The Dinitramide Anion, $N(NO_2)_2^-$ [▽]

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The infrared and Raman spectra of the NH_4^+, K^+, and Cs^+ salts of $N(NO_2)_2^-$ in the solid state and in solution have been measured and are assigned with the help of ab initio calculations at the HF/6-31G* and MP2/6-31+G* levels of theory. In agreement with the variations observed in the crystal structures, the vibrational spectra of the $N(NO_2)_2^-$ anion are also strongly influenced by the counterions and the physical state. Whereas the ab initio calculations for the free $N(NO_2)_2^-$ ion indicate a minimum energy structure of C_2 symmetry, Raman polarization measurements on solutions of the $N(NO_2)_2^-$ anion suggest point group C_1 (i.e., no symmetry). This is attributed to the very small (<3 kcal/mol) N−NO_2 rotational barrier in $N(NO_2)_2^-$ which allows for easy deformation.

Introduction

The dinitramide anion is a highly energetic oxidizer of great interest for halogen-free, high-performance, solid propellants. It was first discovered in 1971 at the Zelinsky Institute in Russia,[1] but was kept a closely guarded secret until its independent rediscovery in the U.S.A. by Bottaro and coworkers in 1989.[2] Part of the earlier Russian work on dinitramide has been summarized in a recent series of papers,[1,3−8] while several papers dealing with theoretical calculations on $N(NO_2)_2^-$ have been published by American authors.[9−11]

Since vibrational spectroscopy is widely used for the identification of propellants, it was important to thoroughly characterize the $N(NO_2)_2^-$ anion. The only published experimental data which could be found in the literature was a very short paper[8] with a listing of frequencies for $KN(NO_2)_2$ and conclusions which significantly deviate from the results of the present study. In the previous theoretical studies, the geometry of $N(NO_2)_2^-$ was calculated at the RHF/6-31G**, MP2/6-31G**, MP2/6-311+G**,[9] and NLDF/GGA/DZVPP[11] levels of theory, but no vibrational frequencies were given. In this paper, the vibrational spectra of $NH_4N(NO_2)_2$ (which is by far the most important dinitramide salt), $KN(NO_2)_2$, and $CsN(NO_2)_2$ are given for both the solid state and solution state, and are compared to the spectra calculated at the HF/6-31G* and MP2/6-31+G* levels of theory.

Experimental Section

The infrared spectra were recorded between 4000 and 200 cm^{-1} on either a Perkin Elmer model 283 double-beam spectrometer or a Mattson Galaxy 5030 FTIR spectrometer. The samples were recorded in KBr, KCl, AgCl, or AgBr pellets. The Raman spectra were recorded on either a Cary model 83 or a Spex model 1403 spectrophotometer using the 488 nm exciting line of an Ar ion or the 647.1 nm line of a Kr ion laser, respectively. Pyrex melting point capillaries or 5 mm Pyrex NMR tubes were used as sample containers for the solids or solutions, respectively. The synthesis of the $NH_4N(NO_2)_2$ has been described previously.[12] The Cs^+ and K^+ dinitramides were prepared from the NH_4^+ salt in the following manner.

Synthesis of $CsN(NO_2)_2$. Cesium fluoride (18 g, 120 mmol) was suspended in 200 mL of dry CH_3CN and treated with $NH_4N(NO_2)_2$ (12.4 g, 100 mmol), and the solution was stirred in the dark under argon for 24 h. The resulting suspension was filtered through a 1 in. × 2 in. plug of silica gel, and all yellow effluent was eluted with CH_3CN. The effluent was concentrated and crystallized from a minimum quantity of hot CH_3CN, giving a first crop of 10 g (∼40% yield) of needles with a melting point of 81 °C. The yield and recovery were not optimized.

Synthesis of $KN(NO_2)_2$. Potassium hydroxide (6.6 g of 85+% purity) was dissolved in 100 mL of dry CH_3OH. Ammonium dinitramide (12.4 g, 100 mmol) was dissolved in another 100 mL aliquot of CH_3OH. The two solutions were combined, and the resulting crystalline precipitate (13 g, 90% yield) of $KN(NO_2)_2$ was collected by filtration.

