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Novel Polynuclear Nickel(II) Complex: Hydrazine, Sulfato, and Hydroxo Bridging in an Unusual Metal Hexamer. Crystal Structure and Magnetic Properties of $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$

Magnus Gustafsson,[†] Andreas Fischer,[‡] Andrey Ilyukhin,[§] Mikhail Maliarik,[*,†] and Per Nordblad[⊥]

[†]*Department of Physics, Chemistry and Biology (IFM), Linköping University, S-581 83 Linköping, Sweden,*
[‡]*Department of Chemistry, Royal Institute of Technology, SE-100 44 Stockholm, Sweden,*
[§]*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science,*
Leninsky Prospect 31, Moscow 119991, Russia, and [⊥]*Department of Engineering Sciences,*
Solid State Physics, SE-751 21 Uppsala, Sweden

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A reaction between nickel(II) sulfate and hydrazine in aqueous solution yields blue crystals of $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$. The compound has been characterized by single-crystal and powder X-ray diffraction, vibrational spectroscopy, as well as variable-temperature magnetic susceptibility. This is the first reported crystal structure of the nickel(II) complex with hydrazine. The complex cation in the compound has a remarkable structure with unusual diversity of bridging groups including hydrazine molecules, sulfate ions, and hydroxo groups. Hydrazine molecules bridge nickel ions into trimers, which are further linked into hexamers through bridging sulfates. The magnetic susceptibility study of the compound reveals antiferromagnetic interaction between nickel(II) ions in the polynuclear complex.

Nickel(II) complexes with hydrazine have recently attracted significant interest because of their applications for the electroless deposition of fine nickel powders,[1-3] thin films of metallic nickel,[2,3] and nanotubes of nickel complexes.[4] The studies have been aimed at the controlled chemical reduction of the complexes in aqueous solution. Although hydrazine is a powerful reducing agent, the reduction of nickel proceeds very slowly unless elevated temperatures and/or catalysts are applied.[5,6]

Because of the kinetic inertness of the redox reaction between nickel(II) and hydrazine, several relatively stable $Ni-N_2H_4$ complexes were previously synthesized and studied both in the solid state and in solution. Thus, two crystalline compounds, bis- and tris(hydrazine)nickel(II) chlorides, are formed in the aqueous $NiCl_2-N_2H_4$ system depending on the molar ratio N_2H_4/Ni^{2+}.[3,7] Both $[Ni(N_2H_4)_2Cl_2]$ and $[Ni(N_2H_4)_3]Cl_2$ compounds are easily dissolved in a solution of aqueous ammonia because of the formation of mixed hydrazine−ammonia complexes: $[Ni(N_2H_4)_n(NH_3)_m]^{2+}$ $(2n + m = 6)$.[7b] The complexes are stable at ambient temperature; however, when the solutions are heated, the effective reduction of nickel(II) takes place.

A study of coordination compounds formed in the aqueous $NiSO_4-N_2H_4$ system was also undertaken. A compound with the general composition $NiSO_4 \cdot 3N_2H_4$ was synthesized and characterized by means of IR spectroscopy and powder X-ray diffraction.[8] A reaction between hydrazine sulfate and $NiSO_4$ in an aqueous solution yielded $Ni(N_2H_5)_2(SO_4)_2$.[9]

Although a number of powder X-ray diffraction studies of nickel(II) complexes with hydrazine were undertaken, no crystal structure of $[Ni(N_2H_4)_n]^{2+}$ was reported. In this paper, we report the synthesis and crystal structure of the $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8](SO_4)(H_2O)_{10}$ compound (**1**) along with its magnetic properties.

Crystalline compounds were obtained from the aqueous nickel(II) sulfate−hydrazine system with N_2H_4/Ni^{2+} molar ratios (n) of 1 and 2.[10] Powder X-ray analysis of the polycrystalline samples of the solids obtained at different n and at

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[*] To whom correspondence should be addressed. Current address: Outotec (Sweden) AB, Gymnasievägen 14, SE-931 27 Skellefteå, Sweden. E-mail: mikhail.maliarik@outotec.com. Tel.: +46 910 87742. Fax: +46 910 89050.

