Synthesis of vicinal bishydroxylamine

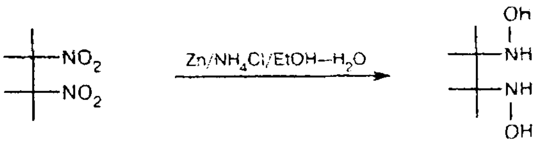
V. I. Ovcharenko,[a]* *S. V. Fokin,*[a] *G. V. Romanenko,*[a] *I. V. Korobkov,*[a] *and P. Rey*[b]

[a]*International Tomography Center, Siberian Branch of the Russian Academy of Sciences,*
630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 33 1399. E-mail: ovchar@tomo.nsc.ru
[b]*C.E.A-Département de Recherche Fondamentale sur la Matière Condensée,*
Service de Chimie Inorganique et Biologique, Laboratoire de Chimie de Coordination (URA CNRS 1194),
17 rue des Martyrs, 38041 Grenoble, France.
Fax: (103 3) 476 88 5090

Reduction of 2,3-dimethyl-2,3-dinitrobutane with Zn in aqueous ethanol in the presence of NH_4Cl affords 2,3-bis(hydroxylamino)-2,3-dimethylbutane together with 2,3-diamino-2,3-dimethylbutane and complex Zn salts. A modified procedure was developed for the synthesis of bishydroxylamine, which involves reduction in a $Zn/NH_4Cl/THF-H_2O$ system.

Key words: reduction of nitro derivatives, hydroxylamine derivatives, nitroxyl radicals, ethylenediamine derivatives, Zn^{II} complexes, X-ray diffraction analysis.

Stable nitroxyl radicals, which exhibit paramagnetism and are convenient subjects for study by ESR spectroscopy, are used as spin labels in molecular biology, biophysics, and analytical chemistry.[1] Of special note is the wide application of stable nitroxyl radicals in the design of molecular ferromagnetics.[1—5] Among them are 2-imidazoline derivatives, the synthesis of which has been developed by Ullman and coworkers.[6—11] The key stage of this procedure involves the preparation of 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**1**), which is then condensed with the corresponding aldehyde (or its synthetic equivalent). Vicinal bis(hydroxylamine) **1**, in turn, is prepared from 2,3-dimethyl-2,3-dinitrobutane (**2**) according to a procedure developed by Lamchen and Mittag.[12] This procedure involves reduction of nitro compound **2** with a Zn powder in the presence of NH_4Cl in aqueous ethanol, which is commonly used in the synthesis of hydroxylamines. However, this procedure often gives poorly reproducible or even negative results. Hence, attempts at modifying this procedure have been undertaken.[13] The reasons for a low yield of bishydroxylamine **1** remain unclear. This has stimulated us into more detailed studies of the processes that occur in the reduction of dinitro compound **2** to bishydroxylamine **1**.[14]



2 **1**

Results and Discussion

It is generally accepted that reduction of dinitro compound **2** to bishydroxylamine **1** is accompanied by the formation of $Zn(OH)_2$.[12] The presence of the latter can be readily explained by assuming that the following reactions occur:

$$C_6H_{12}(NO_2)_2 + 4\,Zn + 8\,NH_4Cl = C_6H_{12}(NHOH)_2 + 4\,ZnCl_2 + 8\,NH_3 + 2\,H_2O,$$
$$4\,ZnCl_2 + 8\,NH_3 + 8\,H_2O = 4\,Zn(OH)_2\downarrow + 8\,NH_4Cl,$$

$$C_6H_{12}(NO_2)_2 + 4\,Zn + 6\,H_2O = C_6H_{12}(NHOH)_2 + 4\,Zn(OH)_2\downarrow.$$

In this case, NH_4Cl acts as a proton carrier, in the absence of which reduction does not occur. Since the suggested zinc hydroxide is usually filtered off and discarded in the course of the synthesis, the true nature of this product was not studied and the behavior of Zn in this system was not considered.

We found that $Zn(OH)_2$ was not formed at all in the reduction of compound **2** to **1** under the conditions reported previously.[12] On the contrary, a white crystalline precipitate that formed was a mixture of $Zn(NH_3)_2Cl_2$ and a product of its partial hydrolysis, *viz.*, $Zn(OH)Cl$, which can be readily identified from its characteristic IR spectrum. The spectrum has overlapping bands of the spectra of $Zn(NH_3)_2Cl_2$ and $Zn(OH)Cl$ (the positions of these characteristic bands in the IR spectrum of this mixture are as follows: for $Zn(NH_3)_2Cl_2$, 3328 (s), 1599 (m), 1243 (s), 665 (s), 423 (m); and for $Zn(OH)Cl$, 3440 (s), 1082 (m), 938 (m), 738 (s), 545 (m), 464 cm^{-1} (m)). Note that the solid phase obtained

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1539—1545, August, 1999.

