

# Synthesis, Characterization, and Crystal Structures of Cu, Ag, and Pd Dinitramide Salts

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**Abstract.** The literature known, but not fully characterized, silver dinitramide transfer reagents AgN(NO<sub>2</sub>)<sub>2</sub> (**1**), [Ag(NCCH<sub>3</sub>)]-[N(NO<sub>2</sub>)<sub>2</sub>] (**2**), and [Ag(py)<sub>2</sub>][N(NO<sub>2</sub>)<sub>2</sub>] (**3**) have been investigated by <sup>109</sup>Ag, <sup>14</sup>N NMR and vibrational spectroscopy (IR, Raman). In addition, the poorly understood [Cu(NH<sub>3</sub>)<sub>4</sub>][N(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**4**) and [Pd(NH<sub>3</sub>)<sub>4</sub>][N(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**5**) have also been prepared and characterized by <sup>14</sup>N NMR and vibrational spectroscopy (IR, Raman).

The structures of **2–5** have also been determined by X-ray diffraction.

**Keywords:** Copper dinitramide; Silver dinitramide; Palladium dinitramide; Crystal structure; NMR spectroscopy (multinuclear); Vibrational spectroscopy

## Synthese, Charakterisierung und Kristallstrukturen von Cu-, Ag- und Pd-Dinitramidsalzen

**Inhaltsübersicht.** Die aus der Literatur bekannten, aber nicht völlig charakterisierten Silberdinitramid-Transferreagenzien AgN(NO<sub>2</sub>)<sub>2</sub> (**1**), [Ag(NCCH<sub>3</sub>)]-[N(NO<sub>2</sub>)<sub>2</sub>] (**2**) und [Ag(py)<sub>2</sub>][N(NO<sub>2</sub>)<sub>2</sub>] (**3**) wurden mittels <sup>109</sup>Ag-, <sup>14</sup>N-NMR und IR- sowie Raman-Spektroskopie

untersucht. Ferner wurden die wenig verstandenen Verbindungen [Cu(NH<sub>3</sub>)<sub>4</sub>][N(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**4**) und [Pd(NH<sub>3</sub>)<sub>4</sub>][N(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**5**) dargestellt und charakterisiert (<sup>14</sup>N-NMR, IR, Raman). Die Strukturen von **2–5** wurden röntgenographisch bestimmt.

### Introduction

Recently, we have undertaken many studies on high energy density materials containing only C, H, N and O atoms e.g. nitrates, azides and azotetrazolates [2]. Due to an interest in extending this chemistry to include dinitramide salts, an appropriate dinitramide transfer reagent was required. Free dinitramine did not appear to be very promising, due to its instability, decomposing at 0 °C [1]. Instead, potassium and silver dinitramide salts are reported as good dinitramide transfer reagents [3]. Potassium dinitramide, has been studied in great detail (including structure determination using X-ray diffraction techniques) by *Gilardi* in the 1990s [4], however in our investigations, transfer of the dinitramide anion using KN(NO<sub>2</sub>)<sub>2</sub> was not successful. Silver dinitramide salts, on the other hand, have proved to be excellent

dinitramide transfer reagents [5]. AgN(NO<sub>2</sub>)<sub>2</sub> (**1**), [Ag(NCCH<sub>3</sub>)]-[N(NO<sub>2</sub>)<sub>2</sub>] (**2**) and [Ag(py)<sub>2</sub>][N(NO<sub>2</sub>)<sub>2</sub>] (**3**) were first prepared by *Lykanov* [1], however, these compounds were only characterized by elemental analysis and melting point. Therefore, we have undertaken the first extensive study of **1–3**, in order to fully characterize these salts and furthermore to investigate their ability to act as dinitramide transfer reagents. Characterization included <sup>109</sup>Ag, <sup>14</sup>N NMR, vibrational spectroscopy (IR, Raman) and X-ray diffraction studies (of **2** and **3** only). The only heavy metal dinitramide salts which have been studied using X-ray diffraction techniques so far are *fac*-[Re(bpy)-(CO)<sub>3</sub>N<sub>3</sub>O<sub>4</sub>] [6], hexaaquamanganese and hexaaquozinc dihydrate dinitramide [7]. Therefore, due to the surprisingly interesting structure of **2**, [Cu(NH<sub>3</sub>)<sub>4</sub>][N(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**4**) [1] and [Pd(NH<sub>3</sub>)<sub>4</sub>][N(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**5**) have also been prepared and characterized by <sup>14</sup>N NMR, vibrational spectroscopy (IR, Raman) and X-ray diffraction studies.

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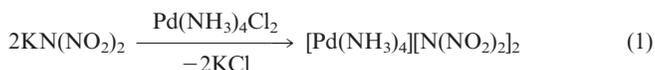
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### Results and Discussion

#### *Preparation and spectroscopic characterization*

All compounds, with the exception of [Cu(NH<sub>3</sub>)<sub>4</sub>]-[N(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**4**), were prepared by a metathesis reaction using KN(NO<sub>2</sub>)<sub>2</sub>. **4** was prepared by the reaction of

CuSO<sub>4</sub>·5H<sub>2</sub>O with ADN (ammonium dinitramide, NH<sub>4</sub><sup>+</sup>N(NO<sub>2</sub>)<sub>2</sub><sup>-</sup>). KN(NO<sub>2</sub>)<sub>2</sub> was prepared according to [8] and the silver and copper dinitramide salts according to [1]. [Pd(NH<sub>3</sub>)<sub>4</sub>][N(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub> was prepared according to equation (1).