Ab initio calculations were performed at the RHF and MP2 levels of theory using the standard 6-31G* and 6-31+G* basis sets, respectively, and the Gaussian 92 program.[13] Harmonic vibrational frequencies were computed for the minimum-energy structures and

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[▽] Dedicated to Prof. Alois Haas on the occasion of his 65th birthday.
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Table 1. Observed[a] and Calculated Geometries[b] for the $N(NO_2)_2^-$ Anion

	observed[b]				calculated		
	$NH_4N(NO_2)_2$	$KN(NO_2)_2$	$CsN(NO_2)_2$−I[c]	$CsN(NO_2)_2$−II[c]	HF/6-31G*	MP2/6-31+G*	NLDF/GGA/DZVPP[d]
N(1)−N(2)	1.376(1)	1.384(3)	1.377(8)	1.383(7)	1.3445	1.3778	1.407
N(1)−N(3)	1.359(1)	1.351(3)	1.360(8)	1.366(7)			1.402
N(2)−O(2A)	1.236(1)	1.227(3)	1.230(7)	1.219(7)	1.2029	1.2523	1.270
N(3)−O(3A)	1.252(1)	1.239(3)	1.232(7)	1.241(7)			1.269
N(2)−O(2B)	1.227(1)	1.227(3)	1.244(7)	1.246(7)	1.2075	1.2575	1.262
N(3)−O(3B)	1.223(1)	1.232(3)	1.235(7)	1.229(7)			1.259
N(2)−N(1)−N(3)	113.20(8)	114.0(2)	115.1(4)	115.3(5)	114.68	112.79	112.4
N(1)−N(2)−O(2A)	113.03(8)	112.1(2)	113.0(5)	112.8(5)	114.10	113.88	113.4
N(1)−N(3)−O(3A)	112.40(8)	113.0(2)	112.6(5)	112.7(5)			113.5
N(1)−N(2)−O(2B)	123.38(8)	124.0(2)	123.4(5)	124.0(5)	123.09	122.67	123.3
N(1)−N(3)−O(3B)	125.14(9)	125.8(2)	124.9(5)	125.9(5)			123.3
O(2A)−N(2)−O(2B)	123.35(9)	123.7(2)	123.1(6)	123.1(6)	122.51	123.14	123.0
O(3A)−N(3)−O(3B)	122.18(9)	121.1(2)	122.4(6)	121.4(5)			
			Torsion Angles				
N(3)−N(1)−N(2)−O(2A)	157.25(8)	162.2(2)	160.4(2)	171.4(5)	151.56	149.93	
N(2)−N(1)−N(3)−O(3A)	162.19(8)	163.9(2)	167.7(5)	168.0(5)	151.56	149.93	
N(3)−N(1)−N(2)−O(2B)	−28.3(1)	−22.6(3)	−26.9(8)	−12.9(8)	−22.27	−23.82	−26.0
N(2)−N(1)−N(3)−O(3B)	−23.7(1)	−19.9(3)	−16.3(8)	−14.4(8)	−22.27	−23.82	−27.8
			Twist and Bend Angles				
N(2) nitro group	25.5 5.1	20.2 4.4	23.3 6.6	10.7 4.0			
N(3) nitro group	20.8 5.3	18.0 3.3	14.3 3.6	13.2 2.1			

[a] Data from ref 14. [b] Bond lengths in Å; angles in deg; twist angles were calculated from the two torsion angles of the NO_2 groups out of the N_3 plane and, if required, subtracting 180° from the torsion angle to bring its value below 90°, and then averaging these two values; the bend angle reflects the degree of pyramidalization of the nitro N atom whereby a zero degree angle represents a planar $N-NO_2$ group. [c] The $CsN(NO_2)_2$ salt contains two different ion pairs. [d] Data from ref 11.

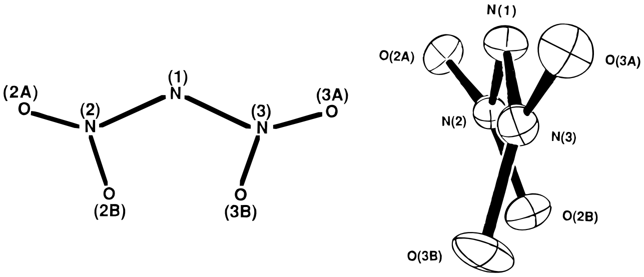

Figure 1. Two views of the dinitramide anion showing the labeling of the atoms and the twist of the NO_2 groups.

scaled by empirical factors to maximize their fit with the experimentally observed frequencies.