upon treatment of a known specimen of $Zn(NH_3)_2Cl_2$ with aqueous ethanol gave exactly the same spectrum. The formation of the above-mentioned mixture as the major component of the precipitate (or the only component in the case of a deficiency of Zn powder) was observed in all cases of reduction of **2**. Consequently, the overall reduction reaction of **2** to **1** would be more correctly represented as follows:

$$\begin{aligned}&C_6H_{12}(NO_2)_2 + 4\,Zn + (6 + x)\,NH_4Cl = \\&= C_6H_{12}(NHOH)_2 + (2 + x)\,Zn(NH_3)_2Cl_2\downarrow + \\&+ (2 - x)\,Zn(OH)Cl\downarrow + (2 - x)\,NH_3 + x\,H_2O.\end{aligned}$$

However, the composition of the solid phase is not the only characteristic feature of the behavior of zinc in the synthesis of **1**. Of even greater importance is the fact that a substantial amount of zinc cations appeared in the solution in the course of reduction of **2** to **1**. These cations can be readily detected by chelatometric titration of aliquots of the filtrate of the reaction mixture in the course and after completion of reduction of **2**. We demonstrated that in an aqueous or in aqueous-ethanolic solution, zinc exists as the complex cation $[Zn(tmEn)_2H_2O]^{2+}$, where tmEn is 2,3-diamino-2,3-dimethylbutane (the reduction product of **1**). In model experiments, poorly soluble $[Zn(tmEn)Cl_2]$, which was obtained by the reaction of $ZnCl_2$ with an equimolar amount of tmEn, readily passed into solution upon treatment with an excess of tmEn and was isolated as crystals of $[Zn(tmEn)_2H_2O]Cl_2 \cdot H_2O$ after concentration of the aqueous solution. The structure of the complex is shown in Fig. 1. The molecular structure of the $[Zn(tmEn)Cl_2]$ complex, which is poorly soluble in water and aqueous ethanol, is shown in Fig. 2. Selected bond lengths and bond angles are given in Table 1. Note that the data on the solubility of the Zn^{II} complexes with tmEn under consideration are in rather good agreement with the published data on Zn^{II} complexes with nonsubstituted ethylenediamine (En). Thus when Zn^{II} salts were mixed with En in a ratio of 1 : 1 or 1 : 2, insoluble $[ZnEnCl_2]$ was always formed. The latter passed into solution only when the Zn^{II} : En ratio was 1 : 3 or less, to form the $[ZnEn_3]^{2+}$ complex cation. Subsequent concentration of aqueous solutions resulted in crystallization of salts with this complex cation.[15–17] The reaction of $ZnCl_2$ with an approximately equimolar amount of tmEn also afforded poorly soluble $[Zn(tmEn)Cl_2]$ as the solid phase. As mentioned above, the latter passed into solution only upon treatment with an excess of

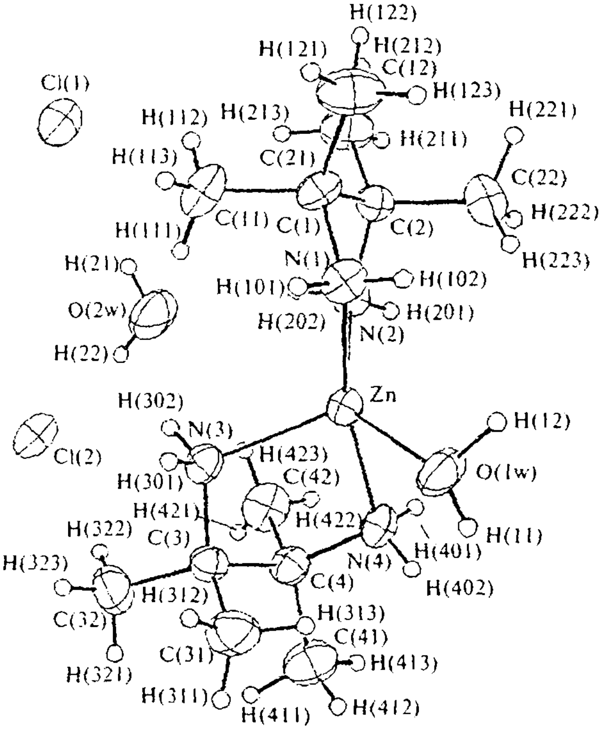


Fig. 1. Structure of $[Zn(tmEn)_2H_2O]Cl_2 \cdot H_2O$.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the structures under study

