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Contribution from the Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, D-4630 Bochum, West Germany, and the Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, West Germany

Reaction between Hydroxylamine and Molybdate(VI): Preparation of the Complexes $[Mo(NO)(CN)_5]^{2-}$, $[Mo(NO)(H_2NO)Cl_4]^{2-}$, and $[Mo(NO)(H_2NO)(N_3)_4]^{2-}$. Crystal Structure of $[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4]\cdot H_2O$

KARL WIEGHARDT,*[1a] GABRIELE BACKES-DAHMANN,[1a] WOLFGANG SWIRIDOFF,[1b] and JOHANNES WEISS*[1b]

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The synthesis of a most probably polymeric nitrosyl complex of molybdenum(II) containing a hydroxylamido(1−) ligand from the reaction of oxoanions of molybdenum(VI) with hydroxylamine in aqueous solution is reported. Reactions of this material with hydrochloric acid, cyanide ions, and azide ions afford the complexes $[Mo(NO)(H_2NO)Cl_4]^{2-}$, $[Mo(NO)(CN)_5]^{2-}$, and $[Mo(NO)(H_2NO)(N_3)_4]^{2-}$, respectively. The complex $[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4]\cdot H_2O$ has been characterized by a single-crystal X-ray diffraction study. The compound crystallizes in the triclinic space group $P\bar{1}$ (C_i^1; No. 2) with $a = 13.129$ (3) Å, $b = 13.761$ (4) Å, $c = 15.596$ (4) Å, $\alpha = 69.23$ (2)°, $\beta = 68.15$ (2)°, $\gamma = 74.85$ (2)°, and $V = 2418$ Å^3, $\rho_{calcd} = 1.401$ g cm^{-3} for $Z = 2$, and mol wt 1022.9. Diffraction data were collected on a Syntex R3 diffractometer using a θ–2θ scan and Mo Kα radiation, and the structure was solved by conventional methods, resulting in a final R factor of 0.053 for 3721 independent reflections. The structure consists of tetraphenylphosphonium cations and the dianion, $[Mo(NO)(H_2NO)(N_3)_4]^{2-}$, with the molybdenum center in a distorted pentagonal-bipyramidal environment of an O,N-coordinated H_2NO^- ligand (d(N–O) = 1.404 (7) Å) and three covalently bound azide groups in equatorial positions (d(Mo–N)$_{av}$ = 2.17 Å); a fourth azide ligand (d(Mo–N) = 2.21 (1) Å) and a linear nitrosyl group (Mo—N—O = 172.4 (5)°, d(N═O) = 1.21 (1) Å, d(Mo—N) = 1.761 (8) Å) occupy the axial positions.

Introduction

Oxoanions of molybdenum(VI) react with hydroxylamine in acidic, neutral, or alkaline aqueous solutions, yielding yellow nitrosyl complexes of the type $\{Mo–NO\}^4$.[2-5] In the presence of excess hydroxylamine and chelating ligands, complexes containing one or two O,N-coordinated hydroxylamido(1−) ligands have been isolated and characterized by X-ray crystallography.[2,3] As an extension of this work, we have studied this reaction with simple monodentate ligands such as chloride, cyanide, and azide. The preparation of a polymeric nitrosyl(hydroxylamido)molybdenum(II) complex[6] containing no added ligands is reported. This material has been found to be a useful starting material for the preparation of nitrosyl complexes of molybdenum of the type $\{Mo–NO\}^4$.[7]

Experimental Section

Preparation of Complexes. When a solution of 4.0 g of $Na_2MoO_4\cdot 2H_2O$ dissolved in 50 mL of water is reacted with 3.2 g of hydroxylammonium chloride at room temperature, a microcrystalline yellow precipitate formed, which was filtered off, washed with ethanol and ether, and air-dried; yield 4.0 g. The composition of this polymeric material does not vary upon small alterations of the above procedure; the complex does not contain chloride ions.

Anal. Found: N, 9.6; H, 3.0; Mo, 35.3.

