The first metal complex with a *vic*-dihydroxyamine and its oxidised derivative

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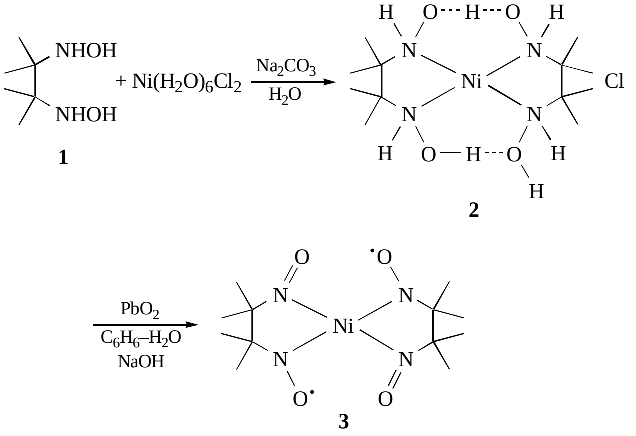
The Ni^{II} complex with a *vic*-dihydroxyamine has been synthesised, characterised by X-ray analysis and oxidised to unusual bischelate containing fully dehydrogenated hydroxyamine groups.

2,3-Dihydroxyamino-2,3-dimethylbutane **1** is widely used for syntheses of nitronylnitroxides.[1,2] However, *vic*-dihydroxyamines were never investigated as ligands. Here, we report on the synthesis and structure of the first Ni^{II} complex with *vic*-dihydroxyamine, which may be oxidised to a bischelate with fully dehydrogenated hydroxyamine groups.

We found that the interaction between aqueous $NiCl_2$ and **1** forms a finely dispersed yellow precipitate of **2** (Scheme 1), which is sparingly soluble in water and organic solvents.[†] The same product crystallised from the reaction mixture on the addition of a base (Na_2CO_3 or NaOH). Compound **2** is stable in the solid state but gradually decomposes in solution during two to three days. The single-crystal study[‡] showed that the structure of the coordination site in **2** is a nearly regular square formed by Ni^{2+} and the N atoms of two bidentately coordinated molecules of **1**, one of which is deprotonated (Figure 1).[§] The chloride ion is not involved in coordination. The cation has two nonequivalent intramolecular H-bonds between the coordinated ligands, because of which **2** is related to classical metal dioximates. However, the Ni–N bond in **2** is much longer (1.92 Å) than that in metal dioximates (~1.87 Å), and **2** is much less stable in solution, where it is readily decomposed by dilute acids.



Scheme 1

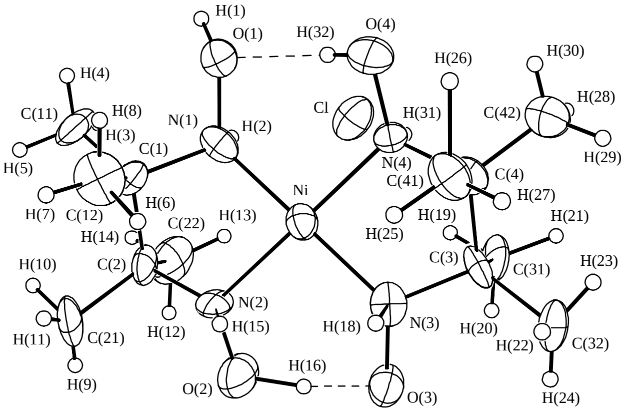


Figure 1 Molecular structure of **2**. Selected bond lengths (Å): Ni–N(1) 1.897(3), Ni–N(3) 1.920(6), Ni–N(2) 1.931(6), Ni–N(4) 1.935(6), O(1)–N(1) 1.449(8), N(2)–O(2) 1.395(8), O(3)–N(3) 1.457(8), N(4)–O(4) 1.396(8), N–C 1.506(9)–1.520(9), O(1)··O(4) 2.504(8), O(2)··O(3) 2.510(8); selected bond angles (°): N(1)–Ni–N(2) 84.0(3), N(3)–Ni–N(4) 84.7(3).