AgN(NO<sub>2</sub>)<sub>2</sub> (**1**) has been reported by *Lykanov* to be quite explosive; whereas [Ag(NCCH<sub>3</sub>)]N(NO<sub>2</sub>)<sub>2</sub> (**2**) and [Ag(py)<sub>2</sub>][N(NO<sub>2</sub>)<sub>2</sub>] (**3**) were reported as being considerably safer to handle. **1** is light sensitive and exposure to light for a few minutes results in the formation of a silver mirror. However, the acetonitrile and pyridine adducts can be handled much more easily. As pyridine is a stronger base, the use of [Ag(NCCH<sub>3</sub>)]N(NO<sub>2</sub>)<sub>2</sub> (**2**) may be preferable and in fact, of all three silver salts, **2** has proven to be the best dinitramide transfer reagent. In fact compound **2** has been used to prepare *N*-methylurotropinium dinitramide, which was produced readily in relatively high yields and is the subject of a future publication [5].

<sup>109</sup>Ag and <sup>14</sup>N NMR data for compounds **1–3** are presented in Table 1.

**Table 1** <sup>14</sup>N and <sup>109</sup>Ag NMR data of compounds **1**, **2** and **3** (δ)

Compound	<sup>109</sup> Ag NMR	<sup>14</sup> N NMR	Solvent
AgN(NO <sub>2</sub> ) <sub>2</sub> ( <b>1</b> )	137 (s)	-17 (s, NO <sub>2</sub> ), -73 (br, N(NO <sub>2</sub> ) <sub>2</sub> ), Δv <sub>1/2</sub> = 1015 Hz)	EtOH
[Ag(NCCH <sub>3</sub> )]N(NO <sub>2</sub> ) <sub>2</sub> ( <b>2</b> )	212 (s)	-16 (s, NO <sub>2</sub> ), -68 (br, N(NO <sub>2</sub> ) <sub>2</sub> ), Δv <sub>1/2</sub> = 580 Hz), -157 (br, NCCH <sub>3</sub> ), Δv <sub>1/2</sub> = 290 Hz)	CH <sub>3</sub> CO <sub>2</sub> Et
[Ag(py) <sub>2</sub> ][N(NO <sub>2</sub> ) <sub>2</sub> ] ( <b>3</b> )	306 (s)	-13 (s, NO <sub>2</sub> ), -91 (br, N(NO <sub>2</sub> ) <sub>2</sub> ), Δv <sub>1/2</sub> = 1450 Hz)	THF

Two signals for the dinitramide anion can be observed in the <sup>14</sup>N NMR spectra for compounds **1–3** and are similar with literature values [9]. The NO<sub>2</sub> group can be observed to lie in the range δ -12 to -17 and the central nitrogen atom [N(NO<sub>2</sub>)<sub>2</sub>]<sup>-</sup> between δ -68 and -91 (it should be noted that varying solvents have been used). The coordinated acetonitrile can be easily observed in the <sup>14</sup>N NMR of **2** at δ -157, differing from free acetonitrile which is found at δ -137 to -139. As pyridine is observed in the same region in <sup>14</sup>N NMR as the central nitrogen atom of the dinitramide anion [N(NO<sub>2</sub>)<sub>2</sub>]<sup>-</sup>, the two cannot be differentiated. However, elemental analysis and Raman spectra confirm the coordination of two pyridine molecules. The <sup>109</sup>Ag NMR spectra of **1–3** show different shifts for each compound, which can be explained by the use of a different solvent in each case. From the <sup>109</sup>Ag NMR spectrum of **2**, it can be deduced that the structure in the solid state differs from that in solution. X-ray diffraction studies show three different silver atoms, however, in solution only one signal can be observed in the <sup>109</sup>Ag NMR spectrum (three signals would have been expected from the solid state structure). This suggests that the Ag atom in solution is no longer coordinated to the dinitramide ion and acetonitrile group, but is instead coordinated to solvent molecules. Compounds **4** and **5** both show signals in <sup>14</sup>N NMR at δ -8 and δ -57 for NO<sub>2</sub> and [N(NO<sub>2</sub>)<sub>2</sub>]<sup>-</sup> respectively. Coordinated ammonia can also be observed in the <sup>14</sup>N NMR spectrum of compound **5** at δ -413.

Raman and IR data for compounds **1–5** are presented in Table 2, where assignments have been made according to [8].

While the coordinated acetonitrile and pyridine in **2** and **3** respectively, can be removed only in high *vacuo* with extensive drying (0.5–1 h), the coordinated ammonia in **4** and **5** can be removed more easily after only a few minutes in *vacuo*. Therefore, accurate elemental analysis of the bulk products of **4** and **5** could not be obtained due to the facile loss of NH<sub>3</sub> on drying.

