General and Inorganic Chemistry

Dinitramide and its salts
3.* Metallic salts of dinitramide

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The preparation and physicochemical properties of salts of dinitramide $HN(NO_2)_2$ with uni- and bivalent metals of groups I, II, VII, and VIII of the Periodic Table are considered.

Key words: dinitramide, metallic salts, complex salts of dinitramide.

Following the preparation of the first representative of a new class of inorganic compounds, *viz.*, the potassum salt of dinitramide,[1] $KN(NO_2)_2$ (K-DNA, KN_3O_4), we started to investigate the synthesis and properties of numerous salts of dinitramide $HN(NO_2)_2$ (DNA, HN_3O_4) with metals and organic bases. Some of these compounds can be used as efficient constituents of solid missile fuels, explosive compositions, and gunpowders. In addition, the synthesis and study of the properties of the salts of a previously unknown oxygen acid of nitrogen are of doubtless scientific interest.

In the present communication, the following methods of preparation of metallic salts of DNA are described:

1. Interaction of metal hydroxides with β-substituted *N*-alkyl-*N*,*N*-dinitramines in ethanol.[1,2]

$$XCH_2CH_2N(NO_2)_2 + MOH \xrightarrow[-XCH=CH_2]{} MN_3O_4 \qquad (1)$$

X = CN, CHO, COR, COOR
M = K, Rb, Cs

This reaction serves as the source of the $N(NO_2)_2^-$ anion and at the same time is a convenient method for synthesizing K-, Rb-, and Cs-salts of DNA, which are poorly soluble in ethanol. Potassium and ammonium salts of DNA obtained by this method[1,2] were used to synthesize other salts by means of ion exchange (see below).

2. Cation exchange in dinitramide salts.

$$MN_3O_4 + M'X_n \rightleftharpoons M'(N_3O_4)_n + n\,MX \qquad (2)$$

Salts and solvents that would shift the equilibrium to the right were used; the reactions were usually carried out in nonaqueous media, for example, in ethanol. In laboratory practice, it is convenient to use the Ag-salt of dinitramide (easily soluble in water and different organic solvents) in combination with halides of an appropriate metal.

3. Treatment of the ammonium salt of dinitramide with solutions of strong bases.

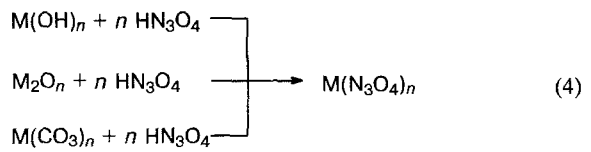
$$NH_4N_3O_4 + M(OH)_n \xrightarrow[-H_2O,\ -NH_3]{} M(N_3O_4)_n \qquad (3)$$

* For part 2, see *Russ. Chem. Bull.*, 1994, **43**, 1200.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1546—1549, September, 1994.

This method is suitable for obtaining dinitramide salts poorly soluble in water or alcohols.

4. Interaction of aqueous or nonaqueous dinitramide solutions with metal hydroxide, oxide, or carbonate.



(4)

Virtually no additional purification is required for metallic salts of dinitramide obtained by this method.

Aqueous solutions of HN_3O_4 with a concentration of 7—10 % can be easily and safely prepared when a solution of KN_3O_4 is passed through a column filled with a cation-exchange resin in the H^+ form. Nonaqueous DNA solutions were obtained[1] by passing dry HCl through a vigorously stirred suspension of KN_3O_4 in absolute ether at 0—5 °C. Concentration of the filtrate in a rotatory evaporator at 0 °C gives dinitramide as a viscous yellowish liguid.* Repeated dissolution in ether with subsequent distillation of the solvent allows one to remove practically all the traces of HCl. However, it is impossible to eliminate the traces of ether. The addition of another solvent after removal of ether, for example, CH_2Cl_2, and distiilation as described above gave a product, which, according to ^1H NMR spectrum, contained ether even after repetition of this procedure two or three times. This fact may be considered as indirect evidence that dinitramide, like many other mineral acids, forms a complex with ether.

