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Complexes of (Hydroxylamido-*O*,*N*)molybdenum(VI). Preparation and Crystal Structures of Dicesium Bis(benzohydroximato)-*cis*-dioxomolybdate(VI) Hydrate and of (Benzohydroxamato)(benzohydroximato)(*N*,*N*-dimethylhydroxylamido-*O*,*N*)oxomolybdenum(VI)

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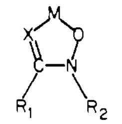
The reaction of *cis*-dioxobis(hydroxylamido-*O*,*N*)molybdenum(VI) complexes with benzohydroxamic acid in chloroform (or ethanol) affords monomeric neutral complexes containing benzohydrox*i*mato(2−) and benzohydrox*a*mato(1−) ligands, the respective N-substituted hydroxylamido(1−) ligand, and a terminal oxo ligand. The complex $[MoO((CH_3)_2NO)(BzH)Bz]$ (BzH = benzohydroxamate, Bz = benzohydroximate) has been characterized by a three-dimensional X-ray diffraction study. The complex crystallizes in the triclinic space group $P\bar{1}$ (C_i^1, No. 2) with $a = 9.063$ (3) Å, $b = 10.442$ (4) Å, $c = 10.618$ (4) Å, $\alpha = 87.46$ (3)°, $\beta = 67.82$ (3)°, $\gamma = 76.71$ (3)°, and $V = 904$ Å^3; $\rho_{calcd} = 1.628$ g cm^{-3} for $Z = 2$ and mol wt 443.3. Diffraction data were collected on a Syntex R 3 diffractometer using θ–2θ scan and Mo Kα radiation, and the structure was solved by conventional methods, resulting in a final R factor of 3.9% for 3819 independent reflections. The structure consists of monomeric complexes of Mo(VI) in a distorted pentagonal-bipyramidal environment containing an *N*,*N*-dimethylhydroxylamido-*O*,*N* ligand, one terminal oxo ligand, the O,O-coordinated dianion of benzohydroxamic acid (benzohydroximate), and an O,O-coordinated benzohydroxamato ligand. The reaction of molybdate(VI) anions with benzohydroxamic acid at pH ~9 yields the bis(benzohydroximato)-*cis*-dioxomolybdate(VI) anion. The cesium salt of the latter has been isolated and the structure has been determined by an X-ray analysis (experimental conditions as before). The complex crystallizes in the monoclinic space group $P2_1$ (C_2^2, No. 4) with $a = 10.749$ (4) Å, $b = 12.357$ (2) Å, $c = 15.679$ (3) Å, $\beta = 107.65$ (3)°, and $V = 1985$ Å^3; $\rho_{calcd} = 2.282$ g cm^{-3} for $Z = 4$ and mol wt 682.0. The structure was solved by conventional methods resulting in a final R factor of 4.2% for 5373 independent reflections. The structure consists of four complex dianions, $[MoO_2Bz_2]^{2-}$ (two of which are crystallographically independent), eight cesium ions, and four molecules of water of crystallization per unit cell. The Mo(VI) ions are in a distorted octahedral environment of two terminal oxo groups in the cis position and of two benzohyroximato(2−) ligands per molybdenum(VI) center. The Mo–O bond distances in the trans position to terminal oxo groups in both structures are relatively longer because of a pronounced trans influence of the oxo ligands.

Introduction

The coordination chemistry of benzohydroxamic acid[2-4] as well as thiobenzohydroxamic acid[5-7] has attracted much interest in the last few years because of the biological relevance of these complexes.[8] These studies have shown that the hydroxamate(1−) anion, the thiohydroxamate(1−) anion, and the thiohydroximate(2−) dianion are coordinated via two oxygen atoms or one oxygen and one sulfur atom to transition metals, respectively, forming five-membered rings.

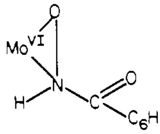


X = O, S
$R_1 = C_6H_5$
R_2 = H, pair of electrons

The crystal structures of a series of tris(benzohydroxamato)metal(III) complexes have been reported (e.g., M = Cr(III),[3] Fe(III)[4]), but to our knowledge no such characterization of a coordinated benzohydroximate dianion has been published to date.[17]

We have investigated the coordination chemistry of N-substituted hydroxylamines with molybdenum(VI) in some detail.[9,10] It was found that hydroxylamido(1−) ligands which are the O-deprotonated forms of the parent hydroxylamines are coordinated via the oxygen and the nitrogen atoms (η^2, "side-on" mode), forming three-membered rings. A complex containing molybdenum(VI) and two coordinated benzohydroxamate ligands has been described previously but without a detailed structural characterization.[11] We describe in this paper the preparation and crystal structure of $Cs_2[MoO_2Bz_2]\cdot H_2O$, a complex of molybdenum(VI) containing the benzohydroximate ligand which is the dianion of benzohydroxamic acid.

At the outset of this study it was hoped to find an example for the η^2 mode of coordination of the hydroxamate anion if molybdenum(VI) is the central transition metal:



Therefore, the reaction of bis(*N*-substituted hydroxylamido)dioxomolybdenum(VI) complexes[9,10] with benzohydroxamic acid was studied. We report the crystal structure of one of the products $[MoO((CH_3)_2NO)(BzH)Bz]$, which contains a benzohydroxamato and a benzohydroximato ligand,

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(2) Chatterjee, B. *Coord. Chem. Rev.* **1978**, *26*, 281.
(3) Abu-Dari, K.; Ekstrand, J. D.; Freyberg, D. P.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 108.
(4) Lindner, V. H. J.; Gottlicher, S. *Acta Crystallogr., Sect. B* **1969**, *B25*, 832.
(5) Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.* **1977**, *16*, 807.
(6) Abu-Dari, K.; Freyberg, D. P.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 2427.
(7) Cliff, C. A.; Fallon, G. D.; Gatehouse, B. M.; Murray, K. S.; Newman, P. J. *Inorg. Chem.* **1980**, *19*, 773.
(8) Raymond, K. N. *Adv. Chem. Ser.* **1977**, *No. 162*, 33-54.
(9) Wieghardt, K.; Holzbach, W.; Weiss, J.; Nuber, B.; Prikner, B. *Angew. Chem.* **1979**, *91*, 582; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 549.
(10) Wieghardt, K.; Hofer, E.; Holzbach, W.; Weiss, J.; Nuber, B. *Inorg. Chem.* **1980**, *19*, 2927.
(11) Dutta, R. L.; Chatterjee, B. *J. Indian Chem. Soc.* **1967**, *44*, 781.