**Table 2** IR and Raman data of compounds **1–5** cm<sup>-1</sup>

assignt	approx mode description	<b>1</b>		<b>3</b>		<b>4</b>		<b>5</b>	
		IR	Raman	IR	Raman	IR	Raman	IR	Raman
A	v <sub>1</sub>	1531 s	1506(2)	1593 vw 1527 s	1570(1)	1599 m 1527 m	1516(2)	1538 s 1527 s	1533(2)
	v <sub>2</sub>	1356 w 1343 w 1316 w	1317(10)	1341 w	1329(2)	1342 m 1325 vw	1326(10)	1343 w	1333(6)
	v <sub>3</sub>	972 m	969(2)	952 vw	943(1)			953 w 928 w	
B	v <sub>4</sub>	827 w	832(4)	825 w	828(2)		823(6)	823 w	824(4)
	v <sub>9</sub>	1455 m 1428 m	1426(2)	1440 s		1428 m	1438(1)	1431 m	
	v <sub>10</sub>	1186 vs 1173 vs	1191(2) 1171(2)	1176 vs	1226(2) 1153(1)	1252 vs 1182 s		1284 w 1256 w 1208 vs 1178 vs	1263(2) 1167(2)
	v <sub>11</sub>	1020 s	1038(2)	1066 vw 1018 m	1073(1) 1039(2)	1024 m	1002(1)	1030 m 1022 m	1032(2)
	v <sub>13</sub>	730 w		728 w				732 w	

**Table 3** Crystal data and structure refinement of **2–5**

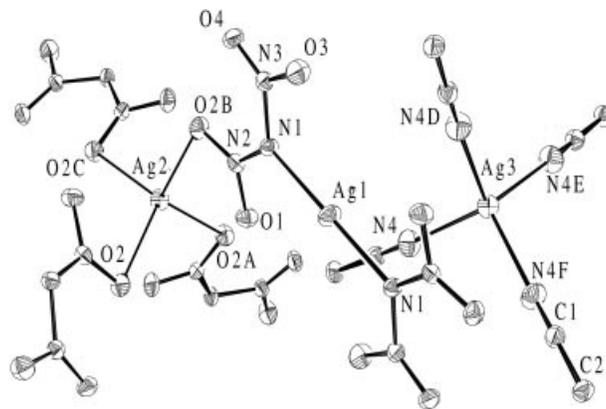
	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Empirical formula	C <sub>8</sub> H <sub>12</sub> Ag <sub>4</sub> N <sub>16</sub> O <sub>16</sub>	C <sub>10</sub> H <sub>10</sub> Ag <sub>1</sub> N <sub>5</sub> O <sub>4</sub>	H <sub>12</sub> CuN <sub>10</sub> O <sub>8</sub>	H <sub>12</sub> N <sub>10</sub> O <sub>8</sub> Pd
Formula mass	1019.82	372.10	343.704	368.58
Temperature [K]	193(2)	193(2)	200(2)	200(2)
Crystal size mm	0.40 × 0.40 × 0.40	0.40 × 0.10 × 0.10	0.15 × 0.09 × 0.02	0.24 × 0.15 × 0.09
Crystal system	tetragonal	triclinic	triclinic	triclinic
Space group	<i>I</i> 4 <sub>1</sub> / <i>a</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> / Å	15.1767(6)	6.189(7)	6.501 (2)	6.857(1)
<i>b</i> / Å	15.1767(6)	7.756(8)	7.384(2)	7.377(1)
<i>c</i> / Å	11.8204(7)	13.95(1)	7.466(2)	7.412(1)
$\alpha$ /°		87.30(2)	97.48(3)	96.82(2)
$\beta$ /°	90	81.17(2)	111.11(3)	117.15(2)
$\gamma$ /°		80.19(2)	113.96(3)	110.06(2)
<i>V</i> / Å <sup>3</sup>	2722.6 (2)	652.0(1)	289.0(1)	295.87 (9)
<i>Z</i>	4	2	1	1
$\rho$ (calcd.) / g/cm <sup>3</sup>	2.488	1.896	1.9750(8)	2.1697(7)
$\mu$ / mm <sup>-1</sup>	2.934	1.568	1.953	2.934
<i>F</i> (000)	1952	368	175	192
2 $\theta$ range/°	4.36–58.54	2.96–57.74	3.1–27.9	3.1–27.9
Index ranges	–18 ≤ <i>h</i> ≤ 18 –19 ≤ <i>k</i> ≤ 19 –15 ≤ <i>l</i> ≤ 13	–7 ≤ <i>h</i> ≤ 7 –8 ≤ <i>k</i> ≤ 9 –17 ≤ <i>l</i> ≤ 17	–8 ≤ <i>h</i> ≤ 8 –9 ≤ <i>k</i> ≤ 9 –9 ≤ <i>l</i> ≤ 9	–8 ≤ <i>h</i> ≤ 8 –9 ≤ <i>k</i> ≤ 8 –9 ≤ <i>l</i> ≤ 9
Reflections collected	7559	3886	2765	2806
Independent reflections	1441 ( <i>R</i> <sub>int</sub> = 0.0245)	2031 ( <i>R</i> <sub>int</sub> = 0.0312)	1281 ( <i>R</i> <sub>int</sub> = 0.0438)	1308 ( <i>R</i> <sub>int</sub> = 0.0197)
Observed reflections	1319	1589	1002	1303
Max. and min. transm.	0.4405 and 0.3273	0.8015 and 0.5795	0.9590 and 0.8215	0.9044 and 0.8140
Data/restraints/parameters	1441/0/121	2031/0/182	1281/0/112	1308/0/112
Goodness-of-fit on <i>F</i> <sub>2</sub>	1.134	1.043	0.913	1.087
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2( <i>I</i> )]	0.0223, 0.0522	0.0465, 0.1077	0.0296, 0.0512	0.0167, 0.0402
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0257, 0.0538	0.0659, 0.1158	0.0469, 0.0514	0.0168, 0.0402
Large. diff. peak/hole / e/Å <sup>3</sup>	0.232/–0.536	0.584/–0.560	0.401/–0.489	0.260/–0.613

### Crystal Structures

The crystal structures of compounds **2–5** are presented in Figures 1–4 and crystal data in Table 3.