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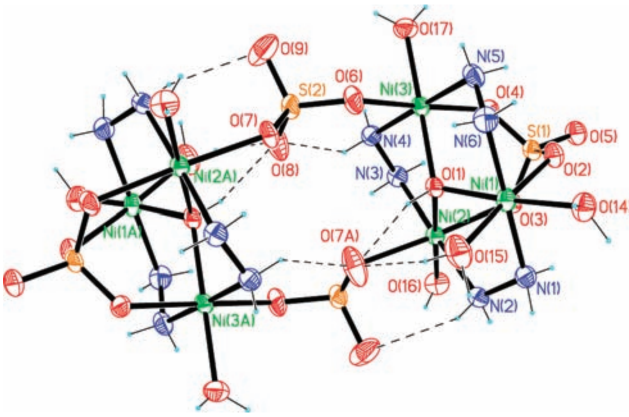

Figure 1. Molecular structure of the complex cation in **1**.

different temperatures[11] shows the identity of the compounds (see Figure S1 in the Supporting Information). The IR spectra of the samples are also similar (Table S1 in the Supporting Information).[12]

The crystal structure of **1** consists of a polunuclear nickel(II) cation, a sulfate anion, and lattice water molecules.[13] The molecular structure of the complex cation is shown in Figure 1. Three crystallographically independent nickel atoms in the structure are linked into trimers by three hydrazine molecules bridging pairs of metal ions. In addition, the trimer unit is strengthened by coordination of a sulfate ion capping the three metal ions and by a hydroxo group, which lies almost in the plane formed by nickel ions. Both the sulfate and hydroxide ions act therefore as tridentate (μ_3) bridging ligands, linking the nickel ions in a trimer. The trimers are further linked into hexamers via two other bridging sulfate anions.

The nickel ions in the complex have pseudooctahedral coordination formed by two nitrogen atoms of bridging hydrazine molecules appearing in trans positions of the polyhedron and four oxygen atoms from two types of bridging sulfate ions, a hydroxo group, and a water molecule of coordination. All three nickel atoms coordinate the same hydroxo group (μ_3-OH) and an oxygen atom of the capping sulfate ion (μ_3-O_3SO). Water molecules of coordination are placed in the trans position to the oxygen of the hydroxo group. The last place in the coordination polyhedron is filled either by an oxygen atom of the coordinated water molecule, like in the case of Ni(1), or by oxygen atoms of bridging sulfates (μ_2-O_2SO_2) for Ni(2,3). The hexamer cation is additionally linked by a network of hydrogen bonds; see Figure 1 and Table S4 in the Supporting Information. The noncoordinated sulfate ion in the crystal structure is disordered about the inversion center. Water molecules of crystallization are partially disordered.

Coordinated sulfate ions in the structure have two different bonding modes: μ_3-O_3SO, capping the nickel atoms in the trimers, and μ_2-O_2SO_2, bridging the trimers in the hexamers. The former bridging mode is rather unusual for the sulfate ion. To the best of our knowledge, the complex cation $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8]^{2+}$ is the first example of the μ_3-O_3SO bonding fashion in the compounds of nickel(II) ions. Although the variety of the bonding modes of sulfato ligands is known,[15,16] metal complexes with μ_3-sulfato groups are very rare. To the best of our knowledge, the only hitherto reported trinuclear complexes with capping μ_3-O_3SO sulfato ligands were formed by titanium(IV).[17] Interestingly, even the μ_6-bridging mode of the sulfato group is possible because it has been recently reported for a vanadium(V) cluster compound with SO_4^{2-} ions capping six vanadium ions.[18]

The hydroxo group in the complex is bound to the three nickel atoms with almost equidistant Ni−O(1) separations, 2.026−2.033 Å. The angles between the Ni−O(1) bonds, Ni(3)−O(1)−Ni(2), Ni(3)−O(1)−Ni(1), and Ni(2)−O(1)−Ni(1), are also almost identical, 112.3−113.3° (Tables S2 and S3 in the Supporting Information).