$Cs_2[Mo(NO)(H_2NO)Cl_4]\cdot H_2O$. A suspension of 0.5 g of the above polymeric material in concentrated hydrochloric acid (30 mL) was stirred at 20 °C until a clear orange solution was obtained. A 2-g sample of CsCl was added in small amounts with stirring. The resulting solution was allowed to stand in the refrigerator for 12 h. A yellow microcrystalline precipitate was filtered off, washed with ethanol and ether, and air-dried; yield 0.3 g.

Anal. Calcd for $Cs_2[Mo(NO)(H_2NO)Cl_4]\cdot H_2O$: H, 0.69; Mo, 16.44; N, 4.8. Found: H, 0.5; Mo, 16.4; N, 4.8.

$[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4]\cdot H_2O$. A suspension of 0.5 g of the above polymeric material and 1.5 g of NaN_3 in 25 mL of water was heated to 60 °C with stirring until a yellow solution was obtained. To this solution was added 0.3 g of tetraphenylphosphonium chloride. When the solution cooled slowly to 0 °C, orange-yellow crystals precipitated, which were filtered off and air-dried. The compound was found to be nonexplosive; yield 0.3 g. Anal. Calcd for $[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4]\cdot H_2O$: C, 56.36; H, 4.34; N, 19.17; Mo, 9.38. Found: C, 56.2; H, 4.3; N, 19.0; Mo, 9.6.

Table I. Summary of Crystal Data and Intensity Collection for $[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4]\cdot H_2O$

A. Crystal Parameters at 22 °C

system	triclinic	V, Å^3	2418.3
a, Å	13.129 (3)	fw	1022.9
b, Å	13.761 (4)	Z	2
c, Å	15.596 (4)	ρ_{calcd}, g cm^{-3}	1.401
α, deg	69.23 (2)	space group	$P\bar{1}$
β, deg	68.15 (2)	μ(Mo Kα), cm^{-1}	3.8
γ, deg	74.85 (2)		

B. Intensity Measurement

cryst dimens, mm	0.3 × 0.3 × 0.2
diffractometer	Syntex R3
radiation	Mo Kα, λ = 0.710 69 Å
temp	22 °C
data colln	θ–2θ
max 2θ, deg	60
std reflctns	2 every 2 h; no decay obsd
data collected	3966
no. of data for $I > 2.5\sigma(I)$	3721
no. of variables	612

$[(C_6H_5)_4P]_2[Mo(NO)(CN)_5]\cdot 3H_2O$. A suspension of 0.8 g of NaCN and 0.5 g of the above polymeric material in 25 mL of water was heated with stirring to 50 °C until a yellow solution was obtained. To this solution was added 0.2 g of $[(C_6H_5)_4P]Cl$. When the solution cooled slowly, pale yellow, needle-shaped crystals precipitated, which were washed with ether and air-dried; yield 0.2 g.

Anal. Calcd for $[(C_6H_5)_4P]_2[Mo(NO)(CN)_5]\cdot 3H_2O$: C, 64.37; H, 4.68; N, 8.49; Mo, 9.70. Found: C, 64.5; H, 4.5; N, 8.6; Mo, 9.9.

The analogous complex **$[(C_6H_5)_4As]_2[Mo(NO)(CN)_5]\cdot 3H_2O$** was prepared according to the above procedure using 0.3 g of $[(C_6H_5)_4As]Cl$ for precipitation.

Anal. Calcd for $[(C_6H_5)_4As]_2[Mo(NO)(CN)_5]\cdot 3H_2O$: C, 59.12; H, 4.30; N, 7.80; Mo, 8.91. Found: C, 59.2; H, 4.3; N, 7.9; Mo, 8.7.

