

Energetic lanthanide complexes: coordination chemistry and explosives applications

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Abstract. Metals are generally added to organic molecular explosives in a heterogeneous composite to improve overall heat and energy release. In order to avoid creating a mixture that can vary in homogeneity, energetic organic molecules can be directly bonded to high molecular weight metals, forming a single metal complex with Angstrom-scale separation between the metal and the explosive. To probe the relationship between the structural properties of metal complexes and explosive performance, a new series of energetic lanthanide complexes has been prepared using energetic ligands such as NTO (5-nitro-2,4-dihydro-1,2,4-triazole-3-one). These are the first examples of lanthanide NTO complexes where no water is coordinated to the metal, demonstrating novel control of the coordination environment. The complexes have been characterized by X-ray crystallography, NMR and IR spectroscopies, photoluminescence, and sensitivity testing. The structural and energetic properties are discussed in the context of enhanced blast effects and detection. Cheetah calculations have been performed to fine-tune physical properties, creating a systematic method for producing explosives with ‘tailor made’ characteristics. These new complexes will be benchmarks for further study in the field of metalized high explosives.

1. Introduction

The role of metal powders as additives to organic energetic molecules has undergone a large amount of research: primarily for creating enhanced blast explosives and more recently for developing explosives that produce low collateral effects. Low collateral effects are typically developed by combining heavy inert metals with explosives like RDX in order to minimize damage in the surrounding area of an explosion. Explosives such as these are important in urban conflicts, where standard munitions would inflict unacceptable levels of extraneous damage and human casualties. Historically, the use of metals in organic explosives was accomplished by superficially mixing the two in a heterogeneous composite, often resulting in poor and unpredictable performance. To mitigate this problem, energetic organic molecules can be coordinated, i.e. directly bonded, to high molecular weight metals, forming a single molecule that contains the beneficial aspects of organic molecular explosives and metals. This approach eliminates the need to form heterogeneous mixtures, and allows for Angstrom-scale separation between metal atoms and oxidizing species.

One important challenge in metalized explosives is that the relationship between the structural properties of metal complexes and explosive performance has not been well studied. We have prepared and characterized a new series of energetic neodymium complexes, as many of the lanthanide salts are relatively heavy, non-toxic, air-stable, and inexpensive in comparison to heavy



metals like tungsten and tantalum. These complexes provide a starting point for future studies, where structural properties may be systematically adjusted in order to improve performance. The complexes are also discussed in the context of low collateral effects and explosives detection.

2. Experimental

Reagents were purchased from Aldrich and solvents from Fisher. UV-Visible spectra were obtained using a Hewlett-Packard 8453 diode array spectrophotometer. IR spectroscopy measurements were taken using a Thermo Nicolet NEXUS 670 FT-IR. Fluorescence measurements were carried out using an Continuum Panther OPO as the excitation source; the resulting fluorescence was dispersed onto a 0.25 m monochromator and detected by either an InGaAs photodiode array or an InP/InGaAs PMT. Elemental analyses, sensitivity testing, and differential scanning calorimetry were performed by the High Explosives Science and Technology Group at Los Alamos National Laboratory.