$[Zn(tmEn)Cl_2]$		$[Ni(tmEn)_2][ZnCl_4]$		$[Zn(tmEn)_2H_2O]Cl_2 \cdot H_2O$			
Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Zn—N	2.038(2)	Ni—N(1)	1.897(4)	Zn—N(1)	2.132(1)	Zn—N(3)	2.054(1)
		Ni—N(2)	1.909(4)	Zn—N(2)	2.079(1)	Zn—N(4)	2.136(1)
Zn—Cl	2.2338(7)	Zn—Cl(1)	2.293(2)	Zn—O(1w)	2.133(1)		
		Zn—Cl(2)	2.267(1)				
		Zn—Cl(3)	2.258(2)				
N—C(1)	1.501(3)	N(1)—C(1)	1.504(5)	N(1)—C(1)	1.492(2)	N(3)—C(3)	1.496(2)
		N(2)—C(2)	1.502(5)	C(2)—N(2)	1.490(2)	C(4)—N(4)	1.497(2)
C(1)—C(1′)	1.559(5)	C(1)—C(2)	1.549(5)	C(1)—C(2)	1.562(2)	C(3)—C(4)	1.569(2)
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
N—Zn—Cl	114.40(7)	Cl(2)—Zn—Cl(1)	107.26(4)	N(1)—Zn—O(1w)	81.98(4)	N(3)—Zn—O(1w)	115.59(4)
		Cl(3)—Zn—Cl(1)	104.84(7)	N(2)—Zn—O(1w)	138.11(4)	N(4)—Zn—O(1w)	87.06(4)
		Cl(3)—Zn—Cl(2)	112.45(4)				
N—Zn—N′	85.3(1)	N(1)—Ni—N(2)	85.2(2)	N(2)—Zn—N(1)	80.97(4)	N(3)—Zn—N(4)	82.23(4)
C(1)—N—Zn	108.2(1)	C(1)—N(1)—Ni	110.2(3)	C(1)—N(1)—Zn	110.39(7)	C(3)—N(3)—Zn	111.25(7)
		C(2)—N(2)—Ni	113.9(3)	C(2)—N(2)—Zn	111.73(7)	C(4)—N(4)—Zn	109.54(7)

tmEn. However, unlike $[ZnEn_3]^{2+}$, the $[Zn(tmEn)_2H_2O]^{2+}$ complex cation contains only two rather than three diamine molecules, which is apparently associated with steric hindrances due to a large number of methyl substituents. As a result, the coordination number of Zn^{II} in the $[Zn(tmEn)_2H_2O]Cl_2 \cdot H_2O$ complex is equal to five. The fifth coordination position is occupied by a water molecule (see Fig. 1). This is consistent with the data considered below that none of the structurally characterized metal complexes with tmEn contains more than two tmEn molecules in the inner coordination sphere. The rather high thermodynamic stability of $[Zn(tmEn)_2H_2O]^{2+}$ is also noteworthy, because $Zn(OH)_2$, which is virtually insoluble in aqueous ethanol, completely passes into solution in the reaction with an excess of tmEn.

$$Zn(OH)_2 + 2\ tmEn + H_2O = [Zn(tmEn)_2H_2O]^{2+} + 2\ OH^-.$$

It is common knowledge that overreduction products (in the case under consideration, 2,3-diamino-2,3-dimethylbutane) are always formed in the reduction of nitro derivatives to hydroxylamines. However, the ability of *vic*-diamine to transfer zinc into a solution should be taken into account in the synthesis of imidazolines where bishydroxylamine **1** is condensed with the corresponding aldehyde or its synthetic equivalent without isolation from the reaction mixture.[2] It is difficult to predict the effect of the presence of substantial amounts of the Zn^{II} complex in a solution on subsequent condensation to form adduct (**3**). This is of particular importance where condensation is promoted by addition of hydrochloric acid. First, the system exhibits buffer properties on gradual addition of the acid owing to neutralization:

$$\begin{aligned}&[Zn(tmEn)_2H_2O]Cl_2 + 2\ HCl = \\ &\quad [Zn(tmEn)Cl_2]\downarrow + tmEn \cdot 2HCl + H_2O\end{aligned}$$

or

$$\begin{aligned}&[Zn(tmEn)_2H_2O](OH)_2 + 4\ HCl = \\ &\quad = [Zn(tmEn)Cl_2]\downarrow + tmEn \cdot 2\ HCl + 3\ H_2O.\end{aligned}$$

It may occur that to make the reaction mixture acidic, which is essential to promote the formation of heterocyclic adduct **3**, it is necessary to add a large amount of acid. Second, when the acid is added, crystallization of **3** is accompanied by passage of poorly soluble $[Zn(tmEn)Cl_2]$ complex to the solid phase, which contaminates the target product and may complicate further oxidation of **3** to nitroxyl **4**. Third, $[Zn(tmEn)Cl_2]$ is dissolved in the presence of an excess of acid:

$$[Zn(tmEn)Cl_2] + 2\ HCl = tmEnH_2^{\,2+} + ZnCl_4^{\,2-}.$$

In this case, protonated 2,3-diamino-2,3-dimethylbutane ($tmEnH_2^{\,2+}$) is formed. This compound can react with an aldehyde to yield the corresponding condensation products (**5**), which contaminate adduct **3** (Scheme 1).

