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Coordination Chemistry and Photoreactivity of the Dinitramide Ion

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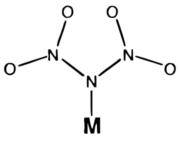
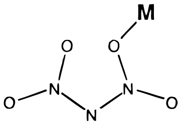
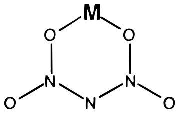
The dinitramide ion ($N_3O_4^-$) is a relatively new simple nitrogen oxyanion of theoretical[1] and practical interest.[2] Despite its potential as a non-chlorine containing, high energy density material, its chemistry is not well understood.[3] Such studies are of importance since possible environmental effects of $N_3O_4^-$ include its ability to act as a potent oxidant and/or nitrating agent.[4] From a published description of X-ray structural studies of several dinitramide salts,[5] it is apparent that $N_3O_4^-$ can act as a ligand to transition metals.[6] For example, three of the possible coordination modes to a single metal are depicted by structures **I**−**III** where only the skeletal atoms are shown, and M represents a transition metal complex fragment. It should be noted that structures **I** and **III** are similar to bonding modes known for the acetylacetonate ion. Prediction of the dominant bonding mode of $N_3O_4^-$ should be facilitated by knowledge of the site of protonation in dinitraminic acid (HN_3O_4); unfortunately this is the subject of debate with structures analogous to **I** and **III** being suggested.[1a,f,2b,d,h,3d]



I



II



III

Here we report the first demonstrated metal complex of $N_3O_4^-$, the first published X-ray structure of the coordinated ion, and an unusual example of an intramolecular photosensitized reaction of a coordinated ligand ($N_3O_4^-$) via a metal-to-ligand charge transfer excited state.

Reaction of KN_3O_4 with the reactive precursor *fac*-Re(bpy)-$(CO)_3OSO_2CF_3$ at room temperature in water gives a yellow microcrystalline solid which when recrystallized slowly from hexanes/CH_2Cl_2 gives thin yellow plates of *fac*-Re(bpy)-$(CO)_3N_3O_4$ in 75% yield.[7] The replacement of triflate by dinitramide is suggested by their relative acidity i.e., −14.6[8] versus −5.6,[1b] respectively.

The X-ray crystal structure[9a] (Figure 1) of *fac*-Re(bpy)-$(CO)_3N_3O_4$ clearly shows that coordination occurs at the central nitrogen of the dinitramide skeleton with the rest of the complex possessing the typical facial geometry exhibited by Re(bpy)-$(CO)_3X$ complexes. The Re−N bond lengths for the bpy ligand are 2.166(10) Å (Re(1)−N(4)) and 2.160(10) Å (Re(1)−N(5)). The Re−bpy bond lengths are typical of those in similar complexes of the type *fac*-Re(bpy)$(CO)_3X$ (for X = OSO_2CF_3[9c] and PO_2F_2[9d] bond lengths are between 2.140 and 2.150 Å). The Re−N_3O_4 (Re(1)−N(2)) bond length is considerably longer, 2.223(10) Å, consistent with its being a weaker donor than pyridine type ligands. A structurally interesting feature is the "tilting" of the planar nitro groups away from each other along the Re(1)−N(2) axis.

fac-Re(bpy)$(CO)_3N_3O_4$ is extremely photosensitive in solution. This is demonstrated in Figure 2 where changes in the UV−visible spectrum in CH_2Cl_2 (2.57×10^{-5} M) after irradiation (436 nm, 1000 W Hg lamp in a one cm cuvette) demonstrate the formation of a new product. Analysis[10] of the spectral changes (436 nm irradiation; monitoring the spectrum between 230 and 550 nm) is best approximated as an $A \rightarrow B \rightarrow C$ process (see inset in Figure 2). Preparative photolysis in CH_2Cl_2 allows the isolation and characterization of C, which is