Neodymium NTO phenanthroline dimer $[Nd_2(NTO)_6(phen)_2]$. NTO (1.8 g, 13.8 mmol) and 1,10-phenanthroline•H₂O (0.914 g, 4.61 mmol) were suspended in a ~1:1 mixture of 400 mL ethanol:CH₃CN, and heated/stirred at ~60 °C until all dissolved. NaOH (1.70 M in H₂O, 8.1 mL) was added dropwise over the course of 15 minutes, followed by addition of a solution of NdCl₃ (1.66 g, 4.63 mmol) in 60 mL ethanol. The solution was stirred and heated at 70 – 80 °C for 30 min, and then reduced to dryness. CH₃CN was added, and the white insoluble solid (NaCl) was filtered off. The volume of the filtrate was then reduced at 60 – 70 °C until the solution became cloudy. A light green precipitate was collected on a Büchner funnel, and washed with CH₃CN and cold ethanol. The solid was dissolved in hot acetone, flash-frozen with N₂ (liq) and layered with diethyl ether. When the ratio of acetone to diethyl ether was greater than 1:1, crystals formed over the course of several days. When more diethyl ether was used, the product precipitated out as a powder. Drying *in vacuo* yielded 1.3 g of $[Nd_2(NTO)_6(phen)_2]$. The product is stable in air and a variety of solvents, and soluble in CH₃CN and acetone upon heating. ¹H NMR (acetone) δ : 3 – 4 broad peaks from 5 – 12 ppm. Elemental analysis, calculated for $[Nd_2(NTO)_6(phen)_2] \cdot 3[(CH_3)_2C=O]$: C, 33.83; H, 2.52; N, 24.55; analyzed: C, 34.30; H, 2.21; N, 24.45. Acetone is seen by NMR (CD₃CN) in both the crystals and the bulk samples, sharp and unshifted from the free position, even after > 24 h of drying under vacuum at 50 °C, or washing with CH₂Cl₂. When the final purification step involved CH₃CN, ether, or ethanol, these solvents also could not be removed under vacuum and appeared in the NMR (unshifted from the free positions), elemental analyses, and crystal structure. IR spectroscopy showed a broad NH peak at ~3100 cm⁻¹, and strong peaks at 1305 cm⁻¹ (NO₂ sym), 1512 cm⁻¹ (NO₂ asym), 1614 cm⁻¹ and 1648 cm⁻¹ (C=O), and 1414 cm⁻¹ (amide). UV-visible absorption (extinction coefficient) in acetone: 513 nm (6.2 M⁻¹ cm⁻¹), 525 nm (10 M⁻¹ cm⁻¹), 583 nm (29 M⁻¹ cm⁻¹), 746 nm (17 M⁻¹ cm⁻¹), 802 nm (24 M⁻¹ cm⁻¹), 865 nm (4.2 M⁻¹ cm⁻¹), 874 nm (5.9 M⁻¹ cm⁻¹).

Neodymium NTO diglyme $[Nd(NTO)_3(diglyme)]$. Following the related procedure above, NTO (1.0 g, 7.69 mmol) was dissolved in 80 mL of equal parts acetonitrile: ethanol at ~75 °C, and 7 mL of 0.963 M NaOH was added to the solution slowly. An excess of diglyme (5 mL) was added, followed by a solution of NdCl₃ (0.92 g, 2.56 mmol) in 10 mL ethanol. The solution was stirred for 30 min at ~75 °C. The solvent was reduced, and 80 mL of acetonitrile was added. A white powder was filtered off, and the volume of the filtrate was reduced until a yellow iridescent precipitate formed, which was collected and washed with acetonitrile (yielding 1.0 g). ¹H NMR (acetonitrile) δ : 3 – 4 broad peaks from 3 – 3.6 ppm. IR spectroscopy showed a broad NH peak at ~3200 cm⁻¹, and strong peaks at 1304 cm⁻¹ (NO₂ sym), 1502 cm⁻¹ (NO₂ asym), and 1613 cm⁻¹, 1634 cm⁻¹, and 1668 cm⁻¹ (C=O).

X-ray data for $[Nd_2(NTO)_6(phen)_2]$. The crystal was placed in Paratone-n oil and mounted in a cryoloop. The reflection data were collected on a Bruker Platform diffractometer with 1k CCD. The instrument was equipped with a sealed, graphite monochromatized MoK α X-ray source (λ = 0.71073 Å). A hemisphere of data was collected using θ scans, with 30 second frame exposures and 0.3° frame

widths. Data collection and initial indexing and cell refinement were handled using SMART software [1]. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT software [2]. The data were corrected for absorption using the SADABS program [3]. Decay of reflection intensity was monitored via analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom they were attached to. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Two disordered diethyl ether solvent molecules per unit cell were treated with PLATON SQUEEZE [4]. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL [5].