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Table I. New Complexes Described in This Paper

compd[a]	color	mp, °C	% Cs		% C		% H		% N		% Mo	
			calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
$Cs_2[MoO_2Bz_2]\cdot H_2O$ (I)	yellow		38.98	39.2	24.66	25.0	1.77	1.8	4.11	4.2	14.07	14.1
$[MoO((CH_3)_2NO)(BzH)Bz]$[b] (II)	red	165			43.35	43.2	3.87	3.9	9.48	9.5	21.64	21.8
$[MoO((CH_3)_2NO)(BzH)Bz]\cdot CHCl_3$	red				36.29	38.0	3.23	3.2	7.47	7.8	17.05	16.8
$Cs_2[WO_2Bz_2]\cdot H_2O$	pale yellow		34.53	34.6	21.84	22.1	1.57	1.5	3.64	3.8	23.88[c]	23.5
$[MoO((C_2H_5)_2NO)(BzH)Bz]$	orange	159			45.87	46.4	4.49	5.2	8.92	9.0	20.36	20.4
$[MoO((C_6H_5CH_2)_2NO)(BzH)Bz]$	red-violet	159–165 dec			56.49	56.9	4.23	4.3	7.06	7.3	16.10	16.4
$[MoO((CH_3)HNO)(BzH)Bz]$	yellow	164			41.97	41.6	2.82	2.7	9.79	10.2	22.35	22.0
$[MoO(((CH_3)_3C)HNO)(BzH)Bz]$	orange	158 dec			45.87	46.4	4.49	4.5	8.92	9.0	20.36	21.0
$[MoO_2(((CH_3)_3C)HNO)_2]$	colorless	170 dec			31.59	31.8	6.63	6.6	9.21	9.4	31.54	31.6

[a] BzH = benzohydroxamate(1−), $C_7H_6NO_2$. Bz = benzohydroximate(2−), $C_7H_5NO_2$. [b] Prepared from ethanol instead of chloroform. [c] % W.

both of which form nearly planar five-membered rings with the molybdenum(VI) center.

Experimental Section

Abbreviations used are as follows: BzH_2 = benzohydroxamic acid, BzH = benzohydroxamate monoanion (O-deprotonated form of BzH_2), and Bz = benzohydroximate dianion (O- and N-deprotonated form of BzH_2).

Microanalyses (Table I) were performed by Beller Microanalytical Laboratory, Göttingen. Melting points (Table I) were determined in capillaries and are uncorrected.

$Cs_2[MoO_2Bz_2]\cdot H_2O$ (I). $Na_2MoO_4\cdot 2H_2O$ (2.4 g) was dissolved in 50 mL of water, and the pH was adjusted to 9.5 with 0.1 M NaOH. To this solution was added benzohydroxamic acid (2.8 g) at 60 °C with stirring. When CsCl (5 g) was added to the now orange solution and the mixture cooled (0 °C), analytically pure yellow crystals precipitated which were filtered off, washed with ethanol and ether, and air-dried; yield 78%.

$Cs_2[WO_2Bz_2]\cdot H_2O$. The preparation was carried out as has been described for the analogous complex of molybdenum by using $Na_2WO_4\cdot 2H_2O$ (3.3 g); yield 75%.

$[MoO_2((CH_3)_3CNHO)_2]$. $Na_2MoO_4\cdot 2H_2O$ (2.4 g) was dissolved in 50 mL of water. Upon addition of *N-tert*-butylhydroxylammonium chloride (2.6 g), a colorless precipitate formed immediately which was filtered off and dried in vacuo over P_2O_5; yield 91%.

Reactions of $MoO_2(R_1R_2NO)_2$ Complexes with Benzohydroxamic Acid. To suspensions (or solutions) of 5 mmol of $[MoO_2(R_1R_2NO)_2]$ in 50 mL of chloroform were added 12.5-mmol amounts of benzohydroxamic acid with stirring at 20 °C. The color of these solutions became rapidly orange-red. When the mixtures were cooled (0 °C), analytically pure crystals precipitated (see Table I) in yields of 60–80%. In one case the product contained chloroform of crystallization (Table I) which could be removed by recrystallization from ethanol (Table I, second complex). The complexes $MoO_2(R_1R_2NO)_2$ were prepared as described previously.[9,10]

Description of the X-ray Diffraction Studies and Solution of the Structures. The crystals selected for the structural analyses were of the following approximate dimensions: I, 0.2 × 0.2 × 0.2 mm; II, 0.5 × 0.2 × 0.2 mm. The unit cell parameters were obtained at ambient temperature of 23 °C by least-squares refinements of the respective angular settings of 25 reflections of each crystal (Table II). Intensity data were collected on an automated diffractometer, Syntex R 3, and were corrected for Lorentz and polarization effects. An empirical correction for adsorption effects was also carried out.[12] The scattering factors for neutral nonhydrogen atoms were corrected for both the real and imaginary components of anomalous dispersion. The function minimized during least-squares refinement was $\sum(|R_o| - |F_c|)^2$. No weighting scheme was applied in the refinement.