An interesting property of **2** is its ability to be oxidised to unusual complex **3**, where the ligand is the product of complete dehydrogenation of hydroxyamine groups. Dehydrogenation occurs readily in the oxidative system **2**–PbO_2–C_6H_6–H_2O–NaOH, whereupon **3** may be isolated from the benzene extract. Compound **3** is stable as a solid but much less stable in solutions

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[†] $[Ni(H_3L)H_4L]Cl$ **2**. A mixture of powdered $Ni(H_2O)_6Cl_2$ (0.45 g) and **1**·H_2SO_4·H_2O[6] (1 g) was dissolved in 15 ml of water, the solution was filtered, and 10 ml of aqueous Na_2CO_3 (0.5 g) was added to the solution. The reaction mixture was allowed to stand at room temperature. Yellow crystals suitable for X-ray diffraction analysis formed in a day. They were filtered off, washed with cold water and ethanol and dried in air. Yield 58%. $T_{decomp.}$ = 186 °C. Found (%): C, 37.1; H, 7.7; N, 14.3; Ni, 14.9; Cl, 8.5. Calc. for $NiC_{12}H_{31}N_4O_4Cl$ (%): C, 37.0; H, 8.0; N, 14.4; Ni, 15.0; Cl, 9.1.

NiL_2 **3**. Benzene (50 ml) was added to **2** (0.4 g), and solid NaOH (0.3 g) and water (5 ml) were added in sequence with vigorous stirring. After 3 min, PbO_2 (3 g) was added to the mixture. The colour of the benzene layer deepened to black green. The reaction mixture was additionally stirred for 1 h, the organic layer was separated and dried with $CaCl_2$. Then, the mixture was filtered, and the filtrate was evaporated to dryness on a rotary evaporator. Yield 43%. When stored in normal conditions, the solid compound is stable. A toluene solution of **3** saturated at room temperature was allowed to stand overnight at –30 °C to give single crystals suitable for X-ray diffraction analysis. $T_{decomp.}$ = 126–128 °C. ^1H NMR (C_6D_6) δ: 0.81 (s, Me). The electronic absorption spectrum [EtOH, λ_{max}/nm (ε)]: 364 (18840), 560 (1920), 927 (6860). Found (%): C, 41.9; H, 7.2; N, 16.1. Calc. for $NiC_{12}H_{24}N_4O_4$ (%): C, 41.5; H, 7.0; N, 16.1. MS, *m*/*z*: 346.11474 (M^+, calc. 346.11509).

[‡] Cambridge Structural Database does not contain any information concerning metal complexes with *vic*-dihydroxyamines.

[§] *Crystal data for* **2**: $C_{12}H_{31}ClN_4NiO_4$, $M = 389.57$, at 293 K crystals are orthorhombic, space group *Pbca*, $a = 13.380(3)$, $b = 12.825(3)$, $c = 21.077(4)$ Å, $V = 3616.8(13)$ Å^3, $Z = 8$, $d_{calc} = 1.431$ g cm^{-3}, μ(MoKα) = = 1.242 mm^{-1}, 2394 reflections were collected (2394 unique) on a Bruker AXS P4, (MoKα, graphite monochromator, $\theta/2\theta$ scan, $1.93 < \theta < 24.91°$, empirical absorption correction). The structure was solved by the program SIR97 and refined by the full-matrix least-square technique in an anisotropic approximation for all non-hydrogen atoms. Positions of all hydrogen atoms were located in a difference Fourier map and then refined in isotropic approximation. The final *R* indexes are $R_1 = 0.0767$, $wR_2 = 0.1084$, for 2394 unique $I_{hkl} > 2\sigma(I)$, GOOF = 0.970. All calculations were carried out using SHELX97 program.

Crystal data for **3**: $C_{12}H_{24}N_4NiO_4$, $M = 347.06$, at 293 K crystals are monoclinic, space group $P2_1/n$, $a = 6.7692(9)$, $b = 9.853(2)$, $c = 11.583(2)$ Å, $\beta = 98.45(1)°$, $V = 764.2(2)$ Å^3, $Z = 2$, $d_{calc} = 1.508$ g cm^{-3}, μ(MoKα) = 1.291 mm^{-1}, 1228 reflections were measured on a Bruker AXS P4 four-circle automated diffractometer (MoKα, graphite monochromator, $\theta/2\theta$ scan, $3.68 < \theta < 24.96°$). The structure was solved by the program SIR97 and refined by the full-matrix least-square technique in an anisotropic approximation for all non-hydrogen atoms. Positions of all hydrogen atoms were located in a difference Fourier map and then refined in an isotropic approximation. The final *R* indexes are $R_1 = 0.0316$ and $wR_2 = 0.0480$ for 1133 unique $I_{hkl} > 2\sigma(I)$, GOOF = 0.765. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/87.