3. Results and Discussion

3.1 Preparation and characterization of neodymium complexes

The common energetic ligand, 5-nitro-2,4-dihydro-1,2,4-triazole-3-one (NTO) [6-9], has been shown to coordinate to transition metals [10,11] and some lanthanides [11,12]. NTO has two acidic sites ($pK_{a1} = 3.76$ and $pK_{a2} = 11.25$) [13], which make it a good candidate for metal coordination. Using a modification of a literature procedure [14] for non-energetic lanthanide complexes, a novel neodymium complex was prepared using in-situ deprotonated NTO, 1,10-phenanthroline, and $NdCl_3$ in ethanol:acetonitrile. The resulting lanthanide complex, $[Nd_2(NTO)_6(phen)_2]$, was purified by recrystallization in acetonitrile and acetone:diethyl ether (figure 1a), and characterized by NMR and IR spectroscopy (figure 1b) and elemental analysis. Light green crystals were grown and characterized by X-ray crystallography, showing a dimeric structure containing two Nd metal centers, with four bridging NTO groups and two terminal NTO and phenanthroline groups (figure 1c). To our knowledge, this is the first neodymium NTO complex that has been synthesized, and more importantly, the only example of any lanthanide NTO complex where no water is coordinated to the metal, demonstrating novel control of lanthanide NTO structures and properties. This complex will direct further study and modifications to adjust for density and energetic properties. The x-ray crystallography data are summarized in table 1. The calculated density of 1.613 g cm^{-3} is fairly low, and indicates that the large coordination environment of lanthanide complexes may preclude their use in low collateral effects explosives.

Table 1. Crystal data and structure refinement for xpl216s

Identification code	xpl216s
Empirical formula	$C_{20}H_{16}N_{14}NdO_{9.50}$
Formula weight	748.71
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P 2_1/c$
Unit cell dimensions	$a = 10.665(2) \text{ Å}$, $\alpha = 90^\circ$ $b = 19.292(4) \text{ Å}$, $\beta = 101.855(3)^\circ$ $c = 15.308(4) \text{ Å}$, $\gamma = 90^\circ$
Volume	$3082.2(12) \text{ Å}^3$
Z	4
Density (calculated)	1.613 Mg/m^3
Absorption coefficient	1.755 mm^{-1}
F(000)	1480
Crystal size	$0.20 \times 0.18 \times 0.18 \text{ mm}^3$
Theta range for data collection	1.72 to 28.88°
Index ranges	$-13 \leq h \leq 14$, $-24 \leq k \leq 25$, $-20 \leq l \leq 20$
Reflections collected	32693
Independent reflections	7593 [$R(\text{int}) = 0.0651$]
Completeness to theta = 25.00°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7430 and 0.7204
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7593 / 0 / 379
Goodness-of-fit on F^2	1.146
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0607$, $wR2 = 0.1410$
R indices (all data)	$R1 = 0.0849$, $wR2 = 0.1478$
Largest diff. peak and hole	1.644 and -2.413 Å^{-3}

3.2 Cheetah calculations

Cheetah 6.0 thermochemical code was used to guide modifications of $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$. Assuming that the density and energy release of $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$ can be approximated by the sum of its parts, NdCl_3 , 3 NTO, and phenanthroline, Cheetah estimates a density of 1.46 g cm^{-3} and calculated shock velocity of 4.5 km s^{-1} . Substituting diglyme for phenanthroline gives a density of 1.65 g cm^{-3} and calculated shock velocity of 5.7 km s^{-1} . Though the calculations are approximate, they show that diglyme may be substituted for phenanthroline in order to improve density and performance. To test this theory, $\text{Nd}(\text{NTO})_3(\text{diglyme})$ has been prepared in an analogous procedure as described for $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$.

3.3 Sensitivity and performance data

Differential Scanning Calorimetry (DSC) was performed under a flow of nitrogen gas for both $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$ and $\text{Nd}(\text{NTO})_3(\text{diglyme})$. For $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$, two peak exotherms are observed for the decomposition of the NTO at 221 and 251 °C: these peaks correspond to mass losses of 18 (NH_4 ; H_2O) and 44 (CO_2 ; N_2O), consistent with energetic materials. For $\text{Nd}(\text{NTO})_3(\text{diglyme})$, a peak exotherm is observed at 275 °C for NTO decomposition. The peak exotherms for the phenanthroline ligand in $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$ occur at 471 and 524 °C. For $\text{Nd}(\text{NTO})_3(\text{diglyme})$, one peak is observed at 619 °C, corresponding to the diglyme ligand. At these higher temperatures, the peak exotherms correspond to mass losses of 44, likely CO_2 . It is noteworthy that the dimeric compound appears to have double peaks for losses of each ligand, supporting the observation that the ligands have multiple coordination environments. Only single peaks are observed for $\text{Nd}(\text{NTO})_3(\text{diglyme})$. Table 2 gives sensitivity thresholds for impact, spark, and friction initiation for the compounds, compared to the standard pentaerythritol tetranitrate (PETN). The data show that both complexes are very insensitive to initiation. In fact, 4 g of pressed pellets of $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$ (at $\frac{1}{2}$ inch diameter, 1.385 g cm^{-3}) could not be initiated with a SE-1-31 detonator. This may in part be due to the small diameter of the pellets and the large critical diameter of NTO. The material appears to burn slowly, forming a low-density light blue solid. More work is needed to determine if $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$ will detonate at larger diameters, and to evaluate the performance of $\text{Nd}(\text{NTO})_3(\text{diglyme})$ and other derivatives.