The structures of I and II were solved via three-dimensional Patterson syntheses which yielded the positions of the heavy atoms cesium and molybdenum, respectively. Fourier syntheses revealed the locations of all remaining nonhydrogen atoms. Refinements[12] were carried out with use of anisotropic thermal parameters for all nonhydrogen atoms. In the case of I, refinement was continued with all hydrogen atoms of the phenyl rings included in calculated, idealized positions (based upon d(C–H) of 0.96 Å) and isotropic temperature factors which were treated as variables (see supplementary material). The location of hydrogen atoms of the water of crystallization has not been possible. Convergence was reached with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.042$.

Table II. Summary of Crystal Data and Intensity Collection for $Cs_2[MoO_2Bz_2]\cdot H_2O$ (I) and $[MoO((CH_3)_2NO)(BzH)Bz]$ (II)

A. Crystal Parameters at 23 °C

	I	II
a, Å	10.749 (4)	9.063 (3)
b, Å	12.357 (2)	10.442 (4)
c, Å	15.679 (3)	10.618 (4)
α, deg		87.46 (3)
β, deg	107.65 (3)	67.82 (3)
γ, deg		76.71 (3)
V, Å	1985	904
cryst system	monoclinic	triclinic
space group	$P2_1$ (C_2^2, No. 4)	$P\bar{1}$ (C_i^1, No. 2)
Z	4	2
ρ_{calcd}, g cm^{-3}	2.282	1.628
mol wt	682.0	443.3
	$Cs_2[MoC_{14}H_{10}N_2O_6]\cdot H_2O$	$[MoC_{16}H_{17}N_3O_6]$

B. Measurement of Intensity Data

diffractometer: Syntex R3
radiation: Mo Kα (λ = 0.7107 Å)
data collcn: θ–2θ mode
2θ range, deg: I, 4–62; II, 4–60
scan rate, deg/min: 2.85–11.4
bkgd estimation: stationary crystal, stationary counter at the extremities of each 2θ scan; each for half the time taken for the 2θ scan
std rflcns: 2 every 2 h; no decay observed
rflcns collected: I, 5373; II, 3819 ($I \geq 2.5\sigma(I)$)
abs coeff, cm^{-1}: I, 42.7; II, 7.56

In the case of II a difference Fourier synthesis revealed the position of all hydrogen atoms. Refinement was continued with these positions and isotropic thermal parameters. Convergence was reached with $R = 0.039$.

Final difference Fourier syntheses were essentially featureless, and the structures of I and II are therefore considered to be complete. The ratio of data to parameters for I is 11.0:1 and for II is 12.6:1.

The final positional parameters are given in Table III for complex I and in Table IV for complex II. A list of observed and calculated structure factors and the respective anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms of structures I and II are available as supplementary material.

Results and Discussion

Preparation and Characterization of the Complexes. The reaction of molybdate(VI) oxoanions in aqueous solution with *N-tert*-butylhydroxylammonium chloride affords a colorless crystalline product, $[MoO_2((CH_3)_3CNHO)_2]$. Two strong ν(Mo=O) frequencies at 900 and 870 cm^{-1} indicate the presence of a *cis*-dioxomolybdenum(VI) moiety. Two *N-tert*-butylhydroxylamido(1−) ligands are thought to be coor-

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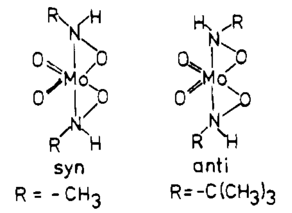
(12) Computations were performed on a NOVA 3 (General Data) computer using SHELX (G. M. Sheldrick, Cambridge, England, 1976).

Table III. Final Positional Parameters for $Cs_2[MoO_2Bz_2]\cdot H_2O$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cs1	0.2155 (2)	0.0000 (1)	0.4468 (1)	Cs3	0.05568 (6)	0.35965 (6)	0.35087 (5)
Cs2	0.2820 (1)	0.60416 (7)	0.5560 (1)	Cs4	0.444407 (8)	0.24133 (6)	0.64854 (5)
Mo1	0.45849 (8)	0.33920 (7)	0.41917 (6)	Mo2	0.0417 (1)	0.26249 (8)	0.58088 (7)
O1	0.4101 (8)	0.1842 (6)	0.3960 (5)	O7	−0.0037 (7)	0.1153 (7)	0.6146 (5)
O2	0.3139 (8)	0.3323 (6)	0.2872 (5)	O8	−0.0841 (7)	0.2887 (6)	0.6635 (5)
O3	0.5185 (7)	0.4820 (5)	0.3958 (5)	O9	0.0809 (8)	0.4191 (7)	0.6029 (5)
O4	0.5764 (8)	0.3146 (6)	0.3327 (5)	O10	0.1865 (8)	0.2746 (6)	0.7069 (5)
O5	0.5813 (7)	0.2946 (7)	0.5091 (5)	O11	0.1555 (7)	0.2040 (7)	0.5369 (6)
O6	0.3426 (9)	0.3877 (7)	0.4657 (5)	O12	−0.0817 (8)	0.2986 (7)	0.4835 (5)
N1	0.3277 (13)	0.1537 (9)	0.3077 (7)	N3	−0.0869 (9)	0.1037 (9)	0.6702 (7)
N2	0.596 (1)	0.4978 (7)	0.3383 (6)	N4	0.1599 (9)	0.4573 (7)	0.6846 (6)
C1	0.294 (1)	0.2329 (9)	0.2639 (8)	C15	−0.1220 (10)	0.2010 (8)	0.6952 (6)
C2	0.197 (1)	0.210 (1)	0.1701 (8)	C16	−0.1996 (10)	0.2082 (9)	0.7600 (7)
C3	0.170 (2)	0.305 (1)	0.1085 (9)	C17	−0.210 (1)	0.299 (1)	0.8010 (9)
C4	0.093 (2)	0.293 (2)	0.018 (1)	C18	−0.276 (2)	0.296 (1)	0.864 (1)
C5	0.044 (2)	0.194 (2)	−0.005 (1)	C19	−0.340 (2)	0.199 (2)	0.884 (1)
C6	0.085 (3)	0.094 (2)	0.055 (1)	C20	−0.320 (1)	0.104 (1)	0.838 (1)
C7	0.134 (2)	0.114 (1)	0.146 (1)	C21	−0.255 (1)	0.106 (1)	0.781 (1)
C8	0.6176 (10)	0.4063 (9)	0.3118 (7)	C22	0.218 (1)	0.373 (1)	0.741 (1)
C9	0.694 (1)	0.4064 (8)	0.2488 (8)	C23	0.291 (1)	0.390 (1)	0.8329 (8)
C10	0.707 (1)	0.305 (1)	0.2056 (8)	C24	0.327 (2)	0.316 (1)	0.892 (1)
C11	0.784 (1)	0.296 (1)	0.142 (1)	C25	0.410 (1)	0.338 (1)	0.9777 (8)
C12	0.835 (1)	0.387 (1)	0.1204 (7)	C26	0.456 (2)	0.436 (1)	0.005 (1)
C13	0.827 (1)	0.480 (1)	0.157 (1)	C27	0.431 (2)	0.505 (2)	0.952 (1)
C14	0.758 (1)	0.492 (1)	0.2295 (8)	C28	0.327 (2)	0.497 (1)	0.864 (1)
O_w	0.513 (2)	0.476 (1)	0.720 (1)	O_w	−0.001 (3)	0.112 (2)	−0.291 (2)