Free dinitramide is very unstable. Immediately after removal of the solvent at 0 °C it decomposes to form colorless and then colored nitrogen oxides. Sometimes this decomposition occurs with explosion. Dinitramide also exploded vigorously when distillation was attempted at 0.5 Torr below +5 °C. Nitric acid is, apparently, the major product of the smooth (without explosion) decomposition of DNA in air. The IR spectrum of the residue treated with alkali supports this statement. However, solutions of DNA not only in water, but also in organic solvents can be stored without noticeable decomposition for several days if their concentration does not exceed ~20 %.

The metallic salts of DNA thus obtained by us (Table 1) are generally stable at ~20 °C and are crystalline substances with low melting or decomposition points. It should be noted, however, that $Fe(N_3O_4)_2 \cdot 7H_2O$ oxidizes and simultaneously decomposes in air. Attempts to obtain Cu^I-, Al^{III}-, Cr^{III}-, and Fe^{III}-salts of DNA failed apparently because of their low thermal stability.

* This procedure is explosion hazardous and requires great caution.

Table 1. Metallic salts of dinitramide and their melting points

Compound	Preparation procedure	M.p./°C
$LiN_3O_4 \cdot H_2O$	2	68—73
LiN_3O_4	2[a]	158 (decomp.)
NaN_3O_4	2	101—107
KN_3O_4	1, 3[1]	127—131
RbN_3O_4	1, 3[1]	102—106
CsN_3O_4	1, 3[1]	85—87
$Cu(N_3O_4)_2 \cdot 3H_2O$	2	51—56[b]
$Cu(N_3O_4)_2 \cdot H_2O$	2[a]	—
AgN_3O_4	2, 4	125—131 (decomp.)
$Mg(N_3O_4)_2 \cdot 6H_2O$	2	89—93 (decomp.)[c]
$Mg(N_3O_4)_2 \cdot 3H_2O$	2[a]	60—65 (decomp.)
$Ba(N_3O_4)_2 \cdot H_2O$	2	74—76 (decomp. at ~130 °C)
$Mn(N_3O_4)_2 \cdot 8H_2O$	2	41—63[c]
$Fe(N_3O_4)_2 \cdot 7H_2O$	2	85 (decomp.)
$Co(N_3O_4)_2 \cdot 6H_2O$	2	82—86[d]
$Ni(N_3O_4)_2 \cdot 6H_2O$	2	80—83 (decomp.)
$Ni(N_3O_4)_2 \cdot 2H_2O$	2[a]	93—97 (decomp.)

[a] With subsequent drying over P_2O_5 in a vacuum-exicator. [b] From ether. [c] From a nitromethane—benzene (3:2) mixture. [d] From a nitromethane—benzene (2:3) mixture.

Salts of DNA are usually easily soluble in water, alcohols, acetonitrile, and other polar organic solvents. The lithium salt and salts of heavy metals are also soluble in solvents of lower polarity, for example, in diethyl ether.

The potassium and cesium salts of DNA are insensitive to mechanical action under the conditions of the standard test for explosives, however, salts of heavy metals, for example, AgN_3O_4, are sensitive to impact and friction. A convenient and safe procedure for preparing AgN_3O_4 solutions consists of the interaction of KN_3O_4 with $AgNO_3$ in MeCN. The Ag-salt of DNA gives a molecular complex which has the composition $AgN_3O_4 \cdot MeCN$ and can be isolated after removal of the solvent. Some other DNA salts are capable of forming molecular complexes with solvents as well. Thus, recrystallization of NaN_3O_4 from dioxane leads to the dioxanate, $NaN_3O_4 \cdot C_4H_8O_2$