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(1) (a) Politzer, P.; Seminario, J. M. *Chem. Phys. Lett.* **1993**, *216*, 348. (b) Brinck, T.; Murray, J. S.; Politzer, P. *J. Org. Chem.* **1991**, *56*, 5012. (c) Politzer, P.; Seminario, J. M.; Concha, M. C.; Redfern, P. C. *J. Mol. Struct. (THEOCHEM)* **1993**, *287*, 235. (d) Leroy, G.; Sana, M.; Wilante, C.; Peeters, D.; Dogimont, C. *J. Mol. Struct. (THEOCHEM)* **1987**, *153*, 249. (e) Leroy, G.; Sana, M.; Wilante, C.; Peeters, D. *J. Mol. Struct. (THEOCHEM)* **1989**, *187*, 251. (f) Redfern, P. C.; Politzer, P. Computational Analyses of Structural Properties of the Dinitramide Ion, $N(NO_2)_2^-$, and Related Molecules; Dinitramine and Trinitroamide. ONR Technical Report AD-A288 139; 1990. (g) Mebel, A. M.; Lin, M. C.; Morokuma, K.; Melius, C. F. *J. Phys. Chem.* **1995**, *99*, 6842.

(2) (a) Bottaro, J. C.; Penwell, P. E.; Schmitt, R. J. *Synth. Commun.* **1991**, *21*, 945. (b) Michels, H. H.; Montgomery, Jr., J. A. *J. Phys. Chem.* **1993**, *97*, 6602. (c) Doyle, R. J. *Org. Mass Spectrom.* **1993**, *28*, 83. (d) Schmitt, R. J.; Krempp, M.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 621. (e) Rossi, M. J.; Bottaro, J. C.; McMillen, D. F. *Int. J. Chem. Kinet.* **1993**, *25*, 549. (f) Pace, M. D. *J. Phys. Chem.* **1994**, *98*, 6251. (g) Pace, M. D. *Mater. Res. Soc. Symp. Proc.* **1993**, *296*, 53−60. (h) Shlyapochnikov, V. A.; Oleneva, G. I.; Cherskaya, N. O.; Lukyanov, O. A.; Gorelik, V. P.; Anikin, O. V.; Tartakovsky, V. A. *J. Mol. Struct.* **1995**, *348*, 103. (i) Brill, T. B.; Brush, P. J.; Patil, D. G. *Combust. Flame* **1993**, *92*, 7788. (j) Yao, D. C. C.; Su, M.; Mill, T. Photolysis Rates and Pathways for the Dinitramide Ion. Presented at the Joint USAF/Amy Contractor/Grantee Meeting on Subsurface Contaminant Fate and Transport, Jun 8, 1995, Boulder, CO. It should be noted that a minor amount of NO_2^- is also observed.

(3) There appears to be a large body of work on dinitramide and dinitraminous acid in the Russian chemical literature. We have only been able to retrieve part of this; some important references are as follows: (a) Lukyanov, O. A.; Anikin, O. V.; Gorelik, V. P.; Tartakovsky, V. A. *Russ. Chem. Bull.* (*Engl. Transl.*) **1994**, *43*, 1457. (b) Lukyanov, O. A.; Gorelik, V. P.; Tartakovsky, V. A. *Russ. Chem. Bull.* (*Engl. Transl.*) **1994**, *43*, 89. (c) Lukyanov, O. A.; Konnova, Yu. V.; Klimova, T. A.; Tartakovsky, V. A. *Russ. Chem. Bull.* (*Engl. Transl.*) **1994**, *43*, 1200. (d) Lukyanov, O. A.; Shlyapochnikov, V. A.; Cherskaya, N. O.; Gorelik, V. P.; Tartakovsky, V. A. *Russ. Chem. Bull.* (*Engl. Transl.*) **1994**, *43*, 1522. (e) Lukyanov, O. A.; Agevnin, A. R.; Leichenko, A. A.; Seregina, N. M.; Tartakovsky, V. A. *Russ. Chem. Bull.* (*Engl. Transl.*) **1995**, *44*, 108. (f) Lukyanov, O. A.; Shlykova, N. I.; Tartakovsky, V. A. *Russ. Chem. Bull.* (*Engl. Transl.*) **1994**, *43*, 1680. (g) Shlyapochnikov, V. A.; Oleneva, G. I.; Tartakovsky, V. A. *Russ. Chem. Bull.* (*Engl. Transl.*) **1995**, *44*, 1449.