Results and Discussion

The experimentally observed[14] and calculated geometries of the dinitramide anion are summarized in Table 1. For comparison, the results of a previous calculation[11] using density functional theory are also given. The labeling scheme used in Table 1 is depicted in Figure 1, together with a view of an actual $N(NO_2)_2^-$ unit, as observed in the crystal structure of $NH_4^+N(NO_2)_2^-$.[14] This figure and the data in Table 1 demonstrate that in the minimum-energy structure of $N(NO_2)_2^-$ the two NO_2 groups are not in the same plane as the N_3 part of the anion but rotated out of this plane by a certain angle to minimize the mutual repulsions between O(2B) and O(3B) and between the two sterically active, free valence electron pairs on the central nitrogen atom N(1) and the electrons of the N(2)−O(2A) and N(3)−O(3A) groups. For the calculated minimum-energy structures, these rotation or twist angles range from 22 to 28°, but it must be kept in mind that the calculated energy differences between these structures and those with either coplanar or perpendicular NO_2 groups are very small and that the rotational barriers are less than 3 kcal/mol.[9] As a consequence of these small energy differences, the torsional angles observed in the crystal structures of different $N(NO_2)_2^-$ salts can vary by as much as 30° [14] due to crystal packing effects and interactions with counterions. A further complication is the slight nonplanarity of the $N-NO_2$ groups. In this paper, the term "bend angle" will be used to describe the degree of pyramidalization of the nitro N atom. Although the minimum-energy structures calculated at the HF/6-31G* and MP2/6-31+G* levels of theory possess C_2 symmetry, one must keep in mind that the 2-fold symmetry can easily be destroyed by small effects such as those encountered in the solid state, in solution, or by ion pairing.

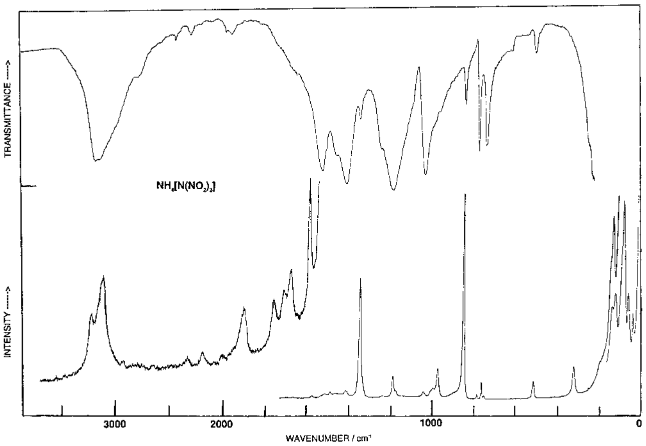

Figure 2. Vibrational spectra of solid $NH_4N(NO_2)_2$. The infrared spectrum was recorded for a KCl pellet. The Raman spectrum was recorded at three different sensitivity levels. The lattice modes were recorded at one-fifth of the sensitivity and the high-frequency range at 50 times the sensitivity of the mid-frequency range, respectively.

The observed vibrational spectra of solid $NH_4N(NO_2)_2$, $KN(NO_2)_2$, and $CsN(NO_2)_2$ and of the $N(NO_2)_2^-$ ion in aqueous solution are shown in Figures 2−5. The observed frequencies are summarized in Table 2 and are assigned by comparison with

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Table 2. Calculated and Observed Vibrational Spectra of the $N(NO_2)_2^-$ Anion in Different Salts and Solutions and Their Assignments in Point Group C_2

