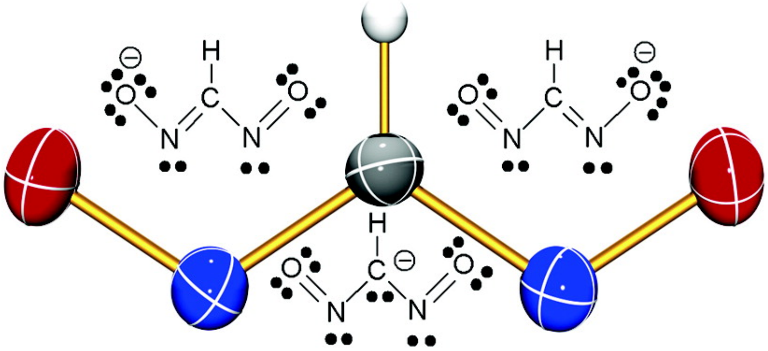
Communication

Blue Alkali Dinitrosomethanides: Synthesis, Structure, and Bonding

Harald Brand, Peter Mayer, Kurt Polborn, Axel Schulz, and Jan J. Weigand

J. Am. Chem. Soc., **2005**, 127 (5), 1360-1361• DOI: 10.1021/ja042877u • Publication Date (Web): 14 January 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Blue Alkali Dinitrosomethanides: Synthesis, Structure, and Bonding

Harald Brand, Peter Mayer, Kurt Polborn, Axel Schulz,* and Jan J. Weigand

Department Chemie und Pharmazie, Ludwig-Maximilians-Universität München,
Butenandtstrasse 5-13 (Haus F), 81377 München, Germany

Received November 25, 2004; E-mail: axel.schulz@cup.uni-muenchen.de

In a series of papers almost a century ago, Wieland described the synthesis of alkali and silver nitrosolates ($M[RC(NO)_2]$, M = metal, R = organic substituent).[1] These nitrosolates can be obtained from unstable *N*,*N*′-dihydroxyamidines by disproportion in ammonia or by oxidation (KIO_4) in basic solution.[1−3] For R = H, these procedures result in the formation of, e.g., potassium dinitrosomethanide when potassium hydroxide is used as a base.[1d,2b]

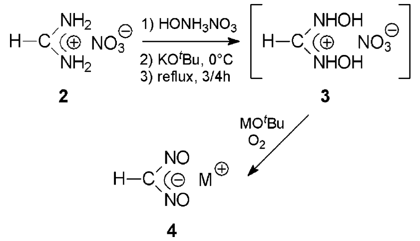
Recently, NO-releasing compounds such as alkali diazeniumdiolates ($[RNH(N(O)NO)]^-$)[4] or methantris(diazene-*N*-oxide-N′-hydroxylates) ($[HC(N(O)NO)_3]^{3-}$)[5] have gained considerable interest due to the discovered biological relevance of nitric oxide.[6] Besides, salts of nitrosodicyanomethanide, $[(ON)C(CN)_2]^-$, and nitrodicyanomethanide, $[(O_2N)C(CN)_2]^-$, are attractive target molecules as propellants on the basis of their theoretically predicted similarity to nitrite and nitrate salts, respectively.[7]

Here we report (i) a new, high-yielding synthetic procedure and for the first time an experimental characterization of potassium dinitrosomethanide (**1**) (IR, Raman, ^1H, ^{13}C, ^{14}N NMR, FAB$^-$ MS, X-ray), (ii) the synthesis and characterization of a number of new highly explosive alkali dinitrosomethanides ($M[HC(NO)_2]$, M = Li, Na, K(18-crown-6), Cs)[8] combined with DFT calculations of the anion, and (iii) the thermal decomposition properties (DSC).

Our two-step synthesis of DNM salts (DNM = dinitrosomethanide) starts from formamidinium nitrate (**2**), which represents an easily accessible source for an NC(H)N unit. Treating a methanolic solution of **2** and hydroxylammonium nitrate (2 equiv) with a methanolic solution of KO^tBu (2 equiv) results in the formation of the labile intermediate *N*,*N*′-dihydroxyformamidinium nitrate (**3**) (Scheme 1). The reaction of **3** with MO^tBu (2 equiv) in the presence of oxygen yields the deep blue alkali DNM salt (**4**), which can easily be purified by recrystallization from methanol (yield 60−70%).