$Cs_2[Mo(NO)(CN)_5]\cdot 3H_2O$. A suspension of 1.6 g of NaCN and 1.0 g of the above polymeric material in 25 mL of water was heated to 50 °C until a yellow solution was obtained. To this solution were

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Table II. Infrared Spectra (cm^{-1})[a] (400–4000 cm^{-1})

complex	
$[(C_6H_5)_4P]_2[Mo(NO)(CN)_5]\cdot 3H_2O$[b]	2120 (m), ν(C≡N); 1645 (s), ν(N=O)
$[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4]\cdot H_2O$[b]	2070 (s), 2040 (s), $\nu_{as}(N_3)$; 1610 (s), ν(N=O); 3200 (w), 3060 (w), ν(N–H); 1334 (w), 1286 (w), $\nu_s(N_3)$
$Cs_2[Mo(NO)(H_2NO)Cl_4]\cdot H_2O$	3450 (b, w), ν(OH); 3270 (m), 3160 (w), ν(N–H); 1590 (s), ν(NO); 1145 (m), $\rho(NH_2)$; 885 (w), 920 (w), 950 (w), 620 (w), 560 (w)
polymeric Mo(NO) complex	3420 (b, s), ν(O–H); 3180 (s), 3070 (s), ν(N–H); 1600 (vs), ν(N=O); 1270 (b, w), 1130 (w), $\rho(NH_2)$; 900 (m, sh), 870 (s), 750 (m, b), 610 (m)

[a] KBr disks. [b] Peaks due to the complex anion only are given. s = strong, m = medium, w = weak, b = broad, and sh = shoulder.

Table III. Spectroscopic Data of $[Mo(NO)(CN)_5]^{n-}$ Complexes (n = 4–2)

complex	ν(N=O), cm^{-1}	$E(N-1s)$[a] eV	μ_{eff}, μ_B	color	ref
$K_4[Mo(NO)(CN)_5]$	1455	401.1	diamagn	violet	11
$[(C_6H_5)_4P]_3[Mo(NO)(CN)_5]$	1585	400.1	1.96	green	12
$[(C_6H_5)_4P]_2[Mo(NO)(CN)_5]\cdot 3H_2O$	1645	399.7	diamagn	pale yellow	this work

[a] Values are relative to $E_{1/2}$(C 1s) = 285.0 eV. We thank Prof. A. Müller (University Bielefeld) for measuring the ESCA spectrum.

added 2.0 g of CsCl and 30 mL of ethanol. At 0 °C a yellow precipitate formed very slowly; this was filtered off, washed with ethanol and ether, and air-dried. The compound is very soluble in water; yield 0.7 g. Anal. Calcd for $Cs_2[Mo(NO)(CN)_5]\cdot 3H_2O$: C, 10.40; H, 1.05; N, 14.59; Mo, 16.66. Found: C, 10.2; H, 0.8; N, 14.2; Mo, 16.8.

X-ray Structural Determination of $[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4]\cdot H_2O$. A crystal of $[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4]\cdot H_2O$ was attached to the end of a glass fiber and mounted on a Syntex R3 four-circle diffractometer. Preliminary examinations showed that the crystal belonged to the triclinic system, space group $P\bar{1}$. The unit cell dimensions were obtained by a least-squares fit of 25 strong reflections. The data are summarized in Table I. Intensity data were measured by θ–2θ scans and were corrected for Lorentz and polarization effects. An empirical absorption correction was carried out.[8] The function minimized during least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ with final convergence to

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.053$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.049$$

The structure was solved via a three-dimensional Patterson synthesis, which yielded the positions of the molybdenum and phosphorus atoms. Subsequent Fourier syntheses revealed the locations of all remaining nonhydrogen atoms. Idealized positions of the H atoms of the phenyl rings were calculated (on the basis of d(C–H) of 0.97 Å and sp^2-hybridized C atoms). The structure was refined to convergence with use of a fixed isotropic thermal parameter for the H atoms (U = 0.08 $Å^2$) and anisotropic thermal parameters for all non-hydrogen atoms. A final difference Fourier synthesis did not reveal the positions of the H atoms of the H_2NO^- ligand and of water of crystallization, and these were not included in the refinement. However, the assignment of the N and O atoms of the three-membered ring given is shown to be correct. A reversed order of the N and O atoms leads to a small increase of the final R factor and unreasonable anisotopic thermal parameters for the N and O atoms. The final atomic parameters are given in Table IV. A list of observed and calculated structure factors and a list of anisotropic thermal parameters are available as supplementary material.