Single crystals of **2** and **3** were obtained from cooling saturated ethyl acetate solutions. X-ray diffraction studies show that in the solid state [Ag(NCCH<sub>3</sub>)] [N(NO<sub>2</sub>)<sub>2</sub>] (**2**) exists as [Ag(NCCH<sub>3</sub>)<sub>4</sub>][Ag<sub>3</sub>[N(NO<sub>2</sub>)<sub>2</sub>]<sub>4</sub>], where three different coordination spheres around the silver atoms can be observed. Metal dinitramide salts synthesized and structurally characterized (X-ray) so far, contain metal ions with two or less non-identical environments (CsN<sub>3</sub>O<sub>4</sub> [4] contains two cesium ions in different environments, whereas in all other structures the environments of the metal ions are identical). The anion {Ag<sub>3</sub>[N(NO<sub>2</sub>)<sub>2</sub>]<sub>4</sub>}<sup>–</sup> contains two types of silver atoms. Both tetrahedral coordination of the Ag atom (Ag2...O2 contacts) to the O2 atom of four dinitramide groups and linear coordination (Ag1–N1, full bonds) of the Ag atom to the central nitrogen atom of two dinitramide groups are present. Each dinitramide anion is connected to both an Ag1 and Ag2 atom as described above, resulting in a three-dimensional network. The [Ag(NCCH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> cation contains a silver atom tetrahedrally bonded to four acetonitrile groups (Fig. 1).

The structure of [Ag(py)<sub>2</sub>][N(NO<sub>2</sub>)<sub>2</sub>] (**3**) consists of an [Ag(py)<sub>2</sub>]<sup>+</sup> cation (with almost coplanar pyridine rings) linked to a dinitramide anion by a single contact between the silver ion and the central nitrogen atom of the

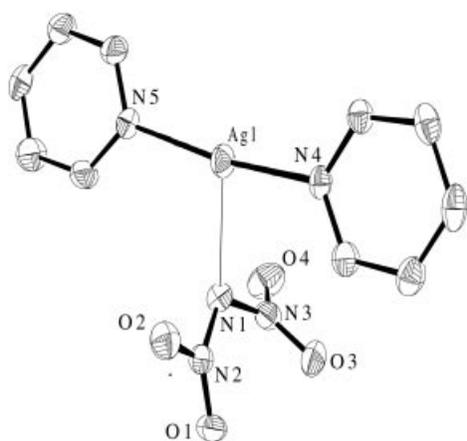


**Fig. 1** ORTEP presentation of the crystal packing of **2** showing the Ag...O and Ag...N contacts drawn at 25 % probability. Selected distances/Å and angles/°:

Ag(1)–N(1) 2.135(2), Ag(3)–N(4) 2.259(3), N(4)–C(1) 1.123(4), C(1)–C(2) 1.449(4), N(1)–Ag(1)–N(1) 180.00(8), N(4E)–Ag(3)–N(4) 114.7(2), N(4D)–Ag(3)–N(4) 106.97(8), Ag(2)–O(2) 2.514(2), O(2A)–Ag(2)–O(2) 116.36(5), O(2)–Ag(2)–O(2B) 96.43(9).

dinitramide ion. The N(4)–Ag–N(5) angle of 168.6(2)° deviates considerably from linearity indicating some Ag...anion interaction (see Fig. 2).

[Cu(NH<sub>3</sub>)<sub>4</sub>][N(NO<sub>2</sub>)<sub>2</sub>] (**4**) forms as a crystalline material on synthesis, when cooled to 0°, with no need for further



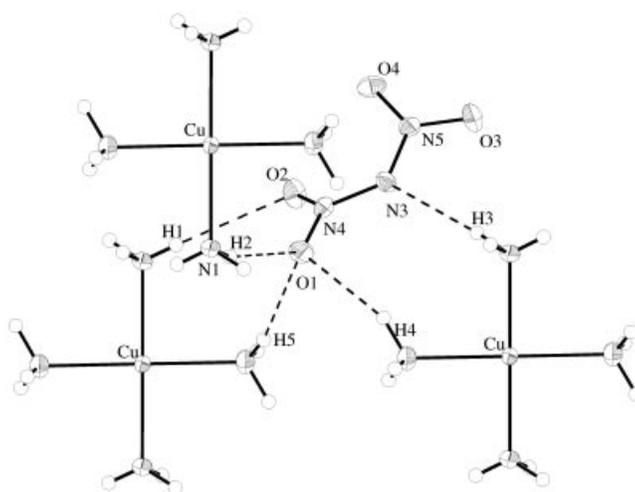
**Fig. 2** ORTEP presentation of the crystal packing of **3** showing the Ag $\cdots$ N contacts drawn at 50 % probability. Selected distances/Å and angles/°:

Ag(1)-N(4) 2.171(5), Ag(1)-N(5) 2.160(4), N(5)-Ag(1)-N(4) 168.6(2), Ag(1) $\cdots$ N(1) 2.641(6), N(5)-Ag(1) $\cdots$ N(1) 93.5(2), N(4)-Ag(1) $\cdots$ N(1) 97.1(2).

recrystallization. Single crystals of [Pd(NH<sub>3</sub>)<sub>4</sub>][N(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**5**) were obtained from a cooled H<sub>2</sub>O solution. Structures **4** and **5** consist of planar [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> and [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> cations, respectively, linked to dinitramide anions by extensive hydrogen bonding, forming a three-dimensional network in each case.