Pure dry alkali DNM salts are stable at ambient temperature, are heat and shock sensitive, and decompose slowly in polar solvents, releasing N_2O gas (detected by ^{14}N NMR experiments).[8a,b] Small amounts of impurities (e.g., KNO_3) considerably decrease the shock and heat sensitivity. It is interesting to note that we were able to detect the DNM anion in a FAB$^-$ mass spectrometry experiment that was carried out with crystals of **1**. To determine the explosion gases of **1**, combined IR and MS pyrolysis experiments were carried out. The only gaseous products observed were N_2O, NO, and HCN. Differential scanning calorimetry experiments of **1** (Table S1, Figure S1, Supporting Information) revealed that **1** undergoes an exothermic decomposition (explosion, $\Delta H = -55.8$ kcal/mol) with an onset of 168.56 °C ($\beta = 5$ °C/min) in a temperature range of 168−186 °C and an estimated activation energy of ca. 48 kcal/mol.[9] It is assumed that the presence of a delocalized π-system probably accounts for the remarkable kinetic stability of **1** (see below). Compared to **1**, nitro- and nitrosodicyanomethanide salts possess a higher thermal stability (Table S1).[7,9c]

Scheme 1



Especially Raman and IR spectroscopy are suitable for identifying DNM salts very fast with the help of the in-phase and out-of-phase NO stretching mode at roughly 1400 and 1390 cm^{-1}, respectively (for approximate assignment of all normal modes on the basis of DFT calculation, see Tables S6−S8, Supporting Information); the C−H stretch can be observed at ca. 3000 cm^{-1}. The ^{13}C and ^1H NMR spectra show a singlet resonance at 190 and 8.7 ppm, respectively. The ^{14}N NMR spectrum displays a resonance at 332 ppm, which is the typical range of NO compounds (cf. $K[(ON)C(CN)_2]$: 381 ppm).[10] Raman and NMR data already indicated the presence of a C−H connectivity. This conclusion was confirmed for the solid state by X-ray structure determination (Figure 1).

1 crystallizes in beautiful Prussian blue octahedrons in the tetragonal space group $I\bar{4}2d$ with eight units per cell. The structure consists of an infinite three-dimensional network of repeating $K[HC(NO)_2]$ units. The crystallographic asymmetric unit contains a potassium atom coordinated to a H−C−N−O unit. Each anion is bonded to seven potassium cations and vice versa (Figure 1). The oxygen atom is coordinated to three potassium centers with K−O bond distances of 2.803(1), 2.849(1), and 2.887(2) Å. The nitrogen atom is coordinated to two neighboring potassium centers with K−N bond distances of 3.070(2) and 3.148(2) Å. Three types of coordination modes are found: (i) monodentate via the O atom, (ii) bidentate via NO, and (iii) bidentate via the two N atoms (N,N′ coordination of the NCN unit). As shown in Figure 1, each potassium center is surrounded by four nitrogen and six oxygen atoms. The bonding interaction of the anion with seven neighboring potassium centers leads to the three-dimensional network arrangement of the ions. Changing the coordination environment on potassium by introducing a crown ether (18-crown-6) leads to observation of linear chains of repeating $K(18\text{-crown-}6)[HC(NO)_2]$ (**5**) units in the solid state instead of the three-dimensional network (Figure 2). The cesium salt crystallizes in the monoclinic space group $P2_1/c$ and also exhibits a three-dimensional network arrangement. In contrast to **1**, the asymmetric unit contains a $Cs[HC(NO)_2]$ (**6**) unit. The anion is also bonded to seven Cs ions, whereas the cesium is surrounded by 13 atoms (5•NO, 2•N, and 1•O atom) as confirmed by MAPLE (Madelung Part of Lattice Energy) calculations (Figures S2−S3, Supporting Information).[11]

As depicted in Figure 1, the DNM anion is planar like all NO-, NO_2-, and CN-substituted methanide anions.[7] In principle, three

10.1021/ja042877u CCC: $30.25 © 2005 American Chemical Society

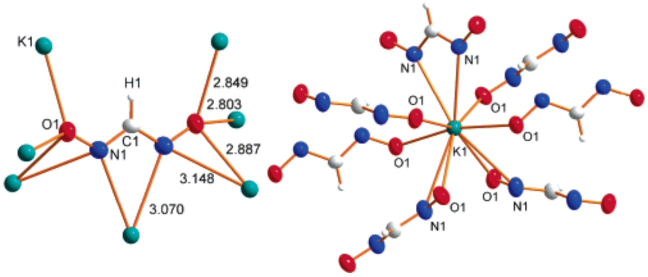


Figure 1. Left: View of DNM coordination environment in **1**. Asymmetric unit is labeled. Right: View of potassium coordination environment; bond lengths in (Å) N−O 1.264(2), C−N 1.321(2); bond angles (deg) O−N−C 116.9 (2), N−C−N 115.4(2), O−N−C−N 180.0.