Results and Discussion

Preparation of Complexes. The reaction between oxoanions of molybdenum(VI) and hydroxylamine in water affords yellow solutions.[2-6] It has been shown previously that, by addition of ligands (e.g., 2,2′-bipyridine,[2] o-phenanthroline,[3] pyridine-2,6-dicarboxylate,[3] terpyridine,[9] oxalate[4]) to such solutions, various nitrosyl complexes of the type $\{Mo–NO\}^4$, containing formally molybdenum(II) centers, can be isolated. These reactions were shown to occur without production of gaseous products such as N_2, NO, N_2O, or NH_3. The reaction of molybdenum(VI) with a large excess of hydroxylamine in the presence of cyanide ions gives the diamagnetic, violet $[Mo(NO)(CN)_5]^{4-}$ ion containing a molybdenum(0) center.[10-12] Lassner[6] reported the preparation of a yellow precipitate from solutions to which no additional ligands were added without describing details of its synthesis or characterization. We can confirm his results. From the elemental analysis (Mo:N = 1:2) and infrared spectrum (Table II) the yellow material appears to be a polymeric nitrosyl complex of molybdenum(II) with one additional hydroxylamido ligand per molybdenum atom (ν(N=O) 1600 cm^{-1}; ν(N—H) 3180, 3070 cm^{-1}). From yellow solutions of the polymeric material in concentrated hydrochloric acid, yellow crystals of $Cs_2[Mo(NO)(H_2NO)Cl_4]\cdot H_2O$ can be precipitated by addition of cesium chloride.[13] Infrared data are summarized in Table II. The presence of a nitrosyl group and a coordinated hydroxylamido ligand is clearly indicted. The reaction of the polymeric material with concentrated hydrobromic acid yields the known orange complex $Cs_2[Mo(NO)Br_5]$,[14] which does not contain hydroxylamine ligands.

Interestingly, the reaction between the polymer and excess sodium cyanide in aqueous solution (pH >8!) at 50 °C also gives a yellow solution. Addition of $[(C_6H_5)_4P]Cl$ yields pale yellow crystals of $[(C_6H_5)_4P]_2[Mo(NO)(CN)_5]\cdot 3H_2O$. This complex is diamagnetic and indefinitely stable in air. It represents the missing link in the series of isostructural anions $[Mo(NO)(CN)_5]^{n-}$ (n = 4–2). The green $[Mo(NO)(CN)_5]^{3-}$ anion is paramagnetic and has only been recently characterized.[12] The dianion has been proposed to exist in solution as an oxidation product of $[Mo(NO)(CN)_5]^{4-}$ by hypobromide.[15] Despite many efforts, it has not been isolated and fully characterized previously. In Table III spectroscopic data are

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(8) Computations were carried out on a NOVA3 (General Data) computer using SHELXTL (Revision 3.0, July 1981) by G. M. Sheldrick, University Göttingen.