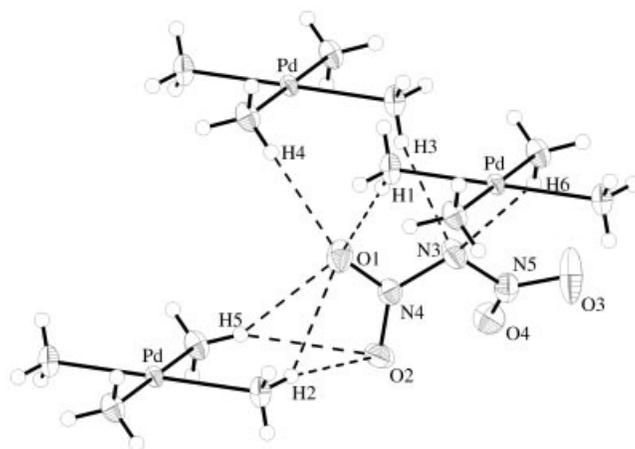
In the structure of **4**, the dinitramide anion accepts five hydrogen bonds from five different NH<sub>3</sub> groups, situated on three different Cu ions. The central nitrogen atom N3, and the O1 atom are hydrogen bonded to a single cation by the H3 and H4 atoms, respectively. A second cation is incorporated as a result of hydrogen bonding between the O1 and O2 atoms to the H5 and H1 atoms. Finally a fifth hydrogen bond links the O1 atom to the H2 atom of a third cation. Hence the O1 atom is involved in three hydrogen bonds, and both the N3 and O2 atoms in one. Of the five hydrogen bonds, only the N1-H3 $\cdots$ N3 interaction can be described as linear with an angle of 177°. The N2-H4 $\cdots$ O1 hydrogen bond is clearly bent (151°), while the other three lie in the region of 162° to 167°. The shortest Cu-O contacts are Cu-O4 with 2.561 Å and Cu-O2 with 3.629 Å with the O4 atom sitting directly above the CuN<sub>4</sub> plane.

The structure of **5** is more complex, as the dinitramide anion accepts eight different hydrogen bonds from six different NH<sub>3</sub> groups, situated on three different Pd ions. In this case, the O1 atom participates in four hydrogen bonds and both the O2 and N3 atoms in two. The central nitrogen, N3, and the O1 atom are hydrogen bonded to one cation by the H3 and H4 atoms, as before, but they are also linked to a second cation by hydrogen bonding to the H6 and H1 atoms. A third cation is involved in four hydrogen bonds, bridging the O1 and O2 atoms by hydrogen bonding to its H2 and H5 atoms. As was the case in **4**, only one hydrogen bond, the N2-H4 $\cdots$ O1 interaction, can be described as linear with an angle of 176°. The majority of hydrogen bonds are bent with N1-H2 $\cdots$ O1, N1-H3 $\cdots$ N3, N2-H5 $\cdots$ O1,



**Fig. 3** ORTEP presentation of the crystal packing of **4** showing the H $\cdots$ N and H $\cdots$ O hydrogen bonds drawn at 50 % probability. Selected distances/Å and angles/°:

Cu-N(2) 2.008(2), Cu-N(1) 2.017(2), N(2)-Cu-N(1) 90.1(1), N(1)-Cu-N(1) 180.0(1), H(4) $\cdots$ O(1) 2.28(4), H(5) $\cdots$ O(1) 2.42(4), H(2) $\cdots$ O(1) 2.26(5), H(1) $\cdots$ O(2) 2.53(4), H(3) $\cdots$ N(3) 2.33(5).



**Fig. 4** ORTEP presentation of the crystal packing of **5** showing the H $\cdots$ N and H $\cdots$ O hydrogen bonds drawn at 50 % probability. Selected distances/Å and angles/°:

Pd-N(2) 2.041(2), Pd-N(1) 2.041 (2), N(2)-Pd-N(1) 90.14(8), N(1)-Pd-N(1') 180.0, H(1) $\cdots$ O1 2.28(5), H(2) $\cdots$ O(1) 2.52(4), H(2) $\cdots$ O(2) 2.57(4), H(3) $\cdots$ N(3) 2.66(5), H(4) $\cdots$ O(1) 2.39(4), H(5) $\cdots$ O(1) 2.49(4), H(5) $\cdots$ O(2) 2.52(4), H(6) $\cdots$ N(3) 2.47(4).

N2-H5 $\cdots$ O2 and N2-H6 $\cdots$ N3 in the region of 142–157°. The hydrogen bond angles N1-H2 $\cdots$ O2 and N1-H1 $\cdots$ O1 are 163° and 166°, respectively.