dinated in the O,N mode found for analogous complexes described previously.[9,10] Two isomers are conceivable which differ in the positions of the two *N-tert*-butyl groups relative to each other: a "syn" form and the corresponding "anti" form.



For the *cis*-dioxobis(*N*-methylhydroxylamido-*O*,*N*)molybdenum(VI) complex the "syn" form has been established in the solid state as well as in solutions of the crystals.[9,10]

The ^1H NMR spectrum of *cis*-dioxobis(*N-tert*-butylhydroxylamido-*O*,*N*)molybdenum(VI) dissolved in $CDCl_3$ at 25 °C exhibits two singlets at δ 1.36 and 1.38 (ratio 1:1), which are assigned to two *tert*-butyl groups and two broad singlets at δ 5.61 and 5.57 (N–H protons; ratio 1:1). Simple recrystallization or fractionated crystallizations from dibromoethane or chloroform did not change the ratio of integrated intensities of these resonances (1:1). When a dimethyl-d_6 sulfoxide solution of this complex was slowly heated to 145 °C, a third signal for a *tert*-butyl group at δ 1.40 arises most probably because of the formation of the "syn" isomer. At this temperature the complex decomposes and the solution becomes blue. These data indicate that the pure "syn" isomer cannot be present in solution and in the solid state (only one singlet for the two *tert*-butyl groups would be detected), but most probably the "anti" isomer is the only isolable product.

The reaction of molybdate(VI) or tungstate(VI) oxoanions in aqueous solution (pH 9.5) with benzohydroxamic acid gives yellow solutions from which yellow crystals can be grown by addition of cesium chloride. The elemental analyses indicate the stoichiometry $Cs_2[MoO_2Bz_2]\cdot H_2O$ and $Cs_2[WO_2Bz_2]\cdot H_2O$, respectively.

$$MoO_4^{2-} + 2BzH_2 \rightarrow [MoO_2Bz_2]^{2-} + 2H_2O \qquad (1)$$

$$WO_4^{2-} + 2BzH_2 \rightarrow [WO_2Bz_2]^{2-} + 2H_2O \qquad (2)$$

This indicates that two benzohydroximato(2−) ligands are coordinated to the molybdenum(VI) and tungsten(VI) centers, respectively. From acidified solutions of these salts, yellow neutral complexes $[MoO_2(BzH)_2]$ and $[WO_2(BzH)_2]$ are obtained. The first has been described previously.[11]

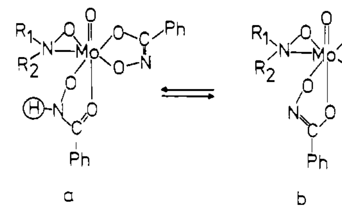
Addition of benzohydroxamic acid to colorless solutions of complexes of the type $[MoO_2(R_1R_2NO)_2]$ in chloroform leads to the formation of orange-red crystalline precipitates of the empirical formula $[MoO(R_1R_2NO)(BzH)Bz]^0$ (eq 3). A

$$[MoO_2(R_1R_2NO)_2] + 2BzH_2 \rightarrow [MoO(R_1R_2NO)(BzH)Bz] + H_2O + R_1R_2NOH \qquad (3)$$

$$R_1R_2NO^- = (CH_3)_2NO^-, (C_2H_5)_2NO^-, (C_6H_5CH_2)_2NO^-, (CH_3)HNO^-, ((CH_3)_3C)HNO^-$$

sharp and strong IR absorption at ~940 cm^{-1} is assigned to ν(Mo═O) stretch frequencies. These complexes are soluble in ethanol, acetone, dimethylformamide, and chloroform but insoluble in water. As is shown from an X-ray study (vide infra), monomeric neutral complexes of molybdenum(VI) are formed containing a hydroxylamido-*O*,*N* ligand, a terminal oxo group, and one benzhydroxamato as well as one benzohydroximato ligand.

In solution two tautomeric species of each of these complexes should exist which might be interconvertible via an intermolecular proton transfer.