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Table IV. Atom Coordinates ($\times 10^4$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo(1)	13338 (1)	4040 (1)	1334 (1)	C(211)	5972 (8)	6866 (7)	2116 (6)
N(2)	13524 (5)	5226 (4)	−10 (4)	C(212)	4914 (8)	7005 (7)	2709 (7)
O(2)	12493 (4)	5403 (4)	677 (4)	C(207)	4709 (7)	6920 (6)	3682 (6)
N(1)	13994 (5)	4709 (4)	1709 (4)	C(214)	2970 (7)	5389 (6)	4082 (6)
O(1)	14451 (5)	5257 (4)	1867 (4)	C(215)	2386 (8)	4597 (7)	4256 (7)
N(20)	13494 (5)	2541 (5)	2408 (5)	C(216)	1422 (8)	4458 (7)	5021 (8)
N(21)	14228 (5)	1840 (4)	2397 (4)	C(217)	1055 (7)	5083 (7)	5619 (7)
N(22)	14922 (6)	1139 (5)	2433 (6)	C(218)	1632 (7)	5841 (7)	5507 (7)
N(30)	12569 (6)	3277 (5)	745 (5)	C(213)	2604 (7)	6024 (6)	4698 (6)
N(31)	12039 (6)	3778 (5)	221 (5)	C(220)	3162 (8)	9115 (7)	3242 (8)
N(32)	11512 (8)	4238 (7)	−273 (7)	C(221)	2597 (12)	10119 (9)	2898 (11)
N(40)	14945 (5)	3355 (5)	537 (5)	C(222)	1462 (13)	10286 (9)	3298 (12)
N(41)	15051 (5)	2721 (5)	133 (5)	C(223)	867 (11)	9516 (9)	3994 (10)
N(42)	15202 (6)	2116 (6)	−261 (6)	C(224)	1423 (8)	8538 (8)	4331 (7)
N(50)	11743 (5)	4166 (5)	2443 (5)	C(219)	2573 (7)	8335 (6)	3955 (7)
N(51)	11222 (5)	3443 (5)	2932 (5)	W(1)	9669 (6)	5468 (6)	1672 (5)
N(52)	10691 (6)	2800 (6)	3437 (6)	H(102)	974	9808	1322
P(1)	8680 (2)	9421 (2)	2008 (2)	H(103)	2677	8710	1271
C(102)	1003 (6)	9058 (5)	1555 (5)	H(104)	2750	6893	1812
C(103)	2005 (7)	8410 (6)	1520 (6)	H(105)	1128	6157	2392
C(104)	2049 (7)	7340 (6)	1837 (6)	H(106)	−590	7203	2541
C(105)	1085 (7)	6907 (6)	2191 (6)	H(108)	−740	10649	2858
C(106)	75 (6)	7518 (6)	2266 (6)	H(109)	−524	12415	2426
C(101)	19 (6)	8611 (5)	1935 (5)	H(110)	−913	13608	1063
C(108)	−882 (7)	11135 (6)	2283 (6)	H(111)	−1478	13066	74
C(109)	−764 (7)	12181 (7)	2031 (7)	H(112)	−1684	11299	429
C(110)	−986 (7)	12884 (7)	1223 (7)	H(114)	−3351	10324	1496
C(111)	−1313 (7)	12564 (6)	634 (7)	H(115)	−4146	9963	522
C(112)	−1405 (6)	11527 (6)	853 (6)	H(116)	−3196	8798	−372
C(107)	−1209 (6)	10792 (6)	1692 (6)	H(117)	−1449	7882	−274
C(114)	−2967 (7)	9813 (6)	1150 (6)	H(118)	−648	8145	734
C(115)	−3423 (8)	9605 (7)	558 (7)	H(120)	−876	8542	3809
C(116)	−2872 (7)	8912 (7)	37 (7)	H(121)	−1935	8194	5428
C(117)	−1839 (7)	8371 (6)	96 (6)	H(122)	−3879	8409	5859
C(118)	−1361 (7)	8528 (7)	691 (6)	H(123)	−4732	9032	4651
C(113)	−1913 (6)	9234 (6)	1213 (5)	H(124)	−3666	9417	3013
C(120)	−1671 (8)	8652 (7)	3982 (7)	H(202)	3219	8701	5287
C(121)	−2292 (11)	8436 (8)	4937 (8)	H(203)	3603	8663	6653
C(122)	−3437 (11)	8570 (9)	5192 (8)	H(204)	3943	7079	7788
C(123)	−3937 (8)	8935 (8)	4476 (8)	H(205)	3884	5521	7562
C(124)	−3308 (7)	9165 (6)	3504 (6)	H(206)	3531	5503	6201
C(119)	−2176 (6)	9029 (6)	3256 (5)	H(208)	5498	6677	4671
P(2)	3308 (2)	7090 (2)	4472 (2)	H(209)	7293	6459	3616
C(202)	3373 (6)	8042 (6)	5741 (6)	H(210)	7601	6515	2050
C(203)	3590 (7)	8014 (7)	6558 (7)	H(211)	6104	6929	1452
C(204)	3788 (7)	7085 (8)	7231 (7)	H(212)	4302	7161	2462
C(205)	3759 (7)	6174 (7)	7090 (7)	H(214)	3627	5501	3538
C(206)	3553 (7)	6156 (6)	6281 (7)	H(215)	2653	4147	3844
C(201)	3381 (6)	7098 (6)	5596 (6)	H(216)	1010	3920	5132
C(208)	5605 (7)	6722 (6)	4014 (6)	H(217)	369	4989	6135
C(209)	6671 (7)	6589 (6)	3386 (7)	H(218)	1388	6239	5963
C(210)	6857 (8)	6638 (6)	2463 (7)	H(220)	3954	8968	2984
H(223)	73	9660	4240	H(221)	2988	10667	2403
H(224)	1020	7998	4824	H(222)	1065	10970	3083

