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# Nitrosonium nitratometallates NO[M($NO_3$)$_3$] (M = Co, Ni): new synthetic approach and crystal structures

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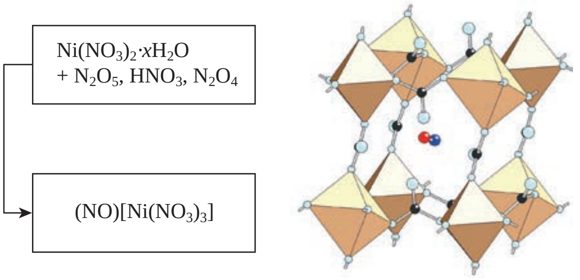
**Monoclinic and triclinic modifications of nitrosonium nitratonickelate NO[Ni($NO_3$)$_3$] as well as triclinic modification of nitrosonium nitratocobaltate NO[Co($NO_3$)$_3$] (isostructural to triclinic NO[Ni($NO_3$)$_3$]) have been synthesized by a new synthetic approach. Single crystal XRD studies revealed the similarity of all these structures in which octahedrally coordinated metal atoms are connected through $NO_3^-$ bridges forming three-dimensional distorted cubic framework with $NO^+$ cations located in the framework cavities.**



Nitrate complexes of *d*-elements adopt the range of unusual extended crystal structures, where metal atoms are linked in chains, ribbons, layers or frameworks by nitrate bridges. Such complexes often exhibit new types of magnetic ordering or frustrated states as a result of the exchange interaction between the metal atoms *via* nitrate bridges {*e.g.*, $Cu(NO_3)_2(H_2O)$, NO[Cu($NO_3$)$_3$], $Ni(NO_3)_2$[1–3]}. Formation of the extended structures is typical of the trinitratometallates A[M($NO_3$)$_3$]: compounds NO[M($NO_3$)$_3$] (M = Cu,[4] Mn[5]) possess layered structures, whereas Ag[Co($NO_3$)$_3$] contains infinite anionic chains.[6] Nitrate complexes NO[M($NO_3$)$_3$] (M = Co, Ni), formulated earlier as $M(NO_3)_2{\cdot}N_2O_4$, have the same stoichiometry but their crystal structures are unknown.[7–9]

Herein we report the synthesis and structural characterization of three nitrosonium nitratometallates: monoclinic (**1**) and triclinic (**2**) modifications of NO[Ni($NO_3$)$_3$] as well as triclinic modification of NO[Co($NO_3$)$_3$] (**3**) which is isostructural to **2**.

For the synthesis of **1**–**3** the calculated amounts of anhydrous nitric acid $HNO_3$ and liquid $N_2O_4$ were added to the freshly prepared $N_2O_5$ followed by a slow addition (~20 min) of partially dehydrated nickel nitrate hydrate $Ni(NO_3)_2{\cdot}2.6H_2O$ or Co powder at 0 °C with stirring. Anhydrous $HNO_3$ and liquid $N_2O_4$ were obtained by published procedure.[10] Nitric anhydride, $N_2O_5$, was prepared by the reaction of the anhydrous $HNO_3$ with $P_2O_5$ according to ref. 10. In a typical experiment, 5–8 mmol of the metal or nitrate were used; the total scale of the reaction mixture was 6–9 g. Molar ratio of the reagents was $Ni(NO_3)_2{\cdot}2.6H_2O : N_2O_5 : N_2O_4 : HNO_3 = 1 : 3 : 4 : 5.5$ for the synthesis of **1** and **2**, and $Co : N_2O_5 : N_2O_4 : HNO_3 = 1 : 3 : 3.5 : 5.4$ for the synthesis of **3**.

The obtained mixture was sealed in a glass ampoule and placed in a Dewar flask filled with 70 °C water for **2** and **3**, and 40 °C for **1**. Crystallization proceeded during gradual cooling of the ampoule to room temperature for *ca*. 3 days yielding the formation of green crystals for **1** and **2** and purple crystals for **3**. Finally, the sealed ampoule was opened, the solution was decanted, and a crystalline precipitate was dried over $P_2O_5$ in a vacuum desiccator. Powder XRD studies (DRON-3M diffractometer; CuKa radiation, graphite monochromator) revealed the formation of new compounds in all three cases. The crystal structures of the compounds were determined by a single crystal XRD study.† A comparison of the powder X-ray data with the calculated XRD patterns based on single crystal data showed that the obtained samples are practically single-phase compounds **1**, **2**, and **3**. All compounds were unstable in air due to their high hygroscopicity. The reactions of **1**−**3** with water were accompanied by the evolution of nitrogen oxides, which indicates the presence of $NO^+$ cations in their crystal structures.