This behavior can be demonstrated from temperature-dependent ^1H NMR spectra of $[MoO((CH_3)_2NO)(BzH)Bz]^0$ dissolved in dimethylformamide-d_7. The ^1H NMR spectrum of this complex exhibits at 230 K two broad signals at δ 11.5 and 11.2 (N–H protons), a multiplet at δ 8.0–7.3 (phenyl protons), and *four* singlets at δ 3.52, 3.48, 3.31, and 3.22, which are assigned to methyl protons. The signals at δ 11.5 and 11.2 broaden at higher temperatures until at 270 K these resonances

Table IV. Final Positional Parameters for $[MoO((CH_3)_2NO)Bz(BzH)]$

atom	*x*	*y*	*z*
Mo	0.32716 (4)	0.19506 (4)	0.31621
O1	0.4759 (3)	0.2504 (3)	0.1410 (2)
O2	0.5454 (3)	0.1593 (3)	0.3308 (2)
O3	0.4138 (3)	−0.0074 (3)	0.2351 (2)
O4	0.2900 (3)	0.0798 (3)	0.4814 (2)
O5	0.1952 (3)	0.2240 (3)	0.2022 (3)
O6	0.2388 (4)	0.3331 (3)	0.418 (3)
N1	0.6835 (4)	0.1777 (4)	0.217 (3)
N2	0.3770 (4)	−0.0482 (3)	0.4502 (3)
N3	0.0916 (4)	0.1769 (4)	0.3200 (3)
C1	0.6330 (5)	0.2257 (4)	0.1218 (4)
C2	0.7492 (5)	0.2555 (4)	−0.0116 (4)
C3	0.6902 (6)	0.3457 (5)	−0.0914 (4)
C4	0.7972 (9)	0.3763 (7)	−0.2173 (5)
C5	0.9598 (9)	0.3157 (9)	−0.2618 (5)
C6	0.0186 (7)	0.2245 (8)	−0.1842 (6)
C7	0.9132 (6)	0.1940 (6)	−0.0570 (5)
C8	0.4410 (4)	−0.0915 (4)	0.3205 (4)
C9	0.5383 (5)	−0.2251 (4)	0.2784 (4)
C10	0.6277 (6)	−0.2544 (5)	0.1386 (4)
C11	0.7256 (7)	−0.3784 (5)	0.0949 (5)
C12	0.7353 (7)	−0.4755 (5)	0.1862 (5)
C13	0.6460	−0.4467 (5)	0.3247 (5)
C14	0.5481 (6)	−0.3229 (5)	0.3714 (4)
C15	−0.0582 (6)	0.2797 (6)	0.3901 (5)
C16	0.0572 (6)	0.0522 (6)	0.2925 (5)
H1	0.405 (6)	−0.088 (5)	0.504 (5)
H3	0.579 (5)	0.389 (5)	−0.063 (5)
H4	0.756 (8)	0.439 (7)	−0.283 (7)
H5	0.041 (8)	0.313 (6)	−0.341 (6)
H6	0.135 (7)	0.178 (6)	−0.214 (6)
H7	0.951 (6)	0.128 (5)	0.001 (5)
H10	0.620 (5)	−0.183 (4)	0.077 (4)
H11	0.807 (6)	−0.395 (5)	−0.000 (5)
H12	0.802 (5)	−0.569 (4)	0.153 (4)
H13	0.650 (6)	−0.515 (6)	0.396 (6)
H14	0.481 (6)	−0.298 (5)	0.484 (5)
H151	−0.128 (5)	0.274 (4)	0.333 (4)
H152	−0.027 (5)	0.368 (4)	0.407 (4)
H153	−0.237 (7)	0.262 (6)	0.477 (6)
H161	−0.021 (6)	0.064 (5)	0.257 (5)
H162	0.035 (6)	−0.002 (5)	0.351 (5)
H163	0.190 (8)	−0.014 (6)	0.240 (6)

are no longer detectable. Above 290 K the four singlets first broaden slightly and at 315 K then give two singlets with chemical shifts of δ 3.48 and 3.30 and an integral intensity ratio of 1:1. These two signals coalesce at 338 K, and only one broad singlet is observed at 345 K. When the complex is cooled to 230 K, the starting spectrum is regained unchanged.

These results can clearly be interpreted if one assumes the two tautomeric forms a and b to be present in solution. Since the two five-membered rings formed by the monoanion and the dianion of benzohydroxamic acid are not equivalent (see structure in Figure 2), two distinct signals for the N–H protons of the tautomeric isomers a and b are observed as well as four signals for the methyl groups (two for each tautomeric form). A protonation–deprotonation mechanism at the nitrogen atoms of the benzohydroxamate ligands affects a rapid isomerization of the $[MoO((CH_3)_2NO)(BzH)Bz]$ complex in solution. At 315 K this process (most probably an intermolecular proton exchange) is rapid on the NMR time scale; i.e., only two distinct resonances for the *N*-methyl groups (the averaged ^1H NMR signals of the two tautomeric forms) are observed. Coalescence of these two signals at still higher temperatures (338 K) is due to a dissociation–recombination mechanism of the *N,N*-dimethylhydroxylamido ligand as has been described previously in detail.[13]

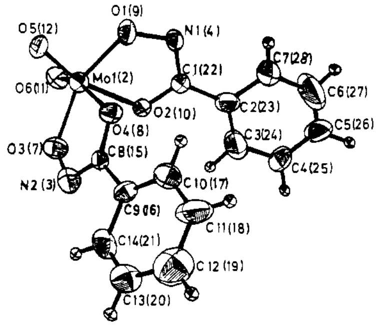


Figure 1. Perspective drawing of the $[MoO_2Bz_2]^{2-}$ anion showing the atom labeling scheme for the crystallographically independent anions.