The hydrazine ligands can bind metal ions in both a unidentate and a bidentate fashion. In contrast to the generally accepted terminology, in the present case, the bidentate mode means that the hydrazine molecules link two metal ions by coordinating to each of the nickel ions via one nitrogen atom. The hydrazine ligand acts therefore as a bidentate bridging group. This binding mode often results in the formation of chain structures of metal ions linked by bridging hydrazine ligands.[19] Polymer two- and three-dimensional structures with hydrazine acting in the bidentate bridging mode were suggested for the series of nickel(II) chloride compounds, $Ni(N_2H_4)_nCl_2$ (n = 2, 3).[7a,20]

The lack of extended chain structures built via bridging hydrazine ligands in the case of the polynuclear cation $[Ni_6(N_2H_4)_6(SO_4)_4(OH)_2(H_2O)_8]^{2+}$, as compared to the structures of $Ni(N_2H_4)_nCl_2$, can probably be attributed to the sulfato group acting as a templating unit for the cluster assembly. The effect is further enhanced by the hydroxo ion operating in the (μ_3-OH) binding mode. Both the SO_4^{2-} and OH^- ligands, therefore, force nickel ions into the trimer units. In contrast to the chloride ion, the sulfate acting as a tridentate ligand is apparently sufficiently strong to compete

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(10) A total of 2.5150 g of $NiSO_4 \cdot 7H_2O$ (8.95×10^{-3} mol) was dissolved in 20 mL of deionized water. A total of 0.50 mL (1.03×10^{-2} mol) of hydrazine monohydrate was added to the solution under intensive stirring. A small amount of a precipitate formed immediately. The mixture was stored under stirring for another 10 min, followed by filtration of the solution. The solution was then gently heated on a hotplate up to 40 °C for 5 h and was then left at room temperature to cool. Blue crystals formed in the solutions within 48 h. The crystals were filtered and washed with a small amount of cold distilled water and methanol. Anal. Calcd for $Ni_6N_{12}S_5O_{40}H_{62}$ (1383.18): Ni, 25.5; N, 12.1; H, 4.5. Found: Ni, 25.8; N, 11.8 H, 4.0.

(11) Powder X-ray diffraction data on the compounds were obtained from a Philips PW 1710 diffractometer, $\lambda = 1.540\,60$ Å (Cu Kα_1, germanium monochromator).

(12) The IR spectra of the compounds were obtained with a Perkin-Elmer 100 FTIR spectrometer. The samples were recorded as KBr pellets.

(13) Data collection was performed at 296 ± 1 K by means of Enraf Nonius CAD-4 diffractometer. Semiemphirical corrections were applied. The structure was solved by direct methods and refined by means of a full-matrix least-squares method on F^2 in *SHELXL-97*.[14] All non-hydrogen atoms were refined anisotropically. Crystal structure data for **1**: $H_{62}N_{12}Ni_6O_{40}S_5$, M_W = 1383.18, triclinic, space group $P\bar{1}$ with a = 10.965(2) Å, b = 11.214(3) Å, c = 11.306(3) Å, α = 60.19(2)°, = 71.96(2)°, = 69.23(2)°, V = 1112.5(5) $Å^3$.

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with hydrazine for the place held by nickel in the coordination sphere. The SO_4^{2-} group takes advantage of its three oxygen atoms to "arrange" nickel ions in the trimer units. A similar template function of the sulfato ligand was also noted in the structure of the vanadium(V) cluster compound with an unprecedented μ_6-bridging mode of the sulfato group.[18]

In the context of mixed-metal complexes with hydrazine and sulfato ligands, it is worth mentioning a family of isostructural compounds $[M(SO_4)_2(N_2H_5)_2]_n$ (M = Cd,[21a] Cr^{II},[21b] Fe^{II},[21c] Zn[21d]). A hydrazinium cation is bound to the metal atoms in the complexes in a monodentate mode. The metal atoms are connected into infinite chains by pairs of sulfate groups. The metal sulfate chains are further cross-linked by N−H···O hydrogen bonds.