The salts of copper(II), manganese(II), iron(II), cobalt(II), and nickel(II) form very stable hydrates. A portion of the water of crystallization remaines even after the salts are dried *in vacuo* over P_2O_5. The monohydrate of DNA Li-salt is completely dehydrated under these conditions, but transforms back to the monohydrate in a humid atmosphere. On the contrary, the Cu-salt trihydrate, $Cu(N_3O_4)_2 \cdot 3H_2O$, is partially dehydrated in

air. Taking into account the ease with which molecular complexes form and the strength of the bonds of the coordinated water in the metallic salts of dinitramide, it was reasonable to suggest that DNA salts should form coordination compounds with amine ligands as well. Indeed, passage of ammonia through ethereal solutions of Ag-, Cu,- and Ni-salts of DNA results in precipitation of the corresponding ammine complexes. The same compounds are precipitated when concentrated aqueous-ammonia solutions of the sulphates of the above mentioned metals are mixed with $NH_4N_3O_4$.

$$M(N_3O_4)_n \cdot mH_2O + NH_3 \longrightarrow [M(NH_3)_p](N_3O_4)_n \quad (5)$$

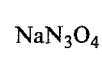
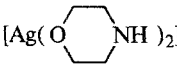
M = Ag: $p = 2$, $n = 1$, $m = 0$
M = Cu: $p = 4$, $n = 2$, $m = 3$
M = Ni: $p = 6$, $n = 2$, $m = 6$

$$MSO_4 + NH_3 + NH_4N_3O_4 \longrightarrow [M(NH_3)_p](N_3O_4)_2 \quad (6)$$

Similarly, complex salts with other nitrogen-containing ligands, in particular with pyridine and morpholine, can be also readily precipitated (Table 2).

It is noteworthy that complex formation remarkably influences the thermal stability of DNA salts, which is increased or decreased. For example, the temperature at which the decomposition of the ammine complex of the Ag-salt of DNA begins is by 70 °C lower and that of morpholinate is 60 °C higher than that of the starting salt.

Table 2. Complex salts of dinitramide

Compound	M.p./°C
$NaN_3O_4 \cdot$ 	119—122
$AgN_3O_4 \cdot MeCN$	68—72
$[Ag(NH_3)_2]N_3O_4$	58—64 (decomp.)
$[Ag(py)_2]N_3O_4$	68—69 (decomp.)
	125—126 (decomp.)*
$[Cu(NH_3)_4](N_3O_4)_2$	178—183 (decomp.)
$[Cu(py)_4](N_3O_4)_2$	138—140 (decomp.)*
$[Ni(NH_3)_6](N_3O_4)_2$	149—155 (decomp.)

* From methanol.

Experimental

The melting points were determined in a metallic block. IR spectra were recorded on a UR-10 instrument (for solid substances, in KBr pellets or on germanium glass, for liquids, in thin films between KBr or NaCl glass). UV spectra were recorded on a Perkin-Elmer R-12 instrument.

Attention! Dinitramide and most of its salts are extremely sensitive explosives; care should be taken when handling them. HN_3O_4 must never be stored without a solvent as the developing decomposition can result in explosion.

Dinitramide, HN_3O_4. A stream of dry HCl was passed through a vigorously stirred suspension of KN_3O_4 (1.45 g, 1 mmol) in abs. ether (25 mL) at 0 °C for 1.5 h. The precipitate was separated, and the filtrate was concentrated *in vacuo* (10—15 Torr) on a rotatory evaporator from a flask immersed in a bath with ice-water. Abs. ether was added at 0 °C to the remaining oily liquid and evaporated again. This procedure was repeated 2—3 times until the test for the Cl^- ions with a $AgNO_3$ solution in MeCN was negative. A yellowish liquid was obtained, which began decomposing several seconds after removal of the solvent. Yield 90—95 %.

Silver dinitramidate, AgN_3O_4. ***A.*** Ag_2CO_3 (5 g) was added at 20 °C to an ethereal solution of HN_3O_4 (from 2.9 g of KN_3O_4) obtained as described above. The mixture was stirred for 1.5 h, and the precipitate was separated and washed on a filter with methanol. The filtrate was concentrated on a rotatory evaporator to give 3.3 g (77 %) of AgN_3O_4. Found (%): N, 20.06. Calculated (%): N, 19.62.