An application of the mixtures of $N_2O_5$, $N_2O_4$, and $HNO_3$ in different proportions allowed us to precisely control the composition of the final products. That contradict previously published synthetic procedures, which use only dinitrogen pentoxide.[11–13] Usually $N_2O_5$ acts as a dehydrating and oxidizing agent producing $HNO_3$ and $N_2O_4$, respectively. The excess of $N_2O_5$ decomposes to $N_2O_4$ and $O_2$ within few days, which leads to the pressure increase in the sealed ampoule; therefore, large excess of $N_2O_5$ should be avoided. According to our studies, if the consumption of $N_2O_5$ results in the $N_2O_4/HNO_3$ molar ratio close to 0.37, the crystallization of NO[Ni($NO_3$)$_3$] occurs. Deviations from this condition lead to the formation of other nitrate species: $Ni(NO_3)_2$ for low $N_2O_4/HNO_3$ ratios (*ca*. 0.1) and $(NO)_6[Ni_4(NO_3)_{12}](NO_3)_2{\cdot}HNO_3$ for $N_2O_4/HNO_3$ ratio of *ca*. 0.66.

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† *Crystal data*. Data collection for single crystals was performed on the CCD diffractometer STADI–VARI Pilatus–100K, for **1** and **2**, and IPDS (Stoe) for **3**.

**1**: monoclinic, space group $P2_1/c$, $a$ = 7.4035(3), $b$ = 10.1944(5) and $c$ = 9.0757(4) Å, $\beta$ = 92.605(3)°, $V$ = 684.27(5) Å$^3$, $Z$ = 4. Refinement with 1968 reflections and 137 parameters to $wR_2$ = 0.0969 and $R_1$ = 0.0387 for 1354 reflections with $F^2 > 2\sigma(F^2)$; ICSD 427984.

**2**: triclinic, space group $P\bar{1}$, $a$ = 6.8622(4), $b$ = 7.1243(4) and $c$ = 8.4433(4) Å, $\alpha$ = 114.715(4)°, $\beta$ = 94.889(4)°, $\gamma$ = 109.114(5)°, $V$ = 342.22(3) Å$^3$, $Z$ = 2; refinement with 2311 reflections and 139 parameters to $wR_2$ = 0.0580 and $R_1$ = 0.0566 for 1867 reflections with $F^2 > 2\sigma(F^2)$; ICSD 427894.

**3**: triclinic, space group $P\bar{1}$, $a$ = 6.8429(6), $b$ = 7.0648(7) and $c$ = 8.4100(8) Å, $\alpha$ = 113.510(7)°, $\beta$ = 94.909(7)°, $\gamma$ = 109.772(7)°, $V$ = 339.19(5) Å$^3$, $Z$ = 2; refinement with 1769 reflections and 140 parameters to $wR_2$ = 0.0593 and $R_1$ = 0.0242 for 1592 reflections with $F^2 > 2\sigma(F^2)$; ICSD 427909.

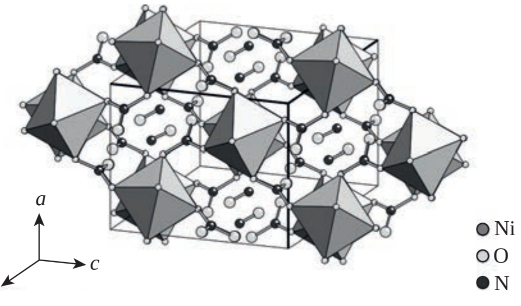

**Figure 1** Crystal structure of **2**. Nickel atoms are located inside of the octahedra.

Single crystal XRD data revealed that monoclinic (**1**) and triclinic (**2**) modifications of NO[Ni($NO_3$)$_3$] have similar crystal structures. Both compounds display a 3D anionic framework [Ni($NO_3$)$_3$]$^-$, which has a structure of a distorted cubic network with nitrosonium cations located in the cavities (Figure 1). Nickel atoms are located at the nodes of the framework and are connected with each other by the nitrate bridges. Each Ni atom is six coordinated which results in a slightly distorted octahedral environment. The structure of **2** contains two crystallographically independent Ni atoms, both located in the inversion centers [Figure 2(*a*),(*d*)].