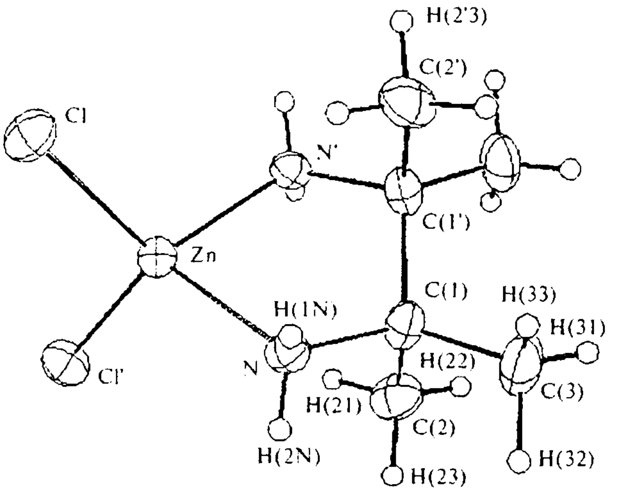
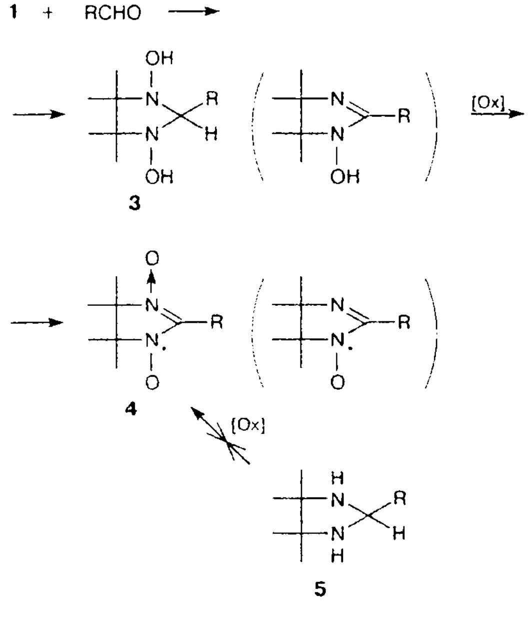


Fig. 2. Structure of $[Zn(tmEn)Cl_2]$.

Scheme 1



The $[Zn(tmEn)Cl_2]$ complex can be readily isolated directly from the reaction mixture under conditions reported previously.[12] Precipitation of this product as a colorless finely crystalline substance starts when the pH of the reaction mixture is decreased to 6—7. However, precipitation occurs rather slowly, which is inconvenient for the separation of tmEn from bishydroxylamine **1** as $[Zn(tmEn)Cl_2]$. We attempted to destroy $[Zn(tmEn)_2H_2O]^{2+}$ with simultaneous consumption of an excess of tmEn in a solution by reaction with a stronger complex-forming agent, *viz.*, with a Ni^{II} salt. We succeeded in isolating compounds with compositions $[Ni(tmEn)_2][ZnCl_4]$ and $[Ni(tmEn)_2]Cl_2 \cdot 2H_2O$ by adding $NiCl_2$ to the reaction mixture. These compounds were also prepared by independent synthesis. However, not only are Ni^{II} complexes with tmEn more stable, but they also are substantially more soluble than $[Zn(tmEn)_2H_2O]^{2+}$, which precludes separation of tmEn from bishydroxylamine in such a manner. The structure of $[Ni(tmEn)_2][ZnCl_4]$ is shown in Fig. 3. The structure of $[Ni(tmEn)_2]Cl_2 \cdot 2H_2O$ has been reported previously.[18] Note that the environment about the Ni^{II} atoms in both complexes is a square. As in the case of Zn^{II}, the coordination number of Ni^{II} is not completed to six through coordination by the third tmEn molecule. No other known structurally characterized metal complexes with sterically hindered tmEn ligands contain more than two tmEn molecules in the inner coordination sphere as well.[19—24]

Lamchen and Mittag described not only the synthesis of free bishydroxylamine **1**, but also the synthesis of its sulfate, which was formed upon addition of an ethanolic solution of H_2SO_4 to pH ≈ 1—2. If the acid is added slowly, a precipitate of $[Zn(tmEn)Cl_2]$ is formed at pH ≈ 6—7. The precipitate is dissolved as pH is further decreased. Actually, a precipitate of the sulfate of **1** is formed at pH ≈ 1—2. However, the precipitate is always contaminated by $(NH_4)_2SO_4$, whose solubility in water is sharply decreased upon addition of even a small amount of ethanol. If bishydroxylamine **1** is reduced to diamine tmEn and the reaction mixture contains an insignificant amount of the target product **1**, only $(NH_4)_2SO_4$ passes into the solid phase upon acidification of the reaction mixture. This may account for the absence of the target bishydroxylamine **1** in the final product. It should be noted that the use of an aqueous-ethanolic medium always favors reduction of **1** to tmEn to a large extent and we failed to obtain bis(hydroxylammonium) sulfate from aqueous-ethanolic media in a yield of higher than 20%.

One more way of decay of vicinal bishydroxylamine **1** should be taken into account when the synthesis is performed with the use of aqueous ethanol. In an aqueous-ethanolic or ethanolic solution, compound **1** gradually oxidizes ethanol to acetaldehyde, reacts with the latter, and is oxidized upon storage in air to the nitroxyl radical (**4**, R = CH_3), which can be readily seen from a gradual increase in the red color of the solution upon its storage for several days. The ESR spectrum of this compound in ethanol is identical to that of the known specimen of radical **4** (R = CH_3): a_N = 7.7 G, $a_{H(2\text{-}CH_3)}$ = 3.3 G. The positions of the absorption bands that appear in the electronic absorption spectrum upon storage of an ethanolic solution of **1** also coincide with the positions of the absorption bands in the spectrum of **4** (R = CH_3).[11] For this reason, it is desirable to avoid the presence of ethanol in the reaction mixture.