Table V. Bond Distances (A) for $Cs_2[MoO_2Bz_2]\cdot H_2O$

	anion I	anion II
Mo1(2)–O1(9)	1.989 (7)	1.989 (9)
Mo1(2)–O2(10)	2.180 (7)	2.117 (6)
Mo1(2)–O3(7)	1.952 (7)	1.995 (8)
Mo1(2)–O4(8)	2.140 (9)	2.163 (9)
Mo1(2)–O5(12)	1.705 (7)	1.750 (7)
Mo1(2)–O6(11)	1.731 (10)	1.734 (9)
O1(9)–N1(4)	1.449 (12)	1.388 (11)
N1(4)–C1(22)	1.188 (16)	1.388 (13)
C1(22)–O2(10)	1.280 (14)	1.328 (13)
C1(22)–C2(23)	1.548 (15)	1.434 (15)
C2(23)–C3(24)	1.490 (20)	1.285 (19)
C3(24)–C4(25)	1.418 (21)	1.396 (18)
C4(25)–C5(26)	1.338 (31)	1.339 (23)
C5(26)–C6(27)	1.537 (32)	1.159 (27)
C6(27)–C7(28)	1.391 (28)	1.495 (24)
C7(28)–C2(23)	1.358 (23)	1.412 (20)
O3(7)–N2(3)	1.416 (14)	1.433 (15)
N2(3)–C8(15)	1.251 (14)	1.353 (15)
C8(15)–O4(8)	1.294 (13)	1.307 (13)
C8(15)–C9(16)	1.461 (17)	1.500 (17)
C9(16)–C10(17)	1.455 (18)	1.313 (18)
C10(17)–C11(18)	1.479 (22)	1.378 (25)
C11(18)–C12(19)	1.336 (23)	1.460 (29)
C12(19)–C13(20)	1.302 (24)	1.427 (27)
C13(20)–C14(21)	1.532 (23)	1.296 (23)
C14(21)–C9(16)	1.355 (19)	1.471 (18)

Description of the Crystal Structures of I and II. The crystal structure of $Cs_2[MoO_2Bz_2]\cdot H_2O$ (I) consists of cesium ions and monomeric anions $[MoO_2Bz_2]^{2-}$ and water of crystallization. There are two crystallographically independent complex anions per unit cell. Figure 1 shows the molybdenum(VI) center to have a distorted octahedral environment of six oxygen atoms: two terminal oxo groups and four oxygen donors, two from each coordinated benzohydroximato ligand. Bond distances and bond angles are given in Tables V and VI.

The benzohydroximate(2−) anions form five-membered rings with the molybdenum(VI) centers. The benzohydroximate rings are nearly planar (see supplementary material). The largest deviation of a single atom from a least-squares plane was found to be 0.07 Å. The MoO_2 moiety has the cis configuration with an average $Mo–O_t$ distance of 1.73 (1) Å and $O_t–Mo–O_t$ angle of 102.6 (4)°. The Mo–O bonds trans to the terminal oxygen atoms have been significantly lengthened, 2.15 Å, as compared to 1.98 (1) Å observed for Mo–O bonds cis to these oxygen atoms. It is of interest to note that the carbonyl oxygen atoms of the hydroximate ligands are coordinated trans to the terminal oxygen atoms, indicating that these atoms are weaker π donors[14] than the oxygen atoms bound to the nitrogen atoms of the chelated ligand. Interestingly, the situation is reversed in the *cis*-dioxobis(*N*-

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[13] Hofer, E.; Holzbach, W.; Wieghardt, K. *Angew. Chem.*, in press.

[14] Butcher, R. J.; Penfold, B. R.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1979**, 668.

Table VI. Bond Angles (Deg) for $Cs_2[MoO_2Bz_2]\cdot H_2O$

	anion I	anion II
O2(10)-Mo1(2)-O1(9)	73.6 (3)	73.3 (3)
O3(7)-Mo1(2)-O1(9)	156.9 (3)	153.8 (4)
O3(7)-Mo1(2)-O2(10)	92.2 (3)	89.2 (3)
O4(8)-Mo1(2)-O1(9)	85.4 (3)	83.6 (3)
O4(8)-Mo1(2)-O2(10)	77.4 (3)	81.2 (3)
O4(8)-Mo1(2)-O3(7)	73.5 (3)	74.3 (3)
O5(12)-Mo1(2)-O1(9)	86.2 (4)	88.2 (3)
O5(12)-Mo1(2)-O2(10)	157.3 (4)	160.8 (3)
O5(12)-Mo1(2)-O3(7)	103.3 (3)	106.4 (3)
O5(12)-Mo1(2)-O4(8)	91.1 (4)	92.2 (4)
O6(11)-Mo1(2)-O1(9)	103.2 (4)	109.7 (4)
O6(11)-Mo1(2)-O2(10)	90.9 (3)	89.6 (3)
O6(11)-Mo1(2)-O3(7)	95.0 (4)	89.1 (4)
O6(11)-Mo1(2)-O4(8)	163.1 (3)	161.0 (3)
O6(11)-Mo1(2)-O5(12)	103.8 (4)	101.5 (4)
N2(3)-O3(7)-Mo1(2)	122.4 (6)	120.0 (7)
C8(15)-N2(3)-O3(7)	106.9 (9)	111.5 (7)
O4(8)-C8(15)-N2(3)	126.6 (6)	118.7 (11)
Mo1(2)-O4(8)-C8(15)	110.5 (7)	115.3 (7)
N2(3)-C8(15)-C9(16)	114.9 (10)	120.7 (10)
C9(16)-C8(15)-O4(8)	118.5 (10)	120.6 (9)
C1(22)-O2(10)-Mo1(2)	108.5 (6)	117.8 (6)
N1(4)-C1(22)-O2(10)	129.1 (11)	114.9 (8)
O1(9)-N1(4)-C1(22)	109.2 (10)	111.3 (8)
Mo1(2)-O1(9)-N1(4)	118.4 (6)	121.9 (6)
O2(10)-C1(22)-C2(23)	116.8 (10)	122.6 (10)
C2(23)-C1(22)-N1(4)	113.6 (11)	122.0 (10)

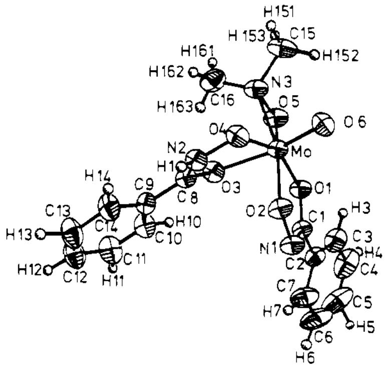


Figure 2. Perspective drawing of the $[Mo((CH_3)_2NO)(BzH)Bz]$ complex showing the atomic labeling scheme.