(4) Trammell, S.; Sullivan, B. P. Unpublished results.

(5) Reported as a personal communication in ref 1c.

(6) Colberg, P. J. S.; Buttry, D. A.; Sullivan, B. P. Abiotic and Biotic Reactions of Quardracyclane and Dinitramide. Presented at the Joint USAF/Amy Contractor/Grantee Meeting Subsurface Contaminant Fate and Transport, Jun 8, 1995, Boulder, CO.

(7) Synthesis of *fac*-Re(bpy)$(CO)_3N_3O_4$. *Caution!* Dintramide derivatives are known to be shock sensitive and explosive.[3a] In 20 mL of deionized water, 0.1 mmol (57 mg) of Re(bpy)$(CO)_3OSO_2CF_3$ was heated to reflux until dissolved in a 100 mL round bottom flask. After the solution was allowed to cool to room temperature, 1.0 mmol (0.145 mg) of $KN(NO_2)_2$ was added and the solution was stirred overnight in the dark. A yellow microcrystalline solid was collected by vacuum filtration and washed with 3 × 15 mL of water and then allowed to air dry. Crystals were grown for X-ray diffraction and elemental analysis by slow diffusion of hexanes into a concentrated solution of product in CH_2Cl_2. Anal. Calcd for $ReC_{13}H_8N_5O_7$: C, 29.33; H, 1.51; N, 13.15. Found: C, 29.53; H, 1.59; N, 12.88. ^1H NMR (δ/ppm, $CDCl_3$): 9.15 (m, 2H), 8.18 (m, 4H), 7.62 (m, 2H). ^1H NMR (δ/ppm, CD_2Cl_2): 9.02 (m, 2H), 8.14 (m, 2H), 8.08 (m, 2H), 7.55 (m, 2H). UV−visible (λ (nm), CH_2Cl_2) (ϵ in M^{-1} cm^{-1}): 246 (19 100), 266 (16 650), 320 (10 700), 370 (3650). IR ($CHCl_3$) (ν (CO) cm^{-1}): 2036, 1940, 1924. IR (CH_2Cl_2) (ν(CO) cm^{-1}): 2036, 1934, 1925.

(8) Jorgensen, C. K. *Naturewissenschaften* **1980**, *67*, 189.

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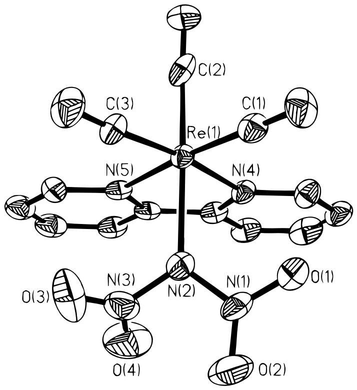


Figure 1. X-ray crystal structure of *fac*-Re(bpy)(CO)$_3$N$_3$O$_4$.

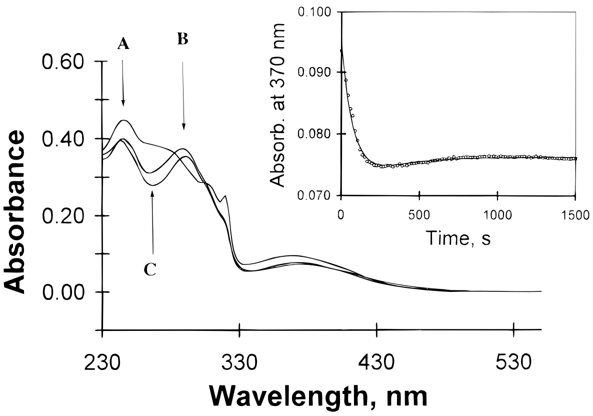
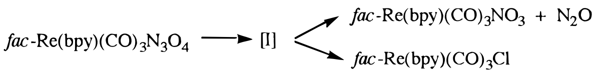


Figure 2. UV−visible spectra of (a) *fac*-Re(bpy)(CO)$_3$N$_3$O$_4$ (A), (b) the intermediate complex (B) formed during photolysis and, (c) *fac*-Re(bpy)(CO)$_3$NO$_3$ plus the minor product (C) (as determined by global analysis of the kinetic process; 2.57×10^{-5} M in CH$_2$Cl$_2$).