It was found that the synthesis of compound **1** was much more efficient with the use of THF as the solvent. Thus the initial dinitro derivative **2** is readily soluble in THF (unlike in an aqueous-ethanolic mixture) and does not precipitate when it comes into contact with an aqueous solution of NH_4Cl (note also that a concentrated solution of NH_4Cl is moderately miscible with THF). In addition, THF virtually does not extract NH_4Cl. In the case of THF, the reduction proceeds more smoothly, which is evidenced by the appearance of a deep blue color of the solution typical of nitroso derivatives.[25] Decolorization of the solution is actually indicative of the completion of reduction, which is convenient for monitoring the process of reduction because the duration of reduction is substantially affected by the quality and particle size of the Zn powder. The only drawback of application of THF is the fact that in THF, as in other solvents, bishydroxylamine **1** is gradually oxidized (though more slowly than in EtOH) by atmospheric oxygen to acetone oxime according to the mechanism of synchronous *trans*-elimination[26] (Scheme 2).

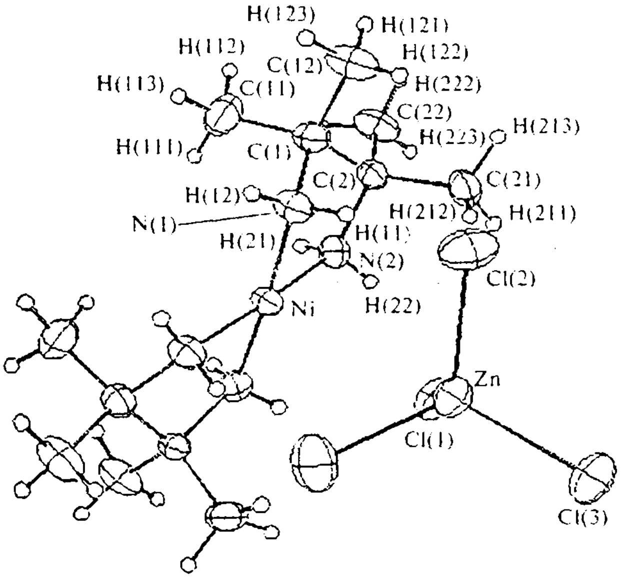
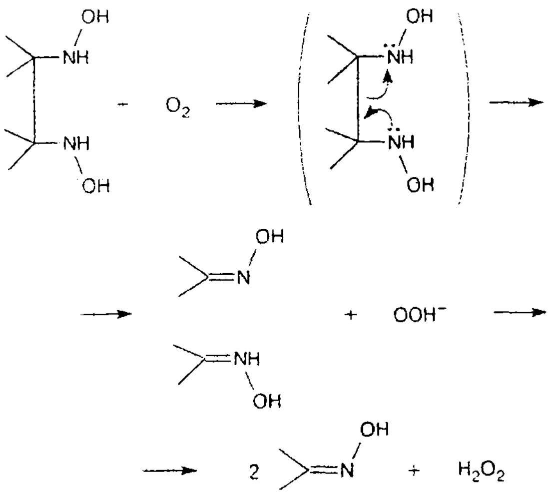


Fig. 3. Structure of $[Ni(tmEn)_2][ZnCl_4]$.

Scheme 2



Nevertheless, the synthesis with the use of THF allowed reproducible preparation of bishydroxylamine sulfate monohydrate in 50—55% yield. We succeeded in isolating the free base from this salt in ~60% yield. In this case, admixtures were removed, which is of prime importance because admixtures catalyze decomposition of free bishydroxylamine.[27—29] Fairly pure, in our opinion, samples of **1** were described in a number of works.[26—28] However, these samples remained unchanged upon storage in air for only several days. The procedure developed in the present work for the synthesis of free bishydroxylamine **1** made it possible to obtain a product which was not decomposed upon storage under ordinary conditions for 4 months or upon storage in a refrigerator at −20 °C for one year In addition, it has been reported[12] that compound **1** is very hygroscopic and volatile and is readily distilled with EtOH or $CHCl_3$ under reduced pressure. In fact, this is true for a decomposition product of **1**, *viz.*, acetone oxime, and for free tmEn. Compound **1** freed from admixtures is absolutely nonhygroscopic and is not distilled off when solutions of **1** in EtOH, MeOH, $CHCl_3$, or THF are concentrated under reduced pressure. When heated in air, the solid product gradually sublimes as the temperature increases to 100—110 °C. At 161—162 °C, the product melts with insignificant decomposition. The IR spectrum of individual compound **1** is shown in Fig. 4.

To summarize, studies of the process of reduction of dinitro compound **2** to bishydroxylamine **1** demonstrated that $Zn(NH_3)_2Cl_2$ and a product of its partial hydrolysis, *viz.*, Zn(OH)Cl, rather than $Zn(OH)_2$, are accumulated in the solid phase in the course of the reaction. In addition, a substantial amount of zinc passes into solution as the coordination cation $[Zn(tmEn)_2H_2O]^{2+}$.