B. Boiling solutions of KN_3O_4 (1.45 g, 0.01 mol) in ethanol (100 mL) and $AgNO_3$ (1.70 g, 0.01 mol) in ethanol (80 mL) were mixed, cooled to 20 °C and filtered. The filtrate was concentrated on a rotatory evaporator to 1/5 of the initial volume, filtered again, and evaporated to dryness to give light-yellow crystals of AgN_3O_4, m.p. 100—105 °C (decomp.).

Lithium dinitramidate hydrate, $LiN_3O_4 \cdot H_2O$. A solution of $NH_4N_3O_4$ in boiling ethanol was treated with an equimolar quantity of solid $LiOH \cdot H_2O$. The mixture was stirred for 0.5 h and concentrated on a rotatory evaporator. The residue was extracted with ether and the extract was evaporated to dryness. The residue was dissolved in 2-propanol and precipitated with CH_2Cl_2 to give $LiN_3O_4 \cdot H_2O$, m.p. 71—73 °C. The anhydrous salt, LiN_3O_4, was obtained by drying $LiN_3O_4 \cdot H_2O$ in a vacuum-exicator over P_2O_5 for 12 h. Found (%): N, 37.61. Calculated (%): N, 37.17.

Sodium dinitramide, NaN_3O_4. A solution of NaBr (4.25 g) in methanol (50 mL) was added to a solution of AgN_3O_4 (obtained from 6.0 g of KN_3O_4 according to procedure ***B***) in methanol (40 mL). The AgBr was filtered off and the filtrate was concentrated on a rotatory evaporator. The residue was extracted with acetone (50 mL) and the extract was evaporated *in vacuo* to give NaN_3O_4 in a quantitative yield. Recrystallization from nitromethane (200 mL) afforded 1.3 g (25%) of NaN_3O_4. Found (%): N, 32.22. Calculated (%): N, 32.55.

Copper(II) dinitramidate trihydrate, $Cu(N_3O_4)_2 \cdot 3H_2O$. A solution of $CuCl_2 \cdot 2H_2O$ (1.1 g) in ethanol (20 mL) was added to a solution of AgN_3O_4 (obtained from 2.0 g of KN_3O_4 according to procedure ***B***) in ethanol (30 mL), the mixture was filtered to remove AgCl, and the filtrate was concentrated on a rotatory evaporator. The residue was extracted with ether (50 mL), and the ether was evaporated to the volume of ~8 mL and cooled to −78 °C. The dark blue crystals that precipitated were separated to yield 0.59 g (25 %). Found (%): N, 25.19; H_2O, 17.18. Calculated (%): N, 25.49; H_2O, 16.39.

Copper(II) dinitramidate monohydrate, $Cu(N_3O_4)_2 \cdot H_2O$. Drying $Cu(N_3O_4)_2 \cdot 3H_2O$ *in vacuo* over P_2O_5 for 24 h gave $Cu(N_3O_4)_2 \cdot H_2O$. Found (%): H_2O, 6.63. Calculated (%): H_2O, 6.12.

Magnesium dinitramidate hexahydrate, $Mg(N_3O_4)_2 \cdot 6H_2O$. Boiling solutions of KN_3O_4 (1.0 g) in methanol (20 mL) and $Mg(ClO_4)_2$ (0.77 g) in methanol (5 mL) were mixed and the mixture was cooled to 20 °C and filtered. The solution was concentrated on a rotatory evaporator, the residue was extracted with ethyl acetate (10 mL), the extract was concentrated on a rotatory evaporator, and the residue was recrystallized from a 3:2 nitromethane—benzene mixture to give 0.32 g (24 %) of $Mg(N_3O_4)_2 \cdot 6H_2O$. Found (%): N, 24.73; H_2O, 31.63. Calculated (%): N, 24.42; H_2O, 31.39.

Magnesium dinitramidate trihydrate, $Mg(N_3O_4)_2 \cdot 3H_2O$. Drying $Mg(N_3O_4)_2 \cdot 6H_2O$ for several days in a vacuum-exicator over P_2O_5 gave $Mg(N_3O_4)_2 \cdot 3H_2O$. Found (%): H_2O, 19.40. Calculated (%): H_2O, 18.64.