identified as the nitrato complex *fac*-Re(bpy)(CO)$_3$NO$_3$. We also observe a minor product which tentatively has been assigned as the chloro complex *fac*-Re(bpy)(CO)$_3$Cl. Independent verification of the nitrato complex is provided by the preparation of this new complex by reaction of *fac*-Re(bpy)(CO)$_3$OSO$_2$CF$_3$ with NaNO$_3$ in water.[11] The stoichiometry of the photolysis was determined by IR and NMR spectroscopic studies of the course of the reaction. After complete consumption of *fac*-Re(bpy)(CO)$_3$N$_3$O$_4$, the product distribution (with respect to the metal) is 90% *fac*-Re(bpy)(CO)$_3$NO$_3$. N$_2$O[12] is also produced, which is consistent with the reaction written in eq 1. The mechanism of formation of the minor product is not



$$\textit{fac}\text{-Re(bpy)(CO)}_3\text{N}_3\text{O}_4 \longrightarrow [\text{I}] \begin{cases} \nearrow \textit{fac}\text{-Re(bpy)(CO)}_3\text{NO}_3 + \text{N}_2\text{O} \\ \searrow \textit{fac}\text{-Re(bpy)(CO)}_3\text{Cl} \end{cases} \quad (1)$$

yet understood and the fate of NO$_3^-$ in the minor pathway has yet to be determined. N$_2$O and NO$_3^-$ have been identified as the dominate photochemical decomposition products of N$_3$O$_4^-$, in aqueous solution.[2j]

The photoreaction in eq 1 is extraordinary. Since irradiation at 436 nm predominantly populates Re(I) to bpy MLCT excited states to the exclusion of dinitramide states (ϕ_{366} = *0.061* for KN$_3$O$_4$ in water), it is apparently a rare example[13,16] of intramolecular chemistry photosensitized by a MLCT excited state. This is made more intriguing by the fact that the quantum yield (ϕ_{436}) is *0.67 ± 0.05*[14] (determined with the ferrioxalate actinometer in air saturated H$_2$O).[15] Our current studies are concentrated on further defining the coordination chemistry and photochemistry of this new ligand.[16]

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Supporting Information Available: For *fac*-Re(bpy)(CO)$_3$N$_3$O$_4$, tables of atomic coordinates and isotropic displacement coefficients (Table 1), bond lengths (Table 2), bond angles (Table 3), anisotropic displacement coefficients (Table 4), hydrogen coordinates and isotropic displacement coefficients (Table 5), crystallographic data collection parameters (Table 6), and solution and refinement parameters (Table 7) (7 pages). Ordering information is given on any current masthead page.

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(9) (a) Single-crystal X-ray data were collected at 23 °C using a yellow crystal of dimensions $0.45 \times 0.20 \times 0.02$ mm on a Siemens P3 diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1) = 0.709\,26$ Å; $\lambda(K\alpha_2) = 0.713\,54$ Å] and a graphite monochromator. The compound crystallized in the centrosymmetric triclinic space group $P\bar{1}$ with two molecules in a cell of dimensions $a = 8.035(2)$ Å, $b = 8.161(2)$ Å, $c = 12.365$ (2) Å, $\alpha = 97.36(3)°$, $\beta = 101.24(3)°$, $\gamma = 91.66(3)°$, and $V = 787.6(3)$ Å^3. A total of 3091 independent reflections were gathered ($R_{int} = 0.023$), the octants collected being $+h, \pm k, \pm l$, using the Wyckoff scan method. Three standard reflections were measured after every 100 reflections collected. The structure was solved by direct methods and refined by full-matrix least-squares techniques using structure solution programs from the SHELXTL system.[9b] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C−H = 0.96 Å) and refined with fixed isotropic thermal parameters. The structure has been refined to conventional R factor values of $R = 0.0478$ and $R_w = 0.0582$ on the basis of 2448 observed reflections with $F < 6\sigma(F)$ in the 2θ range 4−52° ($R = 0.0627$, $R_w = 0.0617$ for all data), giving a data to parameter ratio of 10.4:1. The maximum and minimum residual densities remaining were +2.91 and −3.06 e Å^{-3}, respectively, and located near Re(1). The data were corrected for absorption using semiempirical techniques. (b) Sheldrick, G. M.; *SHELXTL Crystallographic System*, Version 4.2/Iris; Siemens Analytical X-ray Insts. Inc., Madison, WI, 1991. (c) Calabrese, J. C.; Tam, T. *Chem. Phys. Lett.* **1987**, *133*, 244. (d) Horn, E.; Snow, M. R. *Aust. J. Chem.* **1980**, *33*, 2369.