Reduction in THF proceeds rather slowly. It is impossible to increase the rate of reduction by increasing the temperature of the reaction mixture, particularly, in the initial stage, because even local overheating leads to rapid and efficient reduction of **1** to tmEn. The low rate of **2**→**1** reduction results in a gradual decrease in the concentration of bishydroxylamine **1** that formed, due to its fragmentation to acetone oxime. Partial reduction of **1** to tmEn and fragmentation of **1** to acetone oxime result in a decrease in the yield of the target product. Nevertheless, the synthesis of sulfate monohydrate of **1** in aqueous THF is well reproducible and its yield is substantially higher than that in the case of the synthesis in aqueous ethanol. In addition, the procedure developed by us for the isolation of free base **1** from its sulfate makes it possible to obtain **1** in a sufficiently pure form and to store the product without decomposition for a long period.

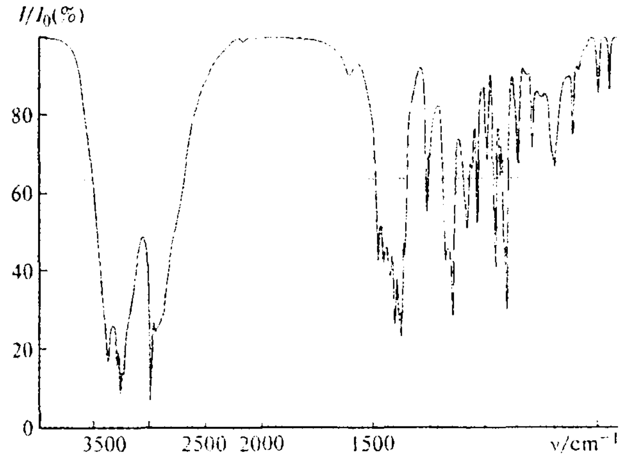


Fig. 4. IR spectrum of bishydroxylamine **1**.

Experimental

The IR spectra of the compounds under study were recorded on a Bruker IFS 66 spectrometer. The ^1H NMR spectra were obtained on a Bruker Avance 300 spectrometer. The electronic absorption spectra were measured on a Shimadzu UV-1202 spectrophotometer. The concentrations of Zn^{II} in solutions and in solid phases were determined by chelatometric titration with the use of Eriochrome Black. 2,3-Dimethyl-2,3-dinitrobutane, 2,3-diamino-2,3-dimethylbutane, 2,3-diamino-2,3-dimethylbutane dihydrochloride, Zn(OH)Cl, and $[Ni(tmEn)_2]Cl_2 \cdot 2H_2O$ were synthesized according to known procedures.[18,30,31] $Zn(NH_3)_2Cl_2$ was prepared by stirring a Zn powder with a solution of NH_4Cl in MeOH for 3 days (the yield was 10%). Found (%): Zn, 38.3. $Zn(NH_3)_2Cl_2$. Calculated (%): Zn, 38,4.

2,3-Bis(hydroxyamino)-2,3-dimethylbutane monosulfate monohydrate ($1 \cdot H_2SO_4 \cdot H_2O$). Water (30 mL) and NH_4Cl (25 g, 0.45 mol) were added to a solution of dinitro compound **2** (20 g, 0.11 mol) in THF (300 mL). The mixture was cooled to 0 °C and Zn (40 g) was added portionwise with stirring over 1 h. Then the reaction mixture was stirred at 10—20 °C for 12—14 h. The solution gradually developed a blue color and turned colorless at the end of the reaction. The mixture was filtered and the precipitate was washed with THF (3 × 100 mL). Tetrahydrofuran in the pale-yellow filtrate was distilled off *in vacuo* and EtOH (200 mL) was added to the residue. The resulting solution was filtered and a 10% H_2SO_4 solution in EtOH was added dropwise with stirring and cooling to 0 °C and pH ≈ 3 (Thymol Blue). The precipitate was filtered off, washed with EtOH, and dried in air. The yield was 15—16 g (50—55%). T_{decomp} = 172—174 °C. Found (%): C, 27.4; H, 7.3; N, 10.6. $C_6H_{16}N_2O_2 \cdot H_2SO_4 \cdot H_2O$. Calculated (%): C, 27.3; H, 7.6; N, 10.6. The Zn powder used for reduction has the following particulate size distribution over the fractions (size, μm/content, %): 54.9—33.7/0.3; 33.7—23.7/3.1; 23.7—17.7/8.4; 17.7—13.6/16.4; 13.6—10.5/10.0; 10.5—8.2/22.7; 8.2—6.4/22.6; 6.4—5.0/4.5; 5.0—3.9/11.1; 3.9—3.0/0.9 (Malvern-3600 E, H_2O).

2,3-Bis(hydroxyamino)-2,3-dimethylbutane (1). Methanol (150 mL) was added to the salt of **1** (10 g, 37.8 mmol) and then solid NaOH (3 g, 75.5 mmol) was added (an excess of alkali should be avoided!) with intense stirring and cooling to 0 °C. After 1 h, the reaction mixture was centrifuged and the solution was decanted from the precipitate and concentrated to dryness *in vacuo*. The residue was dissolved in dry THF, the precipitate was filtered off, and the filtrate was concentrated to dryness. The white finely crystalline precipitate that formed was washed with hexane (10 mL) and dried in air. The yield was 60%. T_{decomp} = 161—162 °C. Found (%): C, 48.5; H, 10.5; N, 18.8. $C_6H_{16}N_2O_2$. Calculated (%): C, 48.6; H, 10.9; N, 18.9.