				observed freq (intens)								
				$KN(NO_2)_2$								
				Ra				$NH_4N(NO_2)_2$[e]			$CsN(NO_2)_2$[f]	
		calculated freq (IR intens) [Ra intens, depol]			solution		IR	Ra		IR	Ra	IR
assignt	approx mode description	HF/6-31G*[a]	MP2/6-31+G*[b]	solid	H_2O	CH_3CN	solid	solid	solution H_2O	solid	solid	solid
A ν_1	ν as NO_2 in phase	1547 (727) [0.05, 0.36]	1620 (337)	1582 (0+) 1525 sh 1516 (1.0) 1505 sh	1530 (0.6, 0.53)	1520 (0.5, pol)	1537 s	1570 (0.2) 1510 (0.2) 1480 (0.2)	1525 (0.5, 0.53)	1526 s	1571 (0.1) 1528 (0.5) 1509 (0.4) 1488 (0.1)	1515 vs
ν_2	ν s NO_2 in phase	1379 (75) [10.0, 0.15]	1350 (45)	1342 (8.0) 1320 (0+)	1335 (8.0, 0.15)	1334 (8.0, pol)	1343 m	1338 (6.0)	1335 (7.1, 0.15)	1344 w	1336 sh 1332 (9.7) 1308 sh	13336 sh 1332 mw 1308 vw
ν_3	ν s N_3	940 (1) [1.3, 0.22]	940 (1)	985 (0.1) 959 (0.7) 932 (0.1)	962 (2.1, 0.04)	962 (1.7, pol)	981 w 953 mw 931 w	978 (0.4) 955 (1.5)	959 (1.3, 0.04)	954 sh	968 (1.4) 952 (0.8) 945 sh	955 mw
ν_4	δ sciss NO_2 in phase	831 (9) [0.8, 0.19]	828 (6)	832 (10)	832 (10, 0.23)	828 (10, pol)	829 mw	832 (10)	830 (10, 0.22)	828 mw	827 (10)	825 mw
ν_5	δ rock NO_2 in phase	731 (13) [0.5, 0.52]	733 (0)	750 (1.8)	759 (0.5, 0.35)	*d*	750 w	742 (0.9)	756 (0.4, 0.35)	738 vw	740 (0.9)	740 mw
ν_6	δ wag NO_2 in phase	464 (0) [0.3, 0.40]	479 (0)	490 (1.6) 472 (0.3)	483 (1.3, 0.23)	470 (0.9, pol)	492 w 471 mw	492 (0.9)	482 (1.0, 0.23)	490 w	480 (1.5) 473 sh 460 (0+)	483 vw 475 vw 463 w
ν_7	δ sciss N_3	274 (0) [0.2, 0.21]	275 (0)	307 (1.8)	301 (2.7, 0.19)	289 (1.5, pol)		295 (1.6)	301 (2.0, 0.19)		298 (1.5) 290 (2.1)	
ν_8	τ NO_2 in phase	81 (1) [0.5, 0.74]	97 (1)	*c*								
B ν_9	ν as NO_2 out of phase	1468 (514) [0.003, 0.75]	1580 (257)	1451 sh 1440 (0.5)	1445 (0.5, 0.75)	1446 (0.5, dp)	1430 ms	1455 (0.1) 1430 (0+)	1435 (0.4, 0.75)	1455 sh	1451 (1.7)	1446 s
ν_{10}	ν s NO_2 out of phase	1253 (1081) [1.7, 0.75]	1218 (1311)	1220 (0+) 1201 (0.7) 1166 (1.1)	1200 (0.6, 0.60)	1195 (0.4, ?)	1224 sh 1204 vs 1178 vs	1220 (0.1) 1175 (1.1) 1159 (0.3)	1190 (0.3, 0.50)	1238 sh 1181 vs	1201 (0.1) 1168 (2.0)	1226 sh 1195 vs 1167 mw
ν_{11}	ν as N_3	1059 (218) [1.1, 0.75]	1035 (207)	1032 (0.4) 1016 (1.4)	1044 (1.8, 0.20)	1035 (1.6, pol)	1032 s 1024 s	1022 (0.3)	1044 (1.3, 0.20)	1025 s	1004 (0.2)	1017 s 1005 sh
ν_{12}	δ sciss NO_2 out of phase	767 (114) [0.6, 0.75]	747 (60)	761 (0.5)	759 (0.5, 0.35)	*d*	763 m	762 (0.2)	756 (0.4, 0.35)	761 m	754 (1.1)	759 m
ν_{13}	δ rock NO_2 out of phase	720 (18) [0.1, 0.75]	716 (38)	735 (0.1)			732 m	727 (0.1)		727 m 722 m	725 (0.1)	728 mw
ν_{14}	δ wag NO_2 out of phase	481 (1) [0.2, 0.75]	503 (1)	490 (1.6) 472 (0.3)	483 (1.3, 0.23)	470 (0.9, pol)	492 w 471 mw	492 (0.9)	482 (1.0, 0.23)	490 w	480 (1.5) 473 sh 460 (0+)	483 vw 475 vw 463 w
ν_{15}	τ NO_2 out of phase	97 (14) [0.01, 0.75]	97 (24)	*c*								