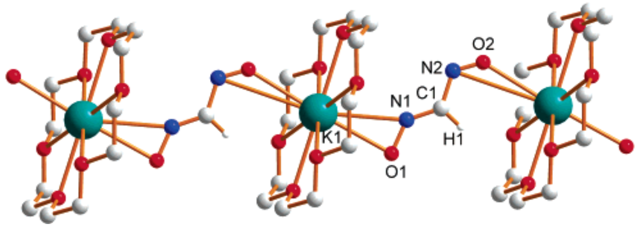


Figure 2. View of the linear chains in **5**.

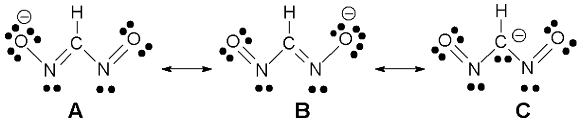


Figure 3. Lewis representation of DNM according to NBO analysis.

different planar structures of DNM are possible: (i) the anti/anti arrangement (as shown in Figure 1), (ii) the syn/anti arrangement, and (iii) the syn/syn arrangement (Figure S4, Supporting Information).[3b] In agreement with the experiment, B3LYP/6-311+G-(3df,2p) calculation revealed that the anti/anti form represents the most stable isomer followed by the syn/anti (+7.5 kcal/mol) and the syn/syn isomer (+13.1 kcal/mol). As expected, the N−O bond distances (**1**, 1.264(2); **6**, 1.277(3) and 1.268(3) Å) are significantly smaller than the C−N bond distances (**1**, 1.321(2); **6**, 1.333(4) and 1.338(4) Å), which is comparable to the situation found in the structure of the nitroso- and nitrodicyanomethanides.[7] These bond distances, together with the planarity, indicate the presence of delocalization of a double bond over the whole anionic species. MO and NBO calculation revealed the existence of a 6π-electron, 5-center bond unit (Figures 3 and S6 (Supporting Information)).[12]

In Figure 3, A and B represent the energetically preferred Lewis representations of DNM according to NBO analysis. Investigation of the intramolecular donor−acceptor interactions utilizing the NBO partitioning scheme clearly indicates a highly delocalized 6π-system according to resonance between Lewis representations A↔B↔C. The calculated natural atomic orbital population (NAO) net charges are $q(\mathrm{O}) = -0.524$, $q(\mathrm{N}) = -0.043$, $q(\mathrm{C}) = 0.008$, and $q(\mathrm{H}) = 0.126e$, which means that the negative charge is mainly found on both O atoms.

The UV−vis spectra of the purple methanolic solution of alkali DNM salts exhibit one very strong characteristic $\pi \rightarrow \pi^*$ and two weak $n \rightarrow \pi^*$ electronic transitions at ca. 331, 503, and 679 nm, respectively, which could be assigned on the basis of TD-B3LYP calculation (Figure S6, Tables S10 and S11, Supporting Information). The purple color arises from the two weak $n \rightarrow \pi^*$ electronic transitions.[3]

The DNM anion can be coined as a resonance-stabilized, nonlinear, planar pseudohalide[13] that forms an insoluble, highly explosive, brownish silver salt upon addition of silver nitrate to an aqueous solution of **1**.[1d] The DNM anion is related to the linear fulminate ion ($\mathrm{CNO^-}$)[14] and can formally be regarded as the addition product of $\mathrm{NO^-}$ to fulminic acid (HCNO). Starting from $\mathrm{CH_4}$, NO-containing nonlinear pseudohalides can be derived by successive substitution of H by NO, e.g., $\mathrm{H_3C(NO)/H_2C(NO)^-}$, $\mathrm{H_2C(NO)_2/HC(NO)_2^-}$, and $\mathrm{HC(NO)_3/C(NO)_3^-}$, whereas the linear pseudohalide $\mathrm{CNO^-}$ is formally formed by replacing three H atoms with one NO unit and deprotonation.

