

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

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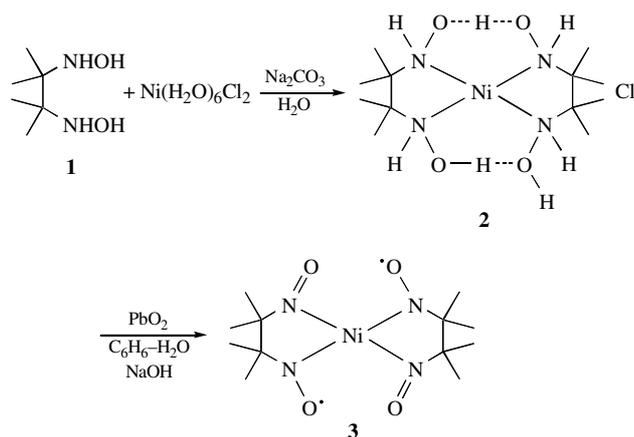
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The Ni<sup>II</sup> complex with a *vic*-dihydroxyamine has been synthesised, characterised by X-ray analysis and oxidised to unusual bischelate containing fully dehydrogenated hydroxyamine groups.

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

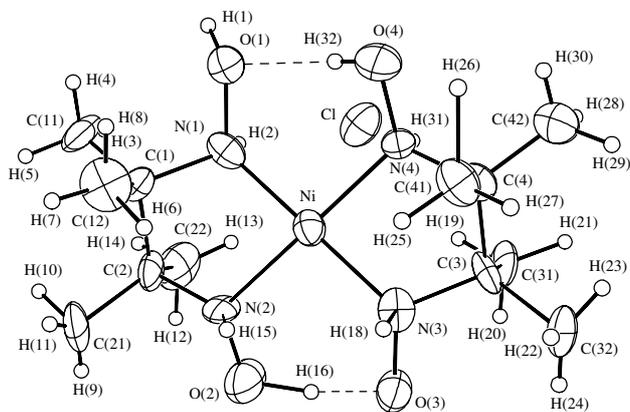
We found that the interaction between aqueous NiCl<sub>2</sub> and **1** forms a finely dispersed yellow precipitate of **2** (Scheme 1), which is sparingly soluble in water and organic solvents.<sup>†</sup> The same product crystallised from the reaction mixture on the addition of a base (Na<sub>2</sub>CO<sub>3</sub> or NaOH). Compound **2** is stable in the solid state but gradually decomposes in solution during two to three days. The single-crystal study<sup>‡</sup> showed that the structure of the coordination site in **2** is a nearly regular square formed by Ni<sup>2+</sup> and the N atoms of two bidentately coordinated molecules of **1**, one of which is deprotonated (Figure 1).<sup>§</sup> The chloride ion is not involved in coordination. The cation has two nonequivalent



<sup>†</sup> [Ni(H<sub>3</sub>L)H<sub>4</sub>L]Cl **2**. A mixture of powdered Ni(H<sub>2</sub>O)<sub>6</sub>Cl<sub>2</sub> (0.45 g) and 1·H<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O<sup>6</sup> (1 g) was dissolved in 15 ml of water, the solution was filtered, and 10 ml of aqueous Na<sub>2</sub>CO<sub>3</sub> (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*<sub>decomp.</sub> = 186 °C. Found (%): C, 37.1; H, 7.7; N, 14.3; Ni, 14.9; Cl, 8.5. Calc. for NiC<sub>12</sub>H<sub>31</sub>N<sub>4</sub>O<sub>4</sub>Cl (%): C, 37.0; H, 8.0; N, 14.4; Ni, 15.0; Cl, 9.1.

NiL<sub>2</sub> **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<sub>2</sub> (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<sub>2</sub>. 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*<sub>decomp.</sub> = 126–128 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ: 0.81 (s, Me). The electronic absorption spectrum [EtOH, λ<sub>max</sub>/nm (ε)]: 364 (18840), 560 (1920), 927 (6860). Found (%): C, 41.9; H, 7.2; N, 16.1. Calc. for NiC<sub>12</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub> (%): C, 41.5; H, 7.0; N, 16.1. MS, *m/z*: 346.11474 (M<sup>+</sup>, calc. 346.11509).

<sup>‡</sup> Cambridge Structural Database does not contain any information concerning metal complexes with *vic*-dihydroxyamines.