[a] All modes were scaled by an empirical factor of 0.8537 to optimize the agreement with the observed frequencies. [b] Stretching mode scaled by an empirical factor of 0.96 to optimize the agreement with the observed frequencies. [c] In the region of ν_8 and ν_{15}, the following Raman bands were observed: 50 (13.5), 60 (3.0), 87 (20), 102 (0.5), 115 (1.5), 142 (4), 163 (0.2). These bands are attributed to lattice vibrations since they were not observed for the solution spectra. [d] Obscured by CH_3CN band. [e] In addition to the bands listed in this table, the following bands were observed: Ra (solid) 3270 (0.05) ν_3 NH_4^+, 3160 (0.1) ν_1 NH_4^+, 1890 (0.05), 1745 (0.04), 1695 (0.03), 1661 (0.05), 1406 (0.2) ν_4 NH_4^+; lattice vibrations at 127 (8), 104 (12), 69 (27.5), 53 (9.5), 34 (5.5); IR (solid) 3255 vs ν_3 NH_4^+, 1407s ν_4 NH_4^+. [f] In addition to the bands listed in this table, the following bands were observed: combination bands in the IR 2924 vw, 2850 vw, 2775 vvw, 2675 vvw, 2610 vw, 2497 vw, 2334 vw, 1977 w; lattice vibrations in the Ra 123 w, 94 m.

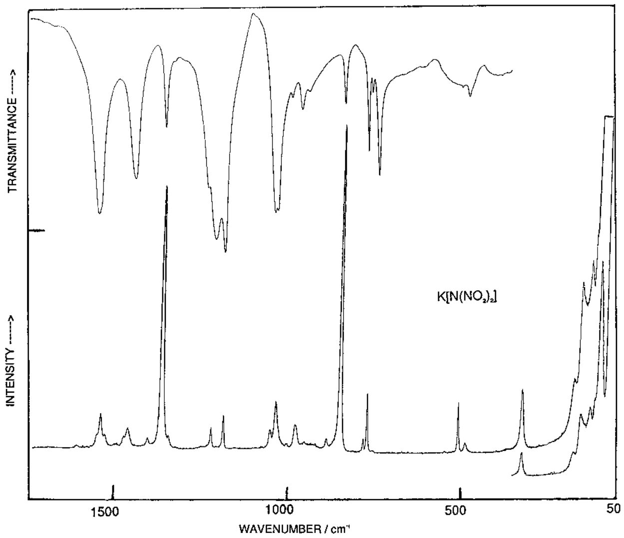

Figure 3. Vibrational spectra of solid $KN(NO_2)_2$.

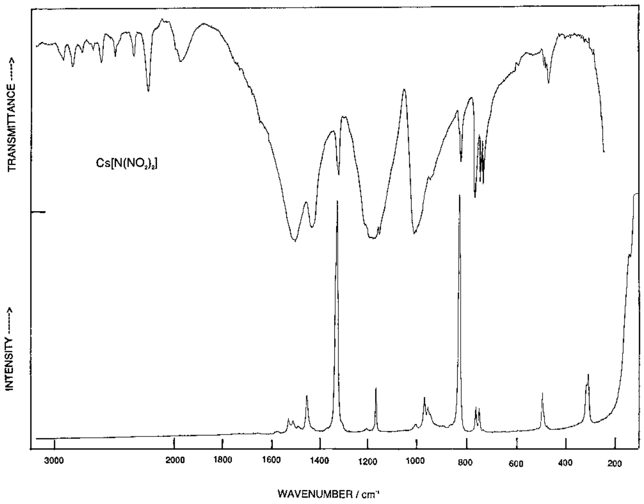

Figure 4. Vibrational spectra of solid $CsN(NO_2)_2$.