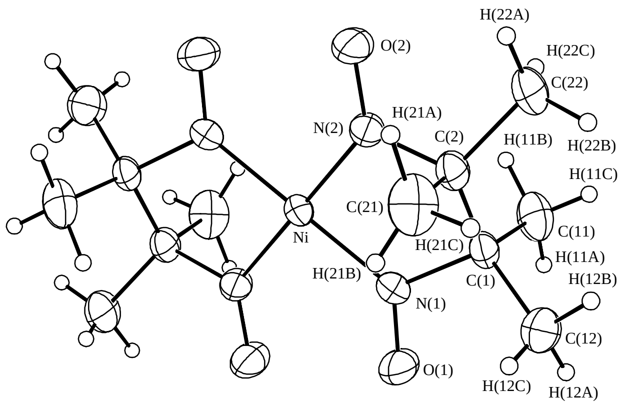

Figure 2 Molecular structure of **3**. Selected bond lengths (Å): Ni–N(1) 1.827(3), Ni–N(2) 1.839(3), N(1)–O(1) 1.230(3), N(2)–O(2) 1.218(3), N(1)–C(1) 1.543(4), N(2)–C(2) 1.531(4), O(1)··O(2′) 2.574(3); selected bond angles (°): N(1)–Ni–N(2) 83.9(1).

(*e.g.*, in benzene, toluene, chloroform and ethanol). When stored for a few days, deep green solutions of **3** are gradually decolourised, and 3,3,4,4-tetramethyl-1,2-diazetine-1,2-dioxide precipitates. Noteworthy, the oxidation of free **1** by Pb^{4+} compounds leads to acetoxime.[3] Formally, **3** may be regarded as a complex with the previously unknown nitrosohydroxyamine radical anion $^{-}\text{O–}^{\cdot}\text{N–CMe}_2\text{–CMe}_2\text{–N=O}$ (Scheme 1). Since **3** is diamagnetic, probably, because of very strong antiferromagnetic exchange interactions between the unpaired electrons of nitroxyl groups, the presence of a radical fragment may be detected using an approach developed for the metal complexes with α-hydroxyaminooximes.[4] This approach consist in the elimination of a ligand from the coordination sphere. Indeed, the addition of an equimolar amount of dimethylglyoxime to a solution of **3** leads to a short-lived quintiplet with $g = 2.006$ and $a_N = 0.70$ mT, which is typical of the EPR spectra of nitronylnitroxides. This indicates strong spin density delocalization in the $^{-}\text{N–}^{\cdot}\text{NNi}^{2+}\text{N=O}$ fragment occurring *via* the metal ion and actually leading to the equivalence of N–O groups in **3**.

The ‘equivalence’ of N–O groups is also indicated by the results of X-ray diffraction analysis of **3**. In the molecule of **3**, the square environment of the metal, which is responsible for the low-spin configuration of Ni^{II}, is formed by four N atoms (Figure 2). The Ni–N bond lengths are similar [1.827(3) and 1.839(3) Å], also indicating strong delocalization and uniform electron density distribution in the {O–N–Ni–N–O} fragment. In contrast to **2**, dimethylglyoximate complexes and metal bischelates with α-hydroxyaminooximes,[5] the molecular structure of **3** contains no intramolecular hydrogen bonds. Nevertheless, the coordination node is planar with much shorter Ni–N distances in **3**, as compared to **2** or classical Ni^{II} dioximates. It is reasonable to assume that this is a consequence of strong delocalization and electron density conjugation in $^{-}\text{O–}^{\cdot}\text{NNi}^{2+}\text{–N=O}$ fragments.

In summary, the interaction of *vic*-dihydroxyamine **1** with Ni^{II} gives rise to bischelate **2**, which contains two nonequivalent intramolecular H-bonds between the coordinated ligands. Compound **2** may be oxidised to unusual bischelate **3** whose structure contains the fragments of **1** with fully dehydrogenated hydroxyamine groups. Note that, the square-planar environment of the central atom was retained in dehydrogenated product **3**, even though a molecule of **3** has no intramolecular H-bonds in contrast to **2**.

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References

1 J. H. Osiecki and E. F. Ullman, *J. Am. Chem. Soc.*, 1968, **90**, 1078.

2 E. F. Ullman, J. H. Osiecki, D. G. B. Boocock and R. Darcy, *J. Am. Chem. Soc.*, 1972, **94**, 7049.

3 G. V. Shustov, N. B. Tavakalyan, L. L. Shustova, A. P. Pleshkova and R. G. Kostyanovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 364 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, 330).

4 V. N. Kirichenko, S. V. Larionov, I. A. Mikhailov, E. G. Boguslavskii and L. B. Volodarskii, *Zh. Neorg. Khim.*, 1984, **29**, 2835 (*Russ. J. Inorg. Chem.*, 1984, **29**, 1624).

5 E. O. Schlemper and R. K. Murmann, *Inorg. Chem.*, 1983, **22**, 1077.

6 V. I. Ovcharenko, S. V. Fokin, G. V. Romanenko, I. V. Korobkov and P. Rey, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1539 (*Russ. Chem. Bull.*, 1999, **48**, 1519).

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