Manganese(II) dinitramidate octahydrate, $Mn(N_3O_4)_2 \cdot 8H_2O$. A solution of $MnCl_2 \cdot 4H_2O$ (1.0 g) in methanol (30 mL) was added to a solution of AgN_3O_4 (2.14 g) in methanol (20 mL). The AgCl was separated, and the filtrate was concentrated on a rotatory evaporator. The residue was extrated with ether, and the solution was evaporated again. Recrystallization from 10 mL of a 3:2 nitromethane—benzene mixture gave 0.45 g (11 %) of the salt; a second recrystallization gave the product with m.p. 38—65 °C. Found (%): N, 21.07; H_2O, 34.36. Calculated (%): N, 20.04; H_2O, 35.04.

Iron(II) dinitramidate heptahydrate, $Fe(N_3O_4)_2 \cdot 7H_2O$. Solutions of AgN_3O_4 (2.14 g) in methanol (30 mL) and $FeCl_2 \cdot 4H_2O$ (1.00 g) in methanol (30 mL) were mixed under argon, the precipitate of AgCl was separated, and the solution was concentrated on a rotatory evaporator. The residue was dissolved in nitromethane, the salt was precipitated with benzene and recrystallized from the nitromethane in an argon atmosphere at a temperature below 50—55 °C. The salt oxidizes and decomposes in air; when heated in a sealed capillary it decomposes at 85 °C. Found (%): N, 21.63; H_2O, 32.08. Calculated (%): N, 21.32; H_2O, 31.98.

Cobalt(II) dinitramidate hexahydrate, $Co(N_3O_4)_2 \cdot 6H_2O$. A solution of $CoCl_2 \cdot 6H_2O$ (0.81 g) in ethanol (20 mL) was added to a solution of AgN_3O_4 (from 1.0 g of KN_3O_4) in ethanol (15 mL). The AgCl was separated, and the filtrate was concentrated on a rotatory evaporator. The residue was extracted with ether, and the extract was concentrated to give 0.9 g (65 %) of the salt. Found (%): N, 22.05; H_2O, 28.68. Calculated (%): N, 22.16; H_2O, 28.50.

Nickel(II) dinitramidate hexahydrate, $Ni(N_3O_4)_2 \cdot 6H_2O$. A solution of $NiCl_2 \cdot 6H_2O$ (1.64 g) in ethanol (30 mL) was added to a solution of AgN_3O_4 (from 2.0 g of KN_3O_4) in ethanol (30 mL). The AgCl was separated, and the filtrate was concentrated on a rotatory evaporator. The residue was extracted with ether, and the extract was concentrated to give 1.76 g (67 %) of the salt, m.p. 76—81 °C after crystallization from a 3:1 mixture of nitromethane and benzene; recrystallization gave a product with m.p. 80—83 °C. Found: (%): N, 22.86; H_2O, 29.32. Calculated (%): N, 22.16; H_2O, 28.50.

Nickel(II) dinitramidate dihydrate, $Ni(N_3O_4)_2 \cdot 2H_2O$. Drying $Ni(N_3O_4)_2 \cdot 6H_2O$ in a vacuum-exicator over P_2O_5 gave $Ni(N_3O_4)_2 \cdot 2H_2O$. Found (%): N, 27.60. Calculated (%): N, 27.36.

Sodium dinitramidate dioxanate, $NaN_3O_4 \cdot C_4H_8O_2$. A solution of NaOH (0.96 g) in methanol (60 mL) was added to a solution of *N*,*N*-dinitro-β-aminopropionitrile[1] (3.85 g) in methanol (25 mL) at 0 °C, and the mixture was stirred for 2 h and concentrated on a rotatory evaporator. The residue was recrystallized three times from a THF—dioxane mixture to give 0.82 g (12.6 %) of the title complex. Found (%): N, 18.10. Calculated (%): N, 19.30. The ^1H NMR spectrum contained only signals of the dioxane protons.