Table 2. Crystallographic characteristics of the compounds and details of X-ray studies

Parameter	$[Zn(tmEn)Cl_2]$	$[Ni(tmEn)_2][ZnCl_4]$	$[Zn(tmEn)_2H_2O]Cl_2 \cdot H_2O$
Space group	*Pccn*	*Pnma*	$P2_1/n$
Z	4	4	4
a/Å	7.705(1)	11.485(4)	10.336(4)
b/Å	8.416(2)	19.114(3)	9.508(3)
c/Å	17.194(3)	9.784(2)	20.149(10)
β/deg			100.60(3)
V/Å^3	1114.9(4)	2147.8(9)	1946.3(14)
d_{calc}/g cm^{-3}	1.504	1.541	1.381
μ/mm^{-1}	2.631	2.492	1.545
2θ/deg	2.37—24.97	2.13—24.95	2.06—24.97
I_{hkl} (independent)	859	1552	3125
GOOF	0.698	0.541	0.934
R ($I_{hkl} > 2\sigma_I$)	$R_1 = 0.0178$, $wR_2 = 0.0356$	$R_1 = 0.0231$, $wR_2 = 0.0298$	$R_1 = 0.0380$, $wR_2 = 0.0913$

Table 3. Atomic coordinates ($\times 10^4$) and equivalent thermal parameters (U_{eq}) in the structure of $[Zn(tmEn)_2H_2O]Cl_2 \cdot H_2O$

Atom	x	y	z	$U_{eq} \cdot 10^3$/Å^2
Zn	1238(1)	3500(1)	1201(1)	27(1)
Cl(1)	2472(1)	−2713(1)	263(1)	46(1)
Cl(2)	33(1)	−2651(1)	2215(1)	46(1)
O(1w)	747(1)	5670(1)	1052(1)	46(1)
O(2w)	1601(1)	−697(1)	1362(1)	66(1)
N(1)	1631(1)	3705(1)	203(1)	33(1)
C(1)	2557(1)	2584(1)	67(1)	31(1)
C(11)	1743(1)	1243(1)	−97(1)	47(1)
C(12)	3172(1)	2989(2)	−541(1)	56(1)
C(2)	3614(1)	2439(1)	725(1)	29(1)
C(21)	4533(1)	1189(2)	693(1)	46(1)
C(22)	4425(1)	3781(1)	874(1)	45(1)
N(2)	2903(1)	2235(1)	1297(1)	29(1)
N(3)	−324(1)	2161(1)	1191(1)	30(1)
C(3)	−981(1)	2417(1)	1782(1)	31(1)
C(31)	−1851(1)	3711(2)	1616(1)	46(1)
C(32)	−1839(1)	1136(2)	1876(1)	50(1)
C(4)	130(1)	2668(1)	2414(1)	32(1)
C(41)	−448(1)	3154(2)	3021(1)	56(1)
C(42)	981(1)	1369(1)	2607(1)	45(1)
N(4)	1018(1)	3785(1)	2226(1)	33(1)

Table 4. Atomic coordinates ($\times 10^4$) and equivalent thermal parameters (U_{eq}) in the structure of $[Zn(tmEn)Cl_2]$

Atom	x	y	z	$U_{eq} \cdot 10^3$/Å^2
Zn	7500	2500	4839(1)	31(1)
Cl	7751(1)	294(1)	4125(1)	44(1)
N	9279(3)	2696(3)	5711(1)	32(1)
C(1)	8326(3)	3034(3)	6454(1)	37(1)
C(2)	7874(4)	4806(3)	6438(2)	51(1)
C(3)	9526(4)	2675(6)	7144(2)	56(1)
H(1N)	9890(3)	1880(3)	5732(16)	34(8)
H(2N)	10050(4)	3370(3)	5664(16)	50(9)
H(21)	7100(3)	5160(3)	6004(14)	55(8)
H(22)	7370(3)	5070(3)	6897(13)	53(7)
H(23)	8890(4)	5410(3)	6407(15)	62(9)
H(31)	9030(3)	2910(3)	7592(14)	53(9)
H(32)	10620(3)	3390(3)	7116(16)	53(8)
H(33)	9950(4)	1640(4)	7130(2)	83(13)

(2,3-Diamino-2,3-dimethylbutane)dichlorozinc(II), $[Zn(tmEn)Cl_2]$. A mixture of powdered $ZnCl_2$ (0.22 g, 1.6 mmol) and tmEn · 2HCl (0.31 g, 1.6 mmol) was dissolved in water (15 mL). The resulting solution was filtered and a 1 *M* aqueous solution of NaOH (3.2 mL) was added. The colorless crystals that immediately formed were filtered off, washed with water, and dried in air. The yield was 75%. Found (%): C, 28.0; H, 6.4; Cl, 27.8; N, 11.2; Zn, 26.1. $C_6H_{16}Cl_2N_2Zn$. Calculated (%): C, 28.5, H, 6.4; Cl, 28.1; N, 11.1; Zn, 25.9.