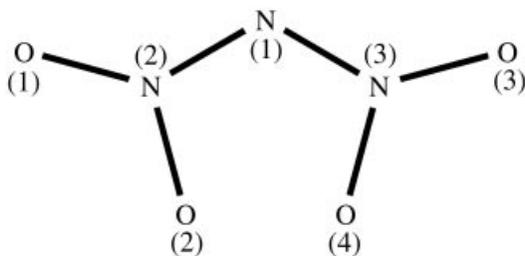
Structures **4** and **5** have an interesting packing arrangement with cations and anions stacking in separate columns. Layers form with alternate rows of cations and anions. The spacing between the anions in a column is 6.501 Å and 7.454 Å and for cations 6.500 Å and 6.857 Å, in **4** and **5**, respectively.

The bond lengths and angles of the dinitramide anions in **2–5** (Table 4) are in good agreement with those of previously determined dinitramide structures [9].

**Table 4** Selected bonds lengths Å and angles ° of the dinitramide anion in compounds **2–5**

	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
N1–N2	1.366(3)	1.345(7)	1.364(3)	1.342(2)
N1–N3	1.401(3)	1.360(7)	1.386(3)	1.407(2)
N2–O1	1.236(3)	1.219(6)	1.255(3)	1.258(2)
N2–O2	1.229(3)	1.236(6)	1.221(3)	1.228(2)
N3–O3	1.225(3)	1.217(6)	1.232(3)	1.220(2)
N3–O4	1.209(3)	1.213(7)	1.230(3)	1.214(2)
N1–N2–N3	118.0(2)	112.2(5)	113.9(2)	113.1(2)
N1–N2–O1	113.2(2)	124.2(6)	111.7(2)	112.8(2)
N1–N2–O2	124.6(2)	113.1(5)	126.1(2)	125.8(2)
O1–N2–O2	122.2(2)	122.4(5)	122.0(2)	121.3(2)
N1–N3–O3	110.8(2)	123.8(6)	112.7(2)	112.6(2)
N1–N3–O4	124.6(2)	114.8(6)	124.1(2)	122.7(2)
O3–N3–O4	124.6(2)	120.9(7)	122.9(2)	124.3(2)

The labeling scheme used in Tables 4 and 5 is depicted in Fig. 5.



**Fig. 5** Labeling scheme of dinitramide anion used for Tables 3–4

As has been observed for other dinitramide structures [4, 6, 7, 10], **2**, **4** and **5** show the “outer” (O1, O3) N–O bonds to be longer than the “inner” (O2, O4) N–O bonds. In contrast, the N–O distances in **3** for the N2 nitro group show the “inner” (O2, O4) N–O bonds to be longer. The N–O bond lengths in all four structures vary from 1.209(3) to 1.258(2) Å. N–N bond lengths vary from 1.342(2) to 1.407(2) Å with the biggest difference within a salt being observed in **5** of 0.065 Å. The N–N–N angles in **3–5** fall close to values previously observed for related compounds [9] and are in the range of 112.2(5) to 113.9(2)°. Whereas in **2**, this value is somewhat larger at 118.0(2)° and is the largest N–N–N angle reported for a dinitramide anion up to now. Torsion, twist and bend angles of the dinitramide anions in **2–5** are presented in Table 5.

Twist angles describe the rotation of the nitro groups out of the NNN plane (calculated by averaging the torsion angles and adding or subtracting 180° to bring the value below 90°) and bend angles describe the pyramidalization of the nitro groups, following the investigations of Gilardi et al [8]. In accordance with almost all reported dinitramide salts [9], the dinitramide anions in compounds **2–5** are

**Table 5** Torsion, twist and bend angles of the dinitramide anion in **2–5**

	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
N3–N1–N2–O1	174.0	–21.9	–172.4	170.3
N3–N1–N2–O2	–7.5	164.1	12.4	–13.8
N2–N1–N3–O3	180.0	–36.7	–159.6	150.2
N2–N1–N3–O4	–1.3	150.6	26.2	–36.9
N(2) nitro group twist	13.5	18.9	10.0	11.75
N(3) nitro group twist	0.65	33.05	23.3	33.35
N(2) nitro group bend	0.9	3.8	–3.1	2.6
N(3) nitro group bend	–0.7	–3.9	3.1	–3.8

asymmetric and there is some difference in the degree of twisting of each nitro group. In **3–5**, both nitro groups are twisted, however in **2**, the N3 nitro group is twisted (torsion angles of 174.0° and –7.5°) and the N2 nitro group is planar (torsion angles 180.0° and –1.3°). This can possibly be attributed to the O2⋯Ag contacts of the N2 nitro group. It has been observed that hydrogen bonding is a major factor in determining whether the dinitramide anion is twisted or planar [10]. Not surprisingly, in **4** and **5** there is less twisting of the N2 nitro group, whose oxygen atoms participate in hydrogen bonding, compared with that of the N3 nitro group where no hydrogen bonding takes place.