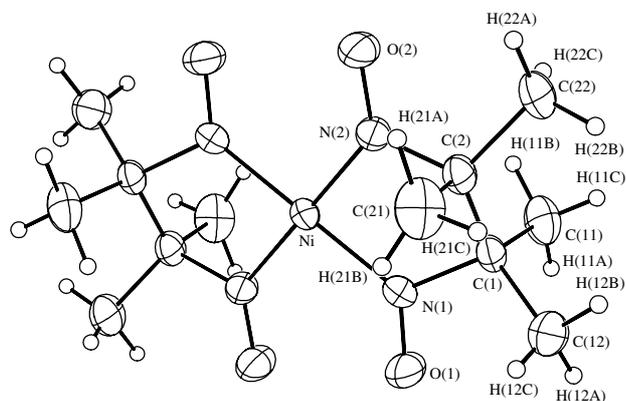
**Figure 1** Molecular structure of **2**. Selected bond lengths (Å): Ni–N(1) 1.897(3), Ni–N(3) 1.920(6), Ni–N(2) 1.931(6), Ni–N(4) 1.935(6), O(1)–N(1) 1.449(8), N(2)–O(2) 1.395(8), O(3)–N(3) 1.457(8), N(4)–O(4) 1.396(8), N–C 1.506(9)–1.520(9), O(1)···O(4) 2.504(8), O(2)···O(3) 2.510(8); selected bond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

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.

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<sub>2</sub>–C<sub>6</sub>H<sub>6</sub>–H<sub>2</sub>O–NaOH, whereupon **3** may be isolated from the benzene extract. Compound **3** is stable as a solid but much less stable in solutions

<sup>§</sup> *Crystal data for 2*: C<sub>12</sub>H<sub>31</sub>ClN<sub>4</sub>NiO<sub>4</sub>, *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<sup>3</sup>, *Z* = 8, *d*<sub>calc.</sub> = 1.431 g cm<sup>–3</sup>, μ(MoKα) = 1.242 mm<sup>–1</sup>, 2394 reflections were collected (2394 unique) on a Bruker AXS P4, (MoKα, graphite monochromator, θ/2θ scan, 1.93 < θ < 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*<sub>1</sub> = 0.0767, *wR*<sub>2</sub> = 0.1084, for 2394 unique *I*<sub>hkl</sub> > 2σ(*I*), GOOF = 0.970. All calculations were carried out using SHELX97 program.

*Crystal data for 3*: C<sub>12</sub>H<sub>24</sub>N<sub>4</sub>NiO<sub>4</sub>, *M* = 347.06, at 293 K crystals are monoclinic, space group *P2<sub>1</sub>/n*, *a* = 6.7692(9), *b* = 9.853(2), *c* = 11.583(2) Å, β = 98.45(1)°, *V* = 764.2(2) Å<sup>3</sup>, *Z* = 2, *d*<sub>calc.</sub> = 1.508 g cm<sup>–3</sup>, μ(MoKα) = 1.291 mm<sup>–1</sup>, 1228 reflections were measured on a Bruker AXS P4 four-circle automated diffractometer (MoKα, graphite monochromator, θ/2θ scan, 3.68 < θ < 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*<sub>1</sub> = 0.0316 and *wR*<sub>2</sub> = 0.0480 for 1133 unique *I*<sub>hkl</sub> > 2σ(*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-diazetidine-1,2-dioxide precipitates. Noteworthy, the oxidation of free **1** by  $\text{Pb}^{4+}$  compounds leads to acetoxime.<sup>3</sup> Formally, **3** may be regarded as a complex with the previously unknown nitrosohydroxyamine radical anion  $-\text{O}-\dot{\text{N}}-\text{CMe}_2-\text{CMe}_2-\text{N}=\text{O}$  (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  $\alpha$ -hydroxyaminooximes.<sup>4</sup> 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 quintuplet with  $g = 2.006$  and  $a_{\text{N}} = 0.70$  mT, which is typical of the EPR spectra of nitronyl nitroxides. This indicates strong spin density delocalization in the  $-\text{N}-\text{NNi}^{2+}\text{N}=\text{O}$  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  $\text{Ni}^{\text{II}}$ , 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  $\{\text{O}-\text{N}-\text{Ni}-\text{N}-\text{O}\}$  fragment. In contrast to **2**, dimethylglyoximate complexes and metal bischelates with  $\alpha$ -hydroxyaminooximes,<sup>5</sup> 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  $\text{Ni}^{\text{II}}$  dioximates. It is

reasonable to assume that this is a consequence of strong delocalization and electron density conjugation in  $-\text{O}-\text{NNi}^{2+}-\text{N}=\text{O}$  fragments.

In summary, the interaction of *vic*-dihydroxyamine **1** with  $\text{Ni}^{\text{II}}$  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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