The measured temperature dependence of the magnetic susceptibility χ and $1/\chi$ shown in Figures 2 and S3 in the Supporting Information does not follow a Curie or Curie−Weiss law.[22] However, from an almost flat region of the $\chi_M(T)T$ vs T plot (Figure S3 in the Supporting Information) at higher temperatures (and assuming Curie behavior), one can extract the value of the Curie constant $C = 8.5$ cm^3 K mol^{-1}. The same C value is also obtained from the Curie−Weiss fit of the high-temperature part of the $1/\chi(T)$ plot (see the inset of Figure 2), which shows a large deviation from the Curie−Weiss behavior at temperatures below 50 K. The effective magnetic moment, μ_{eff}, calculated from the Curie constant,[23] is 3.4 μ_B.

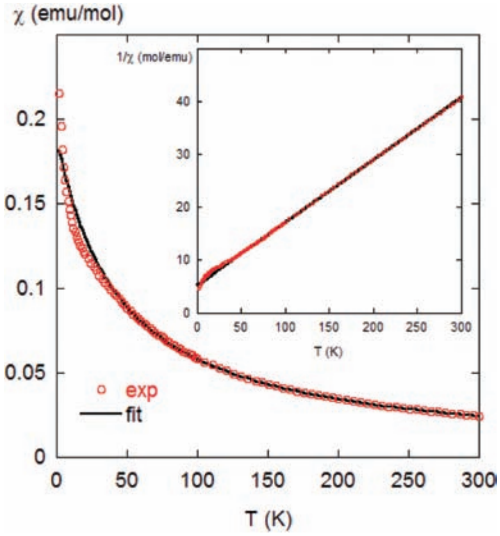

Figure 2. Magnetic susceptibility and inverse magnetic susceptibility (inset) plots versus temperature for **1**.

The fit to the $1/\chi(T)$ plot also yields the Weiss constant θ = 45 K [$\chi = C/(T + \theta)$], implying antiferromagnetic interactions between nickel ions in the complex in the temperature range 50−300 K. One may expect that antiferromagnetic interaction between the three nickel ions in the trimer (Figure 1) occurs through superexchange via the interconnecting oxygen atom [O(1)] of the bridging hydroxo group.

In conclusion, we report a remarkable polunuclear compound where nickel(II) ions are bound in hexamers by hydrazine, sulfato, and hydroxo bridges. Quantum mechanical calculations are clearly needed to gain a deeper insight into the electronic structure and magnetic behavior of this nickel cluster.

Supporting Information Available: Experimental polycrystalline and calculations from the single-crystal data X-ray diffractograms of **1**, FTIR spectrum of **1**, IR data and tentative assignment of the bands for the crystalline samples obtained from the $NiSO_4-N_2H_4-H_2O$ system, X-ray crystallographic data for **1** in CIF format, selected bond lengths and angles as well as hydrogen bonds in the complex cation of **1**, plot of $\chi_M T$ vs T for **1**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have also been deposited with the ICSD database (CSD-number 421462).

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(22) Temperature-dependent magnetic susceptibility measurements on the compound were carried out on a MPMS XL magnetometer over the temperature range 2−300 K. The magnetic field applied was 10 000 Oe. The observed susceptibility data were corrected for underlying diamagnetism. The correction was carried out with the assumption of a temperature-independent diamagnetic contribution from the sample cup (epibond). This contribution has been estimated by assuming Curie−Weiss behavior and using the diamagnetic χ_{dia} as a fitting parameter to achieve a linear high-temperature part of $1/\chi$ vs T. The best linear behavior is found with $\chi_{dia} = -0.0055$ emu mol^{-1}.

(23) $\mu_{eff}{}^2 = 3k_BC/6N_A\mu_B{}^2$ [6 nickel(II) ions mol^{-1}].