Bis(2,3-diamino-2,3-dimethylbutane)aquazinc(II) chloride monohydrate, $[Zn(tmEn)_2H_2O]Cl_2 \cdot H_2O$. A solution of tmEn (1 g, 8.6 mmol) in diethyl ether (15 mL) was added to a solution of $[Zn(tmEn)Cl_2]$ (1 g, 4 mmol) in water (15 mL). After stirring for 1 h, the mixture turned homogeneous. The solution was concentrated with heating to 10 mL and then cooled to ~20 °C. Colorless crystals were filtered off, washed with cold MeOH (10 mL), and dried in air. The yield was 60%. Found (%): C, 35.2; H, 9.3; Cl, 17.2; N, 13.7; Zn, 15.9. $C_{12}H_{36}Cl_2N_4O_2Zn$. Calculated (%): C, 35.6; H, 9.0; Cl, 17.5; N, 13.8; Zn, 16.2.

Bis(2,3-diamino-2,3-dimethylbutane)nickel(II) tetrachlorozincate(II), $[Ni(tmEn)_2)_2][ZnCl_4]$. A solution of NH_4Cl (0.7 g, 13 mmol) in water (10 mL) and a solution of NaOH (0.127 g, 3 mmol) in water (2.5 mL) were successively added to a solution of $NiCl_2 \cdot 6H_2O$ (0.189 g, 0.8 mmol), tmEn · 2HCl (0.3 g, 1.6 mmol), and $ZnCl_2 \cdot 1.5H_2O$ (0.13 g, 0.8 mmol) in water (15 mL). The resulting mixture was kept at ~20 °C for one day. Then concentrated HCl (0.5 mL) was added and orange crystals of the complex were immediately filtered off. The yield was 40%. Found (%): C, 28.5; H, 6.8; Cl, 27.7; N, 11.3. $C_{12}H_{32}Cl_4N_4NiZn$. Calculated (%): C, 28.93; H, 6.47; Cl, 28.46; N, 11.24.

X-ray diffraction studies of the compounds. The crystals of $[Zn(tmEn)_2H_2O]Cl_2 \cdot H_2O$ belong to the monoclinic system. The crystals of $Zn(tmEn)Cl_2$ and $[Ni(tmEn)_2][ZnCl_4]$ belong to the orthorhombic system. The experimental data sets were collected on an automated ENRAF NONIUS CAD-4 diffractometer according to a standard procedure (Mo-Kα

Table 5. Atomic coordinates ($\times 10^4$) and equivalent thermal parameters (U_{eq}) in the structure of $[Ni(tmEn)_2][ZnCl_4]$

Atom	x	y	z	$U_{eq} \cdot 10^3/Å^2$
Ni	7747(1)	2500	5577(1)	24(1)
Zn	7784(1)	2500	9882(1)	33(1)
Cl(1)	9162(1)	2500	8186(1)	37(1)
Cl(2)	6703(1)	3483(1)	9622(1)	53(1)
Cl(3)	8812(2)	2500	11850(2)	50(1)
N(1)	6723(4)	3235(2)	6080(4)	30(1)
C(1)	6924(3)	3863(2)	5186(4)	31(1)
C(11)	6432(5)	3685(3)	3790(6)	51(2)
C(12)	6284(6)	4494(3)	5767(7)	53(2)
N(2)	8734(3)	3228(2)	4914(4)	28(1)
C(2)	8265(3)	3952(2)	5150(4)	29(1)
C(21)	8742(5)	4218(3)	6509(5)	39(1)
C(22)	8668(6)	4437(3)	4017(6)	48(2)
H(11)	6800(3)	3366(19)	7010(3)	43(14)
H(12)	6060(3)	3122(18)	6010(4)	31(14)
H(111)	6820(4)	3290(2)	3240(4)	69(18)
H(112)	6440(4)	4080(2)	3210(4)	59(16)
H(113)	5590(4)	3570(2)	3810(4)	83(19)
H(121)	6480(3)	4884(19)	5190(4)	40(13)
H(122)	6400(4)	4550(2)	6660(4)	42(15)
H(123)	5370(4)	4390(2)	5810(4)	76(16)
H(21)	8810(3)	3161(16)	4080(3)	7(11)
H(22)	9430(3)	3189(16)	5200(3)	25(12)
H(211)	9610(3)	4149(18)	6530(4)	43(13)
H(212)	8530(3)	3980(17)	7220(4)	33(13)
H(213)	8540(4)	4730(2)	6680(4)	63(15)
H(221)	8460(4)	4220(2)	3140(4)	73(19)
H(222)	8400(3)	4879(19)	4130(4)	37(13)
H(223)	9460(4)	4450(2)	4060(4)	80(2)

radiation, graphite monochromator, $\theta/2\theta$ scanning technique) at −20 °C. The structures were solved by direct methods. The positions of the nonhydrogen atoms were refined anisotropically. The positions of the H atoms were located from the difference electron density syntheses and refined isotropically. The final values of the R factors, the crystallographic characteristics of the compounds, and details of X-ray diffraction studies are given in Table 2. The atomic coordinates of the complexes are given in Tables 3—5. All calculations associated with the structure solution and refinement were performed using the SHELX-97 program package.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32229) and by the "Integration" Foundation. We also thank the Russian Foundation for Basic Research for paying for a license for the Cambridge Structural Database, which was used in the present work.

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Received November 4, 1998