## Conclusion

The literature known [1], but not fully characterized silver dinitramide transfer reagents **1–3** were investigated by <sup>109</sup>Ag, <sup>14</sup>N NMR and vibrational spectroscopy (IR, Raman). **2** and **3** have proved to be excellent dinitramide transfer reagents and in comparison with **1** appear to be less explosive and considerably less light sensitive. The crystal structures of **2** and **3** determined by X-ray diffraction show very different structural arrangements in each case. In the solid state, **2** exists as a three dimensional network of anions and cations and has the formula [Ag<sub>3</sub>(NCCH<sub>3</sub>)<sub>4</sub>][Ag<sub>3</sub>[N(NO<sub>2</sub>)<sub>2</sub>]<sub>4</sub>] where three different coordination spheres around the silver atoms can be observed. In contrast the structure of **3** contains only one type of silver atom and is much less complex. The presence of a only one singlet in the <sup>109</sup>Ag NMR spectrum of **2** shows that the solid state structure differs from that in solution and the coordinated acetonitrile group and dinitramide anion are replaced with solvent molecules. **4** and **5** were also prepared and characterized by <sup>14</sup>N NMR and vibrational spectroscopy (IR, Raman). X-ray diffraction studies show both to have similar columnar packing arrangements with hydrogen bridges between the coordinated ammonia ligands and dinitramide anion.

## Experimental

**Caution!** Dinitramide salts are potentially explosive and the appropriate safety precautions should be taken at all times as described in the literature [2a].

## General

All reactions were carried out at ambient temperature and the preparation of silver salts under the exclusion of light. Spectra were recorded on the following instruments: Raman spectra; Perkin Elmer 2000 NIR FT-Raman spectrometer fitted with a Nd-AG laser (1064nm), infrared spectra; Perkin Elmer Spectrum One FT-IR spectrometer (neat solids between KBr plates) and NMR spectra; JEOL Eclipse 400 instrument. Chemical shifts are recorded with respect to  $(\text{CH}_3)_4\text{Si}$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ),  $\text{CH}_3\text{NO}_2$  ( $^{14}\text{N}$ ) and  $\text{AgNO}_3$  ( $^{109}\text{Ag}$ ). Melting points were determined in heated capillaries on a Büchi B540 instrument and elemental analyses performed with a C, H, N-Analysator Elementar Vario EL at the analytical service of LMU.

## X-ray crystallography

Data for **2** and **3** were collected on Siemens SMART Area-detector and **4** and **5** on a STOE IPDS using Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.071073$ ) Å. The structures were solved by direct methods using SHELXL-97 and refinement carried out by means of the full-matrix least squares on  $F^2$ . Further details can be obtained from the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 194343 for **2** and CCDC 194344 for **3**, and from the Fachinformationszentrum Karlsruhe, by quoting the nos. CSD 412606 for **4** and CSD 412607 for **5**.

## Preparations

**AgN(NO<sub>2</sub>)<sub>2</sub> (1)** A saturated solution of  $\text{KN}(\text{NO}_2)_2$  (0.22 g, 1.5 mmol, prepared according to [8]) in boiling EtOH (15 mL) was reacted with a saturated solution of  $\text{AgNO}_3$  (0.25 g, 1.5 mmol) in boiling EtOH (12 mL). A colorless precipitate ( $\text{KNO}_3$ ) was observed immediately and the reaction mixture was stirred for 0.5 h. The  $\text{AgN}(\text{NO}_2)_2$  solution was decanted, and the solvent was reduced to 1/5 of the original volume in high vacuum yielding a white solid [1]. Yield 75 %.

IR (KBr): 2290 m, 2259 m, 1531 s, 1455 m, 1428 m, 1356 w, 1343 w, 1316 w, 1186 vs, 1173 vs, 1020 s, 972 m, 827 w, 761 w, 730 w  $\text{cm}^{-1}$ .  $^{14}\text{N}$  NMR ( $\text{CD}_3\text{OD}$ ):  $\delta = -17$  (s,  $\text{NO}_2$ ),  $-73$  (br,  $\Delta\nu_{1/2} = 1015$  Hz,  $\text{N}(\text{NO}_2)_2$ ).  $^{15}\text{N}$  NMR (EtOH):  $\delta = -17.6$ .  $^{109}\text{Ag}$  NMR (EtOH):  $\delta = 137$ (s).

**[Ag(NCCH<sub>3</sub>)]N(NO<sub>2</sub>)<sub>2</sub> (2)** A saturated solution of  $\text{KN}(\text{NO}_2)_2$  (0.29 g, 2.0 mmol), prepared according to [6]) in MeCN was reacted with a saturated solution of  $\text{AgNO}_3$  (0.33 g, 2.0 mmol) in MeCN. Colorless  $\text{KNO}_3$  precipitated immediately and the reaction mixture was stirred for 1h. The resulting  $[\text{Ag}(\text{MeCN})_4][\text{Ag}_3[\text{N}(\text{NO}_2)_2]_4]$  solution was decanted, solvent was removed in high vacuum and the product extracted with MeOH. [1]. Colorless crystals were obtained from re-dissolving the product in ethyl acetate/hexane mixtures. Yield 46 %. Calcd. for  $\text{C}_8\text{H}_{12}\text{Ag}_4\text{N}_{16}\text{O}_{16}$ : C, 9.42; H, 1.19; N, 21.98. Found: C, 8.81; H, 1.46; N, 21.25 %.