Table V. Bond Lengths (Å)

Mo(1)-N(2)	2.125 (5)	Mo(1)-O(2)	2.048 (5)
Mo(1)-N(1)	1.761 (8)	Mo(1)-N(20)	2.166 (6)
Mo(1)-N(30)	2.211 (10)	Mo(1)-N(40)	2.173 (6)
Mo(1)-N(50)	2.176 (5)	N(2)-O(2)	1.404 (7)
N(2)-Mo(1)	2.125 (5)	O(2)-Mo(1)	2.048 (5)
N(1)-O(1)	1.210 (11)	N(1)-Mo(1)	1.761 (8)
N(20)-N(21)	1.171 (8)	N(20)-Mo(1)	2.166 (6)
N(21)-N(22)	1.143 (9)	N(30)-N(31)	1.183 (11)
N(30)-Mo(1)	2.211 (10)	N(31)-N(32)	1.138 (14)
N(40)-N(41)	1.198 (12)	N(40)-Mo(1)	2.173 (6)
N(41)-N(42)	1.139 (13)	N(50)-N(51)	1.213 (9)
N(50)-Mo(1)	2.176 (5)	N(51)-N(52)	1.143 (10)

Table VI. Bond Angles (deg)

N(2)-Mo(1)-O(2)	39.3 (2)	N(2)-Mo(1)-N(1)	90.8 (3)
O(2)-Mo(1)-N(1)	93.0 (3)	N(2)-Mo(1)-N(20)	162.0 (2)
O(2)-Mo(1)-N(20)	155.0 (2)	N(1)-Mo(1)-N(20)	96.9 (3)
N(2)-Mo(1)-N(30)	84.9 (3)	O(2)-Mo(1)-N(30)	84.5 (3)
N(1)-Mo(1)-N(30)	175.5 (2)	N(20)-Mo(1)-N(30)	86.9 (3)
N(2)-Mo(1)-N(40)	82.0 (2)	O(2)-Mo(1)-N(40)	121.2 (2)
N(1)-Mo(1)-N(40)	90.3 (3)	N(20)-Mo(1)-N(40)	81.7 (2)
N(30)-Mo(1)-N(40)	87.8 (3)	N(2)-Mo(1)-N(50)	116.7 (2)
O(2)-Mo(1)-N(50)	77.5 (2)	N(1)-Mo(1)-N(50)	96.0 (3)
N(20)-Mo(1)-N(50)	78.8 (2)	N(30)-Mo(1)-N(50)	87.2 (3)
N(40)-Mo(1)-N(50)	168.1 (2)	O(2)-N(2)-Mo(1)	67.4 (3)
N(2)-O(2)-Mo(1)	73.3 (3)	O(1)-N(1)-Mo(1)	172.4 (5)
N(21)-N(20)-Mo(1)	129.9 (5)	N(20)-N(21)-N(22)	176.7 (7)
N(31)-N(30)-Mo(1)	121.4 (6)	N(30)-N(31)-N(32)	178.0 (9)
N(41)-N(40)-Mo(1)	123.0 (6)	N(40)-N(41)-N(42)	177.0 (9)
N(51)-N(50)-Mo(1)	124.6 (5)	N(50)-N(51)-N(42)	175.2 (10)