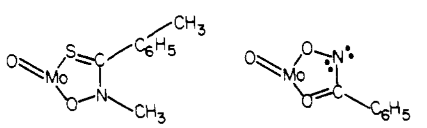
Table VII. Bond Distances (A) for $[MoO((CH_3)_2NO)Bz(BzH)]$

Mo-O1	1.995 (2)	C5-C6	1.377 (10)
Mo-O2	1.991 (3)	C5-H5	0.88 (6)
Mo-O3	2.171 (3)	C6-C7	1.401 (7)
Mo-O4	2.047 (3)	C6-H6	0.99 (5)
Mo-O5	1.969 (3)	C7-H7	0.99 (5)
Mo-O6	1.685 (3)	C8-C9	1.454 (5)
Mo-N3	2.172 (4)	C9-C10	1.403 (5)
O1-C1	1.323 (5)	C9-C14	1.400 (6)
O2-N1	1.417 (4)	C10-C11	1.376 (7)
O3-C8	1.285 (5)	C10-H10	0.98 (4)
O4-N2	1.369 (4)	C11-C12	1.382 (7)
O5-N3	1.399 (4)	C11-H11	0.99 (4)
N1-C1	1.296 (6)	C12-C13	1.391 (7)
N2-C8	1.329 (4)	C12-H12	1.02 (4)
N2-H1	0.78 (6)	C13-C14	1.378 (6)
N3-C15	1.478 (5)	C13-H13	1.02 (6)
N3-C16	1.471 (8)	C14-H14	1.13 (5)
C1-C2	1.482 (5)	C15-H151	1.04 (6)
C2-C3	1.389 (7)	C15-H152	1.07 (5)
C2-C7	1.379 (6)	C15-H153	0.94 (6)
C3-C4	1.399 (7)	C16-H161	0.91 (6)
C3-H3	0.94 (4)	C16-H162	0.82 (6)
C4-C5	1.367 (10)	C16-H163	1.17 (6)
C4-H4	1.05 (8)		

Table VIII. Bond Angles (Deg) for $[MoO((CH_3)_2NO)Bz(BzH)]$

O1-Mo-O2	74.9 (1)	H1-N2-C8	120 (3)
O1-Mo-O3	89.3 (1)	Mo-N3-O5	62.6 (2)
O1-Mo-O4	150.5 (1)	Mo-N3-C15	120.5 (4)
O1-Mo-O5	76.5 (1)	Mo-N3-C16	123.9 (3)
O1-Mo-O6	105.5 (1)	O5-N3-C15	110.9 (3)
O1-Mo-N3	115.6 (1)	O5-N3-C16	112.1 (3)
O2-Mo-O3	82.2 (1)	O15-N3-C16	113.2 (4)
O2-Mo-O4	78.8 (1)	O1-C1-N1	121.0 (3)
O2-Mo-O5	149.5 (1)	O1-C1-C2	117.9 (4)
O2-Mo-O6	98.2 (2)	C2-C1-N1	121.1 (4)
O2-Mo-N3	163.5 (1)	C1-C2-C3	119.0 (4)
O3-Mo-O4	74.0 (1)	C1-C2-C7	120.8 (4)
O3-Mo-O5	86.9 (1)	C3-C2-C7	120.3 (4)
O3-Mo-O6	164.8 (1)	C4-C3-C2	120.2 (5)
O3-Mo-N3	85.1 (1)	C5-C4-C3	119.4 (6)
O4-Mo-O5	125.2 (1)	C6-C5-C4	120.6 (5)
O4-Mo-O6	91.2 (1)	C7-C6-C5	120.6 (5)
O4-Mo-N3	87.6 (1)	C6-C7-C2	119.0 (5)
O5-Mo-O6	99.6 (1)	O3-C8-N2	115.8 (3)
O5-Mo-N3	39.1 (1)	O3-C8-C9	122.4 (3)
O6-Mo-N3	91.3 (2)	C9-C8-N2	121.8 (4)
C1-O1-Mo	116.3 (2)	C8-C9-C10	117.8 (4)
N1-O2-Mo	119.5 (2)	C8-C9-C14	122.6 (3)
C8-O3-Mo	113.8 (2)	C14-C9-C10	119.6 (4)
N2-O4-Mo	113.7 (2)	C9-C10-C11	119.6 (4)
N3-O5-Mo	78.3 (2)	C10-C11-C12	121.1 (4)
C1-N1-O2	107.8 (3)	C11-C12-C13	119.4 (4)
C8-N2-O4	118.3 (3)	C12-C13-C14	120.8 (5)
H1-N2-O4	120 (4)	C13-C14-C9	119.6 (4)

methyl-*p*-tolylthiohydroxamato)molybdenum(VI) complex in which the thiolate donor atoms lie cis to the two terminal oxo groups,[7] because in this case the sulfur atom is a stronger π donor than the oxygen atom.



The crystal structure of $[MoO((CH_3)_2NO)(BzH)Bz]$ (II) consists of well-separated monomers. There are no significant intermolecular nonbonded contacts in the unit cell. Figure 2 shows the complex to have pentagonal-bipyramidal geometry with an *N*,*N*-dimethylhydroxylamido(1−) ligand coordinated via the oxygen and nitrogen atom in equatorial positions.[15] The hydroxylamido ligand adopts the well-known O,N-coordination[9,10] with an N–O bond distance of 1.399 (4) Å and an average N–C distance of 1.475 (7) Å (Table VII), indicating normal N–O and C–N single bonds. A benzohydroximate(2−) ligand occupies two equatorial coordination sites whereas the oxygen atoms of the coordinated benzohydroxamate(1−) ligand occupy the fifth equatorial and one axial position of the pentagonal bipyramid, respectively. Interestingly, in the solid state only one tautomeric form (a) is present. This may be due to an energetically slightly more favorable packing of tautomer a in the solid state.

