K the crystals proved to be quite suitable for X-ray structural analysis. Our following reasoning concerns hydroxamic acid **1** hydrochloride, whose molecular structure is shown in figure 3. Incorporation of OH influences the geometric parameters of N-hydroxyhomoazaadamantanone molecule in comparison with starting lactam [26]. Analysis of the data of X-ray crystallography (table 2) shows that the changes in geometric characteristics are small and refer only to the N–C=O group. A decrease in N1–C1 bond length (1.2993(16) Å) in comparison with lactam (1.331 Å) and in N1–C1–O1 angle (117.29(11)° in comparison 120.6° in lactam) is observed. The hydrogen chloride is a proton donor for the carbonyl, as shown by FTIR for acetohydroxamic acid [27]. In lactam crystals, two types of intermolecular hydrogen bonds have been found, through which the molecules form dimers that differ from one another. The N-hydroxyhomoazaadamantanone hydrochloride molecules, however, form a chain-like supramolecular structure stabilized by strong O–H···Cl hydrogen bonds and weaker C–H…Cl and C–H…O interactions (table 3, figure 4).

The hydroxamic acid and corresponding hydrochloride described above proved to be relatively unstable during storage; therefore, a method for the purification and stabilization of **1** through preparation of a copper complex was employed, as described for a number of cycloalkyl hydroxamic acids [28]. Complex **3** can be easily purified; the crystals obtained are suitable for X-ray structural analysis and can be stored for a long time (for many months without changes) under ordinary conditions. Starting hydroxamic acid is isolated by passing hydrogen sulfide through a suspension of copper complex in methanol. IR spectra of **3** exhibit a strong absorption at 1598 cm^{-1}, similar to that described earlier for cyclic hydroxamato copper(II) complex (1615 cm^{-1}) [29]. The broad absorption at 3103 cm^{-1}, which is observed in hydroxamic acid, is absent from the copper complex. IR spectroscopic data corroborate the chemical structure of **3** shown in scheme 1.

As expected according to the data of an X-ray structural analysis, copper in the complex is coordinated by four oxygens of two ligands and has square-planar coordination (figure 5). The metallocycle is perfectly planar. The Cu1–O1 and Cu1–O2 bond lengths are 1.9151(8) and 1.9038(8) Å, respectively, the C1A–N1A bond length is 1.3022(14) Å,

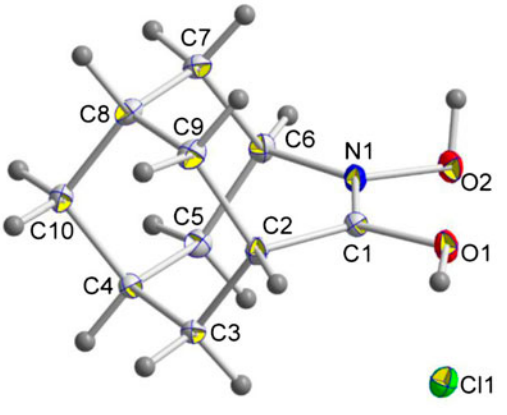

Figure 3. Molecular structure of N-hydroxyhomoazaadamantanone hydrochloride.