Three types of infinite chains can be discriminated in the crystal structures of **1** and **2**, each chain passes *via* Ni atom connecting *trans* vertices of [$NiO_6$] octahedra (Figure 1). Two of these chains have similar structures and consist of Ni atoms lying almost on a straight line [Figure 2(*a*),(*b*)] and $NO_3^-$ bridges of the *anti-anti* type.[14] Ni···Ni distances are 6.0 Å for the chains of the first type [Figure 2(*a*)] and 5.7 Å for the chains of the second type [Figure 2(*b*)]. The most significant differences can be seen between the structures of chains of the third type with the shortest Ni···Ni distance of 5.25 Å in **1** and 5.20 Å in **2**. In these chains Ni atoms are bound by $NO_3^-$ groups of the *sin-anti* type[14] and form a zig-zag chain in case of structure **1** [Figure 2(*c*)], and have linear arrangement in the structure **2** [Figure 2(*d*)].

The chains of the types 2 and 3 with short Ni···Ni distances can be considered as forming layers in both triclinic and monoclinic modifications of NO[Ni($NO_3$)$_3$]. Ni atoms in these layers form a rectangular network, which is similar to the network in the structure of Ni($NO_3$)$_2$($H_2O$)$_2$.[15,16] The layers are connected with each other *via* nitrate bridges of the *anti-anti* type (type 1 chains, Ni···Ni distance of *ca*. 6.0 Å), which leads to the formation of a three-dimensional framework. The N–O bond lengths in $NO^+$ cations [0.989(6) Å in **1** and 1.031(3) Å in **2**] are typical of $NO^+$ containing compounds.[5]

Even though **1** and **2** are polymorphs, the phase transition from one modification to another has not been observed. Since the single-phase samples of **2** were obtained in most syntheses and taking into account the fact that only triclinic modification was obtained for M = Co, we conclude that the triclinic modification is more stable under our synthesis conditions.

In summary, previously unknown polymorphic modifications of nitrosonium nitratonickelate NO[Ni($NO_3$)$_3$] (monoclinic **1** and triclinic **2**), and triclinic modification of nitrosonium nitratocobaltate NO[Co($NO_3$)$_3$] (**3**, isostructural to **2**), have been obtained using the new synthetic approach. Single crystal X-ray diffraction studies have revealed similar extended structures with octahedrally coordinated Ni atoms connected through $NO_3^-$ bridges for both modifications of NO[Ni($NO_3$)$_3$]. The cavities of the three-dimensional framework are occupied with $NO^+$ cations. Minor structural differences between **1** and **2** originate from different orientations of $NO_3^-$ bridges and small displacements of metal atoms. An existence of different polymorph modifications makes these compounds interesting objects for the investigations of magnetic properties, as even small structural differences may substantially affect the nature of magnetic exchange interactions.

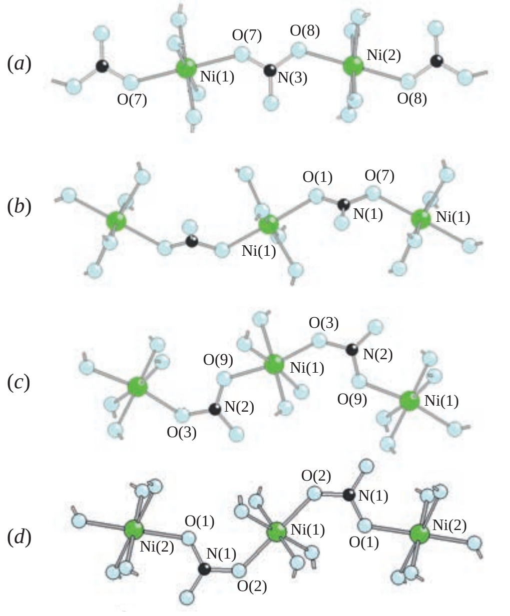

**Figure 2** Chains in the crystal structures of **1** and **2**. Chains with *anti-anti* $NO_3$ groups: (*a*) type 1 for **2** and (*b*) type 2 for **1**. Chains with *sin-anti* $NO_3$ groups (type 3) for (*c*) **1** and (*d*) **2**.

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