the calculated spectra. Although in the solid state and also in solution the 2-fold symmetry axis of $N(NO_2)_2^-$ is destroyed, the assignments were made in C_2 symmetry to allow a better comparison with the calculated spectra. The fact that the C_2 axis of $N(NO_2)_2^-$ is destroyed even in solution is somewhat surprising but well supported by the polarization data which show only one depolarized band for the seven vibrations which would belong to the B species. In the solid state, many fundamental vibrations show splittings. This is not surprising on the basis of the known crystal structures (see Table 1) which exhibit slight distortions and asymmetry of the NO_2 groups and unit cells containing more than one molecule or, as in the case of the Cs^+ salt, containing two nonequivalent $N(NO_2)_2^-$ ions.[14] The low energy barrier toward rotation of the NO_2 groups is also reflected by the low frequency values of about 90 cm^{-1} for the two NO_2 torsion modes.

An interesting observation was made for the infrared spectra of $NH_4N(NO_2)_2$ in KBr pellets. In some cases the spectra showed variations and in two cases were identical to those observed for $KN(NO_2)_2$, indicating an ion exchange in the KBr matrix during the pressing operation. For KCl or AgCl pellets, no similar effects were observed.

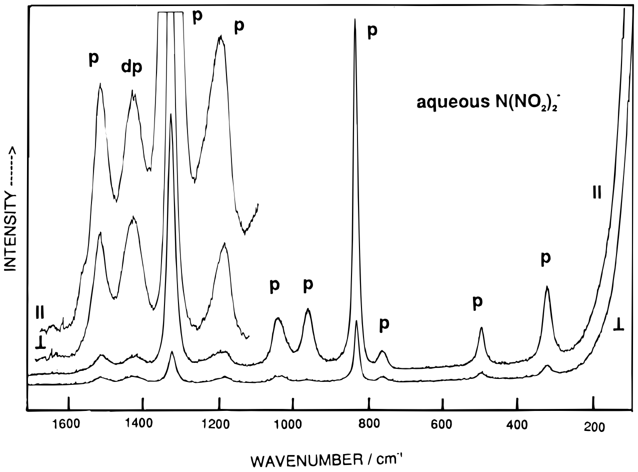

Figure 5. Raman spectrum of an aqueous solution of $NH_4N(NO_2)_2$ at two different sensitivity levels, where p, dp, ||, and ⊥ stand for polarized, depolarized, parallel, and perpendicular, respectively.

The overall agreement between the observed and calculated frequencies and intensities is very good and accurately supports the given assignments. As expected from the variations in the crystal structures, the vibrational spectra of the solid $N(NO_2)_2^-$ salts also differ significantly for different salts but are identical for their solutions. For the solution spectra, no detectable changes were observed for different concentrations, suggesting that ion pairing is not significant.

A comparison of the results from this study with those given previously[8] for $KN(NO_2)_2$ in a short paper show significant discrepancies. Raman bands at 583 cm^{-1} in the aqueous solution and at 640 and 204 cm^{-1} in the solid state were not observed in this study and, therefore, do not belong to the sample. The previous polarization data given for the 1520 and 1436 cm^{-1} bands are reversed. The 1520 cm^{-1} band should be polarized, and the one at 1436 cm^{-1} should be depolarized. Numerous Raman frequencies, relative intensities, and polarization ratios are also in poor agreement with the present data, while the agreement of the corresponding infrared data is better. Also, the previous conclusion that $N(NO_2)_2^-$ in solution has C symmetry is ambiguous because no subscript was given. Furthermore, without stating which two structures were being considered, the previous study preferred an incorrect planar structure. Finally, no data were given on other salts and no assignments were proposed.

Conclusions

The vibrational spectra of the $N(NO_2)_2^-$ anion have been recorded for three different salts and firmly assigned by comparison with computed spectra. The $N(NO_2)_2^-$ anion is easily deformed from the ideal C_2 symmetry causing significant changes in the spectra from salt to salt and in different physical states. It is shown that, even in solution, the $N(NO_2)_2^-$ anion has no symmetry (i.e., belongs to point group C_1). Evidence for ion exchange between $NH_4^+N(NO_2)_2^-$ and K^+Br^- during pellet pressing has been observed and can result in bands due to $KN(NO_2)_2$.

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