summarized. The ν(N=O) stretching frequency increases as expected from 1455 cm^{-1} for the $[Mo(NO)(CN)_5]^{4-}$ species (containing Mo(0)) to 1645 cm^{-1} for the $[Mo(NO)(CN)_5]^{2-}$ anion (a Mo(II) species).

When an aqueous suspension of the polymeric material and sodium azide is heated to 60 °C, a clear yellow solution is obtained. Upon addition of $[(C_6H_5)_4P]Cl$ and cooling to 0 °C, yellow crystals precipitate. The elemental analysis and infrared data (Table II) are in agreement with its formulation

Table VII. Summary of Structure Data of $\{Mo-N=O\}^4$ Complexes

		Mo–N=O		Mo(H_2NO)		
complex	CN[a]	*d*(Mo–N), Å	*d*(N=O), Å	*d*(Mo–N), Å	*d*(N–O), Å	ref
$[Mo(NO)(bpy)(H_2NO)_2]Cl$	7	1.773 (4)	1.210 (6)	2.105 (5)	1.412 (7)	2
$(phen)[Mo(NO)(phen)_2(H_2NO)]I_2 \cdot H_2O$	7	1.69 (3)	1.21 (3)	2.06 (2)	1.33 (3)	3
$[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4] \cdot H_2O$	7	1.761 (8)	1.21 (1)	2.125 (5)	1.404 (7)	this work
$[Mo(NO)(HNO)(CN)(terpy)] \cdot H_2O$	7	1.802 (7)	1.209 (9)	2.044 (7)	1.422 (9)	*c*
$K_3[Mo(NO)(C_2O_4)_3] \cdot 4H_2O$	7	1.780 (5)	1.188 (7)			4
$[(C_6H_5)_4As]_2[Mo(NO)Cl_5] \cdot 2CH_2Cl_2$	6	1.75 (3)	1.12 (4)			*b*
$[Mo(NO)Cl_3(POCl_3)]_2$	6	1.808 (6)	1.080 (7)			*b*
$[(C_6H_5)_4P]_2[Mo(NO)(ONC(CH_3)_2)(NCS)_4]$	7	1.77 (1)	1.19 (1)	2.086 (8)	1.36 (1)	5

[a] Coordination number: 7 = pentagonal bipyramid; 6 = octahedron. [b] Dehnicke, K.; Liebelt, A.; Weller, F. *Z. Anorg. Allg. Chem.* **1981**, *474*, 83. [c] Wieghardt, K.; Holzbach, W.; Weiss, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, in press.

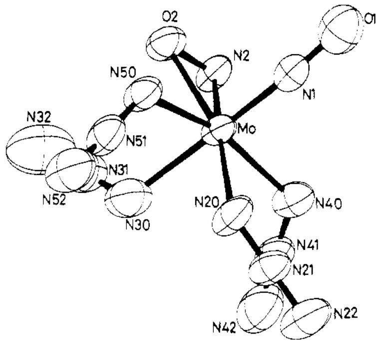

Figure 1. ORTEP view of the $[Mo(NO)(H_2NO)(N_3)_4]^{2-}$ dianion (50% probability).

as $[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4] \cdot H_2O$. Interestingly, Müller et al. have isolated the related $[Mo(NO)(H_2NO)(NCS)_4]^{2-}$ dianion.[5]