Raman (250 mW): 2955(1), 2267(1), 1506(2), 1426(2), 1317(10), 1191(2), 1171(2), 1038(2), 969(2), 832(4),  $\nu\text{N}(\text{NO}_2)_2$ , 753(2), 493(3), 324(3), 162(4)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta = 2.13$  (s,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = 119.9$ , 119.8 (CN), 3.2, 1.8, 0.5,  $-0.9$  ( $\text{CH}_3$ ).  $^{14}\text{N}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -16$  (s,  $\text{NO}_2$ ),  $-68$  (br,  $\Delta\nu_{1/2} = 580$  Hz)  $-157$  (br,  $\Delta\nu_{1/2} = 290$  Hz).  $^{109}\text{Ag}$  NMR ( $\text{CH}_3\text{CO}_2\text{Et}$ ):  $\delta = 212$  (s).

**[Ag(py)<sub>2</sub>]N(NO<sub>2</sub>)<sub>2</sub> (3)** A saturated solution of  $\text{AgN}(\text{NO}_2)_2$  (0.32 g, 1.50 mmol) in boiling EtOH was reacted with pyridine (0.3 mL, 3.68 mmol). A colorless precipitate was observed immediately and the reaction mixture was cooled to 0 °C. The solvent was removed in *vacuo* and the product washed in EtOH. Colorless crystals were

obtained from re-dissolving the product in ethyl acetate and cooling to  $-20$  °C. [1]. Yield: 60 %. Calcd. for  $\text{C}_{10}\text{H}_{10}\text{AgN}_5\text{O}_4$ : C, 32.28; H, 2.71; N, 18.82. Found: C, 31.76; H, 2.99; N, 18.55 %.

IR (KBr): 1593 vw, 1527 s, 1481 w, 1440 s, 1341 w, 1176 vs, 1066 vw, 1018 m, 952 vw, 825 w, 759 w, 751 w, 728 w, 698 m, 619 vw,  $\text{cm}^{-1}$ . Raman (250 mW): 3075(4), 1601(2), 1570(1), 1329(2), 1226(2), 1153(1), 1073(1), 1039(2), 1012(10), 943(1), 828(2), 650(1), 630(1), 464(1), 119(4)  $\text{cm}^{-1}$ .  $^{14}\text{N}$  NMR (THF):  $\delta = -13$  (s,  $\text{NO}_2$ ),  $-91$  (br,  $\Delta\nu_{1/2} = 1450$  Hz  $\text{N}(\text{NO}_2)_2$ ).  $^{109}\text{Ag}$  NMR (THF):  $\delta = 306$  (s).

**[Cu(NH<sub>3</sub>)<sub>4</sub>]N(NO<sub>2</sub>)<sub>2</sub> (4)** A saturated solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.37 g, 1.5 mmol) in  $\text{NH}_3(\text{aq})$  (5mL) was reacted with a saturated solution of  $\text{NH}_4\text{N}(\text{NO}_2)_2$  (0.37 g, 3.0 mmol) in  $\text{H}_2\text{O}$  and cooled to 0 °C producing violet crystals. [1]. Removing all of the solvent in high vacuum removed the coordinated  $\text{NH}_3$ , therefore, elemental analysis could not be obtained. Yield: 65 %.

IR (KBr): 3291 m, 3229 m, 3152 m, 1599 m, 1527 m, 1428 m, 1342 m, 1325 vw, 1252 vs, 1182 s, 1024 m, 689 m  $\text{cm}^{-1}$ . Raman (250 mW): 3284(2), 1516(2), 1438(1), 1326(10), 1002(1), 823(6), 757(1), 481(3), 433(3), 306(3), 126(3)  $\text{cm}^{-1}$ .  $^{14}\text{N}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -8$  (s,  $\text{NO}_2$ ),  $-60$  (br,  $\text{N}(\text{NO}_2)_2$ ,  $\Delta\nu_{1/2} = 577$  Hz),  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = 4.90$ , 4.02, 2.15.

**[Pd(NH<sub>3</sub>)<sub>4</sub>]N(NO<sub>2</sub>)<sub>2</sub> (5)** A saturated solution of  $\text{KN}(\text{NO}_2)_2$  (0.44 g, 3.0 mmol) in  $\text{H}_2\text{O}$  was reacted with a saturated solution of  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ , prepared according to [11], (0.37 g, 1.50 mmol) in  $\text{H}_2\text{O}$ . A colorless precipitate was observed immediately. The solution was filtered, the solvent was removed and colorless crystals were obtained from boiling  $\text{H}_2\text{O}$  solution. Removing all solvent in high vacuum removes the coordinated  $\text{NH}_3$ , therefore, elemental analysis could not be obtained. Yield: 70 %. m.p. 168–174 °C (dec).

IR (KBr): 3233 m, 3146 m, 2088 w, 1604 w, 1538 s, 1527 s, 1431 m, 1343 w, 1284 w, 1256 w, 1208 vs, 1178 vs, 1030 m, 1022 m, 953 w, 928 w, 823 w, 795 w, 761 w, 732 w  $\text{cm}^{-1}$ . Raman (250 mW): 3113(5), 2510(10), 1533(2), 1333(6), 1263(2), 1167(2), 1032(2), 824(4), 754(2), 500(6), 465(2), 284(3), 261(2), 222(2), 164(4), 137(4)  $\text{cm}^{-1}$ .  $^{14}\text{N}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -9$  (s,  $\text{NO}_2$ ),  $-62$  (br,  $\text{N}(\text{NO}_2)_2$ ,  $\Delta\nu_{1/2} = 722$  Hz),  $-413$  (s,  $\text{NH}_3$ )

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