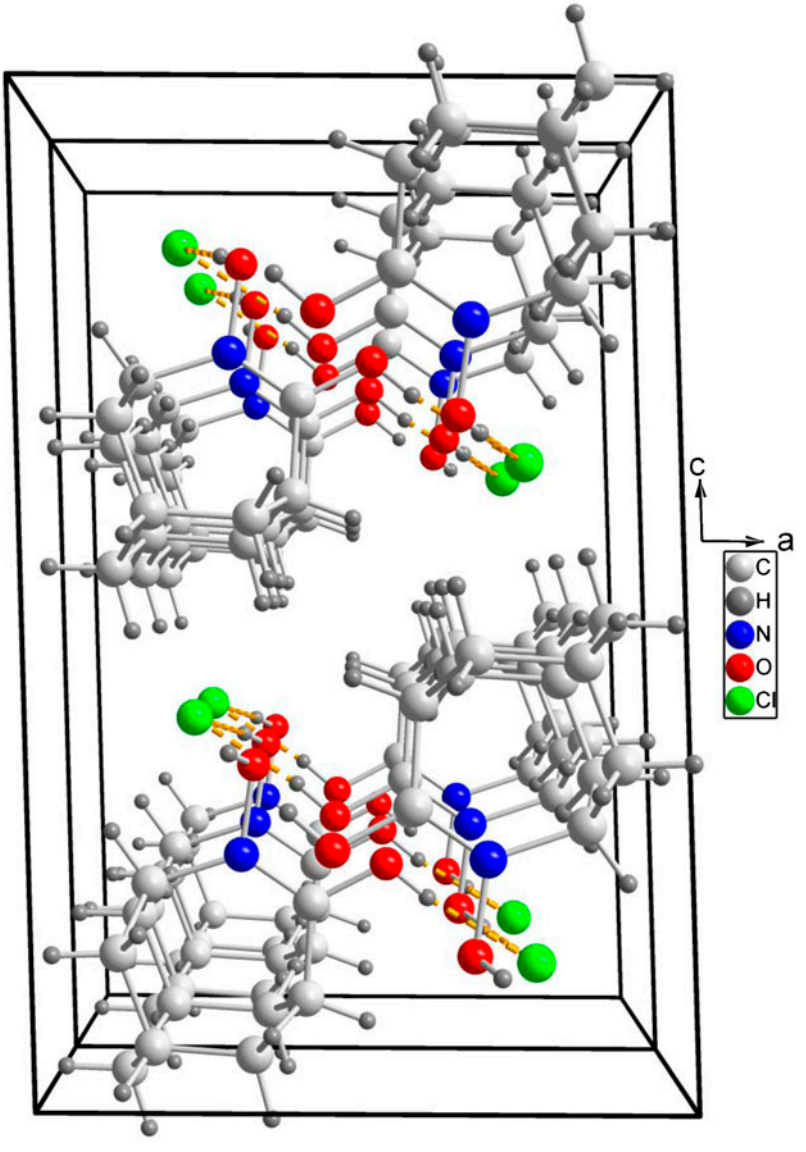

Figure 4. Crystal packing projection for N-hydroxyhomoazaadamantanone hydrochloride. The dashed lines indicate H-bonds.

the O2–Cu1–O1 angle is 84.95(3)° (table 2). These geometric parameters are close to those found for complexes of bis(N-methyl-benzohydroxamato-O,O′)copper(II) [30]. The O1–C1A and O2–N1A bond lengths are 1.3275(12) and 1.3386(12) Å, respectively, the former being noticeably larger and the latter smaller in comparison with those of the corresponding bonds in the above analogs, which is accounted for by the different constituents at C and N in the complexes. The molecules of the complex form a crystal through van der Waals forces.

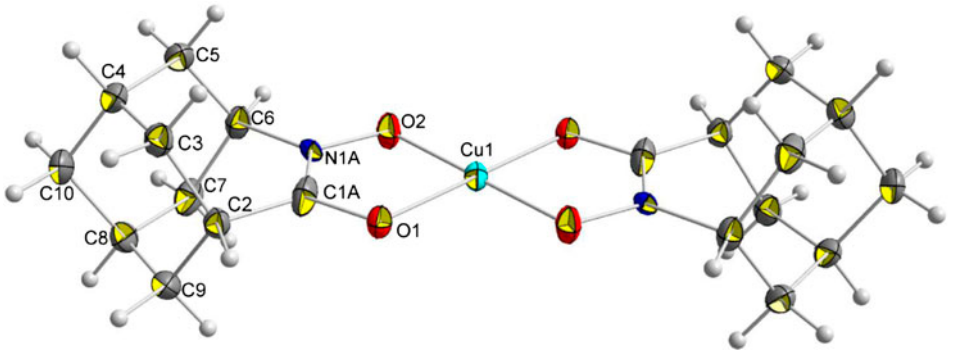

Figure 5. Molecular structure of **3**.

4. Conclusion

A hydroxamic acid **1** of a new type has been synthesized, which combines several significant structure peculiarities: cage skeleton, heterocyclicity, and rigidly fixed *cis*-orientation of oxygens of the hydroxamate fragment of the molecule. Complexes of the above compound with dioxo-molybdenum(VI) **2** and copper(II) **3** have also been synthesized. **1**, **2**, and **3** have been characterized by spectroscopic methods. X-ray structural analyses of N-hydroxyhomoazaadamantanone hydrochloride, **2,** and **3** have been carried out. In spite of the different structures of the coordination polyhedron of **2** and **3,** and considerable differences in the chemical nature of the compounds under investigation, polar hydrochloride and covalent bis-chelate **3**, hydrochloride and binuclear molybdenum complex **2**, the geometry of the hydroxamate fragment of molecules remains practically unchanged. Compound **1** has a peculiar structure, and therefore it can possess new properties in contrast to the known hydroxamic acids (bioligands).

Supplementary material

CCDC 895434, 895435, and 914940 contains the supplementary crystallographic data for proligand (**1**) hydrochloride, **2,** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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