Diamminesilver(I) dinitramidate, $[Ag(NH_3)_2]N_3O_4$. This was obtained as a crystalline residue when NH_3 was passed through a solution of AgN_3O_4 in ethyl acetate, m.p. 58—64 °C (decomp.). Found (%): N, 27.98. Calculated (%): N, 28.22.

An alternative procedure consists of treatment of a concentrated ammonia solution of silver oxide with a saturated solution of $NH_4N_3O_4$ in ethyl acetate at 50 °C for 15 min with subsequent recrystallization from aqueous ammonia, m.p. 58—60 °C. Found (%): N, 29.03.

Di(pyridine)silver(I) dinitramidate, $[Ag(py)_2]N_3O_4$. Solutions of AgN_3O_4 (1.07 g) in ethanol (5 mL) and of pyridine (1.6 mL) in ethanol (3 mL) were mixed, and the mixture was cooled to 0 °C and filtered to give 1.41 g (75 %) of the salt. Found (%): C, 32.25; H, 2.89. Calculated (%): C, 32.26; H, 2.69.

Di(morpholine)silver(I) dinitramidate, $[Ag(C_4H_9NO)_2]N_3O_4$. Morpholine (1 mL) was added to a solution of AgN_3O_4 (1.07 g) in methanol (5 mL), and the residue was separated and washed with methanol and ether to give 1.82 g (93.8 %) of the salt. Found (%): C, 25.18; H, 4.75; Ag, 28.66. Calculated (%): C, 24.81; H, 4.65; Ag, 28.40.

(Acetonitrile)silver(I) dinitramidate, $AgN_3O_4 \cdot MeCN$. Saturated solutions of KN_3O_4 and $AgNO_3$ in acetonitrile (equimolar amounts) were mixed, the precipitate was separated, and the filtrate was concentrated to 1/4 of the initial volume on a rotatory evaporator. Then it was filtered again, and the filtrate was concentrated to dryness. The resudue was recrystallized from a 4:1 ethyl acetate—hexane mixture. Found (%): Ag, 42.47. Calculated (%): Ag, 42.00.

Tetraamminecopper(II) dinitramidate, $[Cu(NH_3)_4](N_3O_4)_2$.

A. A stream of NH_3 was passed for 10 min through a solution of $Cu(N_3O_4)_2 \cdot 3H_2O$ in ether and the violet residue was separated to give the title compound with m.p. 174—180 °C (decomp.). in a quantitative yield. Found (%): N, 40.56. Calculated (%): N, 40.69.

B. Concentrated solutions of $CuSO_4 \cdot 5H_2O$ (13.5 g) in aqueous ammonia and $NH_4N_3O_4$ (12.4 g) in water were mixed, the mixture was cooled to 0 °C, and the residue was separated, m.p. 178—183 °C (decomp.). Yield 13.0 g (78 %). Recrystallization from aqueous ammonia did not change the melting point.

Tetra(pyridine)copper(II) dinitramidate, $[Cu(py)_4](N_3O_4)_2$. A solution of pyridine (1.8 mL) in ether (5 mL) was added to a solution of $Cu(N_3O_4)_2 \cdot 3H_2O$ (1.54 g) in ether (10 mL), and the violet residue was separated and washed with ether. Yield 2.04 g (73.9 %). Found (%): C, 40.44; H, 3.53; Cu, 10.83. Calculated (%): C, 40.54; H, 3.38; Cu, 10.81.

Hexaamminenickel(II) dinitramidate, $[Ni(NH_3)_6](N_3O_4)_2$. Concentrated solutions of $NiSO_4 \cdot 7H_2O$ (14.0 g) in aqueous ammonia and $NH_4N_3O_4$ (12.4 g) in water were mixed, the mixture was cooled to 0 °C, and the residue was separated. Yield 11.5 g (62 %). Recrystallization from aqueous ammonia did not change the decomposition point. Found (%): N, 45.20. Calculated (%): N, 45.04.

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Received April 26, 1994