Crystal Structure of $[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4] \cdot H_2O$. The structure consists of four tetraphenylphosphonium cations, two complex dianions of $[Mo(NO)(H_2NO)(N_3)_4]^{2-}$, and two molecules of water of crystallization per unit cell. Bond distances and bond angles of the dianion are listed in Tables V and VI. The molecular geometry and the atomic labeling scheme for the complex anion are shown in Figure 1. The tetraphenylphosphonium cations do not exhibit any unusual features. The molybdenum(II) center in the dianion has pentagonal-bipyramidal geometry with an O,N-coordinated hydroxylamido(1–) ligand and three N_3^- ligands in equatorial positions; the nitrosyl and a fourth azide ligand occupy the axial positions. Seven-coordination with pentagonal-bipyramidal geometry is now well established for a series of nitrosyl complexes of the type $\{M-N=O\}^4$ (M = V(I), Mo(II)) all of which have a linear M–N=O moiety.[2-5] In Table VII relevant structural data for complexes characterized by X-ray crystallography are summarized. The Mo–N bond of the Mo–NO entity shows considerable multiple-bond character, as does the nitrogen–oxygen bond (1.21 (1) Å). The O,N-coordination of the hydroxylamido(1–) ligand is also well established in a series of complexes.[2,3,5] The bonding situations are in all cases very similar. A nitrogen–oxygen single bond of ~1.40 Å and Mo–N and Mo–O single-bond lengths of 2.125 (5) and 2.048 (5) Å, respectively, justify the description of the three-membered ring as an O,N-coordinated hydroxylamide(1–).[20] The small chelate bite of 39.3° makes the H_2NO^- ligand ideally suited to occupy two equatorial positions of the pentagonal bipyramid. The structural relationship of the H_2NO^- and the O_2^{2-} ligand has been pointed out previously.[16]

The azide ions are each covalently bound to the molybdenum(II) center via one nitrogen;[17] three N_3^- ligands occupy equatorial positions with an average Mo–N bond length of 2.17 (1) Å. The fourth N_3^- ligand is trans to the nitrosyl group, which exerts a trans influence (Mo–N_α bond length 2.21 (1) Å). The average Mo–N bond length of 2.17 (1) Å is significantly longer than is observed for related azido complexes of molybdenum(VI): 2.03 Å for $[MoN(N_3)_3(bpy)]$[18] and 2.01–2.11 Å for $[MoN(N_3)_4]^-$.[19] The bond angles at the N_α atoms (Mo–N_α–N_β–N_γ) span the range 121–129° indicating sp^2 hybridization of N_α atom, as had been observed for many azido complexes of transition metals.[17] The N_α–N_β bond lengths as well as the N_β–N_γ distances are very similar for all four azido ligands: 1.19 and 1.14 Å, respectively.

The nitrogens of one azide group (N(20), N(21), N(22)) show only small deviations from the best equatorial plane defined by the atoms Mo, N(2), O(2), N(20), N(40), and N(50).

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Registry No. $Cs_2[Mo(NO)(H_2NO)Cl_4]$, 84751-31-5; $[(C_6H_5)_4P]_2[Mo(NO)(H_2NO)(N_3)_4]$, 84751-34-8; $[(C_6H_5)_4P]_2[Mo(NO)(CN)_5]$, 84751-36-0; $[(C_6H_5)_4As]_2[Mo(NO)(CN)_5]$, 84751-37-1; $Cs_2[Mo(NO)(CN)_5]$, 84751-38-2; Na_2MoO_4, 7631-95-0; hydroxylammonium chloride, 5470-11-1.

Supplementary Material Available: Listings of the observed and calculated structure factor amplitudes and anisotropic thermal parameters for all non-hydrogen atoms (24 pages). Ordering information is given on any current masthead page.

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(20) Since the hydrogen atoms of the H_2NO^- ligand were not located from the present x-ray structure, the assumed position of both H atoms on the nitrogen atom may be questioned. However, the O,N-coordinated H_2NO^- ligand has been fully characterized by an X-ray study of $[VO(dipic)(H_2NO)(H_2O)]$[21] and a neutron diffraction study of $[UO_2(H_2NO)_2(H_3NO)_2] \cdot 2H_2O$.[22]

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