The terminal oxo ligand in the second axial position exerts again a strong influence upon the Mo–O bond distance trans to it. Since there is only one terminal oxo ligand, the Mo–O_t distance is shorter (1.685 (3) Å) than is observed for *cis*-dioxomolybdenum(VI) complexes;[16] but it also indicates the existence of additional strongly bonded ligand atoms which weaken the π bonding of Mo–O_t.[16] The oxygen atom trans to the terminal oxo ligand is a carbonyl oxygen atom of the

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(15) The first statement regarding the stereochemistry of oxomolybdenum(VI) made by the authors of ref 14 that these complexes are "almost invariably six-coordinate distorted octahedral complexes" should not be taken too strictly. There are now a number of seven-coordinate pentagonal-bipyramidal complexes with bidentate hydroxylamido(1−) ligands known.[10]

(16) Schröder, F. A. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2294 and references therein.

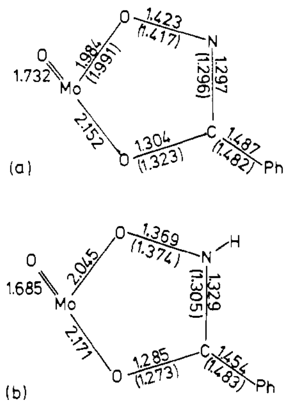
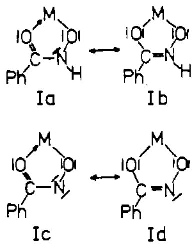


Figure 3. (a) Comparison of the average bond lengths of the coordinated benzohydroximato ligands in the $[MoO_2Bz_2]^{2-}$ anions and in $[MoO((CH_3)_2NO)(BzH)Bz]$ (bond lengths for the latter are given in parentheses). (b) Comparison of the bond distances of the coordinated benzohydroxamato ligand in $[MoO((CH_3)_2NO)(BzH)Bz]$ and average bond lengths in tris(benzohydroxamato)chromium(III)[3] (values for the latter in parentheses).

benzohydroxamate(1−) anion which is again a weaker π donor than the N-bonded oxygen atom.

In general, some lengthening of all bonds might be expected due to increased crowding when seven-coordinate structures are compared with similar six-coordinate complexes. This appears not to be the case in complex II as can be deduced from Figure 3a where the Mo–O bond lengths of the coordinated benzohydroximato ligand of structures I are compared with the respective values of II. The same is true for the coordinated hydroxylamido(1−) ligand of II: the Mo–O and Mo–N bond distances are very similar to those observed in a six-coordinate complex $[MoO_2((CH_3)HNO)_2]^0$.[9]

A unique feature of II is the presence of a benzohydroximate(2−) dianion and of a benzohydroxamate(1−) anion coordinated to the same metal center. This allows a direct comparison of bond distances within the respective five-membered rings (Figure 3a,b). It is noted that the bond distances within the benzohydroxamate ligands do not depend strongly on the nature of the metal ion to which they are coordinated (Figure 3b), e.g., chromium(III),[3] iron(III),[4] or molybdenum(VI). The mode of bonding for the benzohydroxamate(1−) ligands are depicted in formulas Ia and Ib show that the C—N and C—O bond distances are intermediate between single and double bonds. The observed bond distances indicate that the canonical form Ia carries relatively more weight than



Ib because the C—O bond distance (1.285 Å, Figure 3b) is close to a C═O double bond. Bond distances of the benzohydroximate(2−) ligand demonstrate a slight preference for the canonical form Id over Ic. Thus the observed small changes of bond distances upon deprotonation of a benzohyroxamate ligand are consistent with a transition of resonance structure Ia to Id: the C–N bond is contracted by 0.03 Å whereas the C–O bond distance is lengthened by 0.02 Å. The N–O bond distance increases by 0.05 Å upon deprotonation. This effect is best accounted for by an increased electron density at the nitrogen atom due to its deprotonation which leads to a more pronounced repulsion between the nitrogen and oxygen atoms. The same pattern of behavior has been observed for coordinated thiohydroxamate anions and thiohydroximate dianions.[6,17]

Acknowledgment. Financial support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. I, 75701-10-9; II, 75716-25-5; $Cs_2[WO_2Bz_2]$, 75701-11-0; $MoO_2((CH_3)_3CNHO)_2$, 75701-12-1; $MoO((C_2H_5)_2NO)(BzH)Bz$, 75701-13-2; $MoO((C_6H_5CH_2)_2NO)(BzH)Bz$, 75701-14-3; $MoO((CH_3)HNO)(BzH)Bz$, 75701-15-4; $MoO(((CH_3)_3C)HNO)(BzH)Bz$, 75701-16-5; $MoO_2((CH_3)_2NO)_2$, 74081-85-9; $MoO_2((C_2H_5)_2NO)_2$, 74081-86-0; $MoO_2((C_6H_5CH_2)_2NO)_2$, 74081-87-1; $MoO_2((CH_3)HNO)_2$, 70631-31-1.

Supplementary Material Available: Tables of least-squares planes, anisotropic thermal parameters of nonhydrogen atoms, positional and isotropic parameters for hydrogen atoms, and structure factor amplitudes (observed and calculated) for structues I and II, respectively (65 pages). Ordering information is given on any current masthead page.

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(17) After this paper had been accepted for publication an article (Abu-Dari, K.; Raymond, K. *Inorg. Chem.* **1980**, *19*, 2034) appeared describing the molecular structures of two salts of *cis*- and *trans*-tris(benzohydroximato)chromium(III). Where comparable, the bond distances for the coordinated benzohydroximato ligands of our and their studies are in excellent agreement.