(10) Data analysis was done using the Specfit package of Spectrum Associates, Chapel Hill, NC 27514.

(11) (a) Synthesis of *fac*-Re(bpy)(CO)$_3$NO$_3$. In 20 mL of deionized water, 0.26 mmol (147 mg) of Re(bpy)(CO)$_3$OSO$_2$CF$_3$ was heated to reflux until dissolved in a 100 mL round bottom flask. After the solution was allowed to cool to room temperature, 22.6 mmol (220 mg) of NaNO$_3$ was added and the solution was stirred for 15 min. A yellow microcrystalline solid was collected by vacuum filtration and washed with 200 mL of CH$_2$Cl$_2$. The complex is slighly soluble in CH$_2$Cl$_2$; 10 mg/100 mL. Anal. Calcd for ReC$_{13}$H$_8$N$_3$O$_6$: C, 31.97; H, 1.65; N, 8.6. Found: C, 32.00; H, 1.67; N, 8.58. ^{1}H NMR (δ/ppm, CD$_2$Cl$_2$): 9.02 (m, 2H), 8.17 (m, 2H), 8.09 (m, 2H), 7.54 (m, 2H). UV-visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 246 (16 100), 268 (13 700), 368 (3480). IR (CH$_2$Cl$_2$) (ν (CO) cm^{-1}): 2030, 1928, 1902. IR (ATR Cell) (ν (ONO$_2$) cm^{-1}):[17] 1476[11b] ν_5, 1280 ν_1, 1001 ν_2. (b) The exact band energy is somewhat uncertain because it overlaps a nearby bpy-ligand band.

(12) N$_2$O was confirmed as a photolysis product by its corresponding IR peak at 2222 cm^{-1} in both CH$_2$Cl$_2$ that was saturated with N$_2$O(g) and the photolysis (excitation at 436 nm) of *fac*-Re(bpy)(CO)$_3$N$_3$O$_4$ in CH$_2$Cl$_2$. N$_2$O(g) has an IR absorption at 2223.8 cm^{-1} ν_1.[17]

(13) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood Press: New York, 1991.

(14) The quantum yield (ϕ_{436}) of the photodecomposition of *fac*-Re(bpy)(CO)$_3$N$_3$O$_4$ in CH$_2$Cl$_2$ that has been deoxygenated with N$_2$ is *0.92 ± 0.05*.

(15) Rabek, J. F. *Experimental Methods in Photochemistry and Photophysics, Part 2*; John Wiley and Sons: New York, 1982; pp 937−946.

(16) Electrochemical studies of N$_3$O$_4^-$ in H$_2$O[6] show a series of reductive processes in the range of −0.3 to −0.82 V (vs Ag/AgCl) that give rise to *nitrite* but not nitrate. No oxidative processes are observed to the solvent limit (ca. +1.2 V). Given this, it is very unlikely that intramolecular reductive quenching can occur in the Re(I) complex with a significant rate. Thus, the mechanism could be intramolecular oxidative quenching that yields a coordinated but reduced N$_3$O$_4^-$ that fragments in a different fashion than direct electrochemical reduction at an electrode (back electron transfer would then be required to reduce Re(II) to Re(I) via a product of N$_3$O$_4^-$ decomposition). Alternatively, the mechanism could be energy transfer sensitization which gives the same state that is responsible for photodecomposition of free dinitramide ion.[2j]

(17) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; pp 112, 256.