Caution: Like fulminates, $\mathrm{M^+DNM^-}$ salts (M = Na, K, Cs) are explosives and thermally unstable species; moreover, DNM salts are highly toxic, and appropriate safety precautions should be taken.

Acknowledgment. A.S. thanks Prof. Dr. T. M. Klapötke (LMU München) for his generous support and advice. We also wish to thank the Leibniz Rechenzentrum for a generous allocation of computer time. We are indebted to Prof. Dr. W. Beck for helpful advice and Dr. G. Fischer for measuring the mass spectra.

Supporting Information Available: Crystallographic data of **1**, **5**, and **6** (CIF files, Tables S2−S3, Figures S2−S3 (PDF)) and experimental (Tables S1−S3, Figure S1 (PDF)) and computational details (Tables S5−S11, Figures S4−S6 (PDF)). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Wieland, H. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 1445. (b) Wieland, H. Bauer, H. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 1480. (c) Wieland, H. *Liebigs Ann. Chem.* **1907**, *353*, 65. (d) Wieland, H.; Hess, H. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 4175−4191.

(2) (a) Armand, J.; Minvielle, R.-M. *C. R. Hebd. Seances Acad. Sci.* **1964**, *258*, 207. (b) Armand, J.; Minvielle, R.-M. *C. R. Hebd. Seances Acad. Sci.* **1965**, *260*, 2512−2515.

(3) (a) Vetter, G.; Klar, G. *Z. Naturforsch.* **1973**, *28b*, 287−292. (b) Vetter, G.; Kopf, J.; Klar, G. *Z. Naturforsch.* **1973**, *28b*, 293−299. (c) Olbrich, F.; Zimmer, B.; Kastner, M.; von Schlabrendorff, C.; Vetter, G.; Klar, G. *Z. Naturforsch.* **1992**, *47b*, 1571−1579.

(4) Saavedra, J. E.; Bohle, D. S.; Smith, K. N.; George, C.; Deschamps, J. R.; Parrish, D.; Ivanic, J.; Wang, Y.-N.; Citro, M. L.; Keefer, L. K. *J. Am. Chem. Soc.* **2004**, *126*, 12880−12887.

(5) Arulsamy, N.; Bohle, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 10860−10869.

(6) (a) Keefer, L. K. Annu. *Rev. Pharmacol. Toxicol.* **2003**, *43*, 585−607 and references therein. (b) Rehse, K.; Herpel, M.; Piechocki, D. *Arch. Pharm. Pharm. Med. Chem.* **1996**, *329*, 83−86. (c) Moncada, S.; Palmer, R. M.; Higgs, E. A. *Pharmacol. Rev.* **1991**, *43*, 109−142.

(7) Arulsamy, N.; Bohle, D. S.; Doletski, B. G. *Inorg. Chem.* **1999**, *38*, 2709−2715.

(8) (a) ^{13}C ([D6]DMSO, 101 MHz, 25 °C): $\delta = 190$ (s). ^{1}H ([D6]DMSO, 400 MHz, 25 °C): $\delta = 8.7$ (s). ^{14}N ([D6]DMSO, 28.9 MHz, 25 °C): $\delta = 332$ (s, $\Delta\nu^{1/2} = 346$ Hz); for experimental details, see Supporting Information. (b) The stability of alkali DNM salts decreases along Cs > K > Na > Li. The LiDNM is only stable in solution.

(9) (a) E_A was estimated by the method of Ozawa (48.05 kcal/mol). (b) Ozawa, T. Bull. *Chem. Soc. Jpn.* **1965**, *38*, 1881. (c) *ASTM Designation E698-99: Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials*; ASTM International: 1999.

(10) Witanowski, M.; Stefaniak, L.; Webb, G. A.. *Annu. Rep. NMR Spectrosc. (Nitrogen NMR Spectrosc.)* **1993**, *25*, 1−480.

(11) (a) Hoppe, R. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 25. (b) Hübenthal, R. *Program for the Calculation of Maple Values*, version 4; University of Giessen: Germany, 1993.

(12) (a) *NBO*, version 3.1; Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. (b) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41. (c) Weinhold, F.; Carpenter, J. E. *The Structure of Small Molecules and Ions*; Plenum Press: New York, 1988, p 227.

(13) Golub, A. M.; Köhler, H. *Chemie der Pseudohalogenide*; VEB Deutscher Verlag der Wissenschaften: Berlin, 1979.

(14) Beck, W. *Eur. J. Inorg. Chem.* **2003**, 4275−4288.

JA042877U