3.4 Fluorescence data

The detection of explosives is an area of increasing importance to airport security and national security. Explosives taggants like 2,3-dimethyl-2,3-dinitrobutane (DMNB) are still difficult to detect using common techniques [15]. A promising future direction for this work is to develop energetic materials that fluoresce in order to avoid compatibility and lowered performance issues that can result from mixing an inert organic additive to an existing explosive. The f-elements undergo $4f - 4f$ transitions that decay slowly due

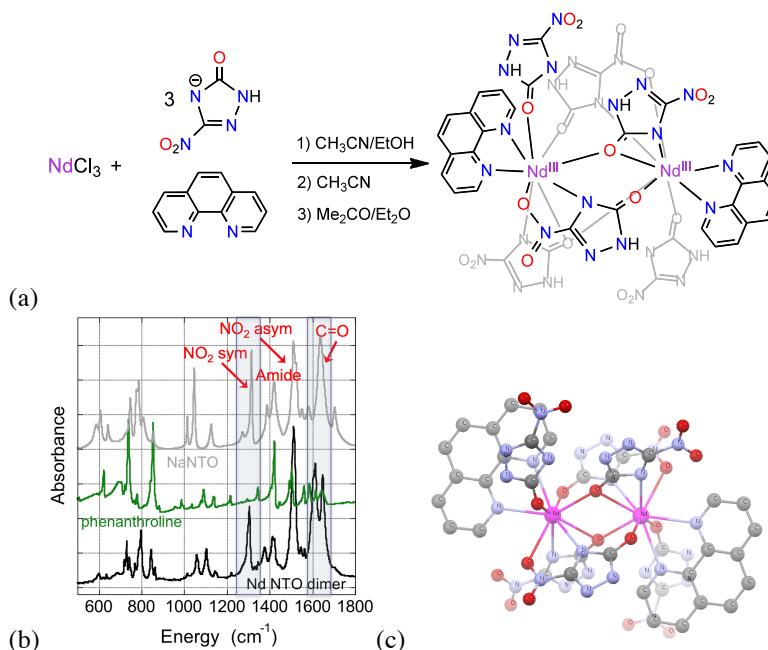


Figure 1. (a) Synthesis of a new neodymium NTO dimer. (b) Infrared spectroscopy of deprotonated NTO (NaNTO), 1,10-phenanthroline, and $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$. (c) X-ray crystal structure of $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$.

Table 2. Sensitivity of neodymium complexes.

Compound	ERL Type 12 Impact ^a	BAM Friction ^b	ABL Electrostatic Discharge ^c
Nd ₂ (NTO) ₆ (phen) ₂	> 320	> 360	0.125
Nd(NTO) ₃ (diglyme)	> 320	> 360	0.125
PETN	14.7	94	0.0625

^a 50% Height (cm). ^b 50% Load (N). ^c TIL (J).

to the fact that the $4f$ orbitals are contracted relative to the filled $5s^25p^6$ orbitals, resulting in metal-centered orbitals that have sharp absorption and luminescence bands [16-18]. Most of the lanthanides display these luminescent properties; in particular, neodymium emits in the near-IR region (1060 nm^{17}), which is useful for identification purposes because of the distinct region of the spectrum.

Fluorescence measurements were recorded from $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$ and $\text{Nd}(\text{NTO})_3(\text{diglyme})$ while pumping at $\sim 520\text{ nm}$ for both compounds at liquid N_2 and room temperatures. Figure 2a displays a time-resolved luminance waveform recorded from $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$ taken while monitoring the largest feature in the emission spectrum at $\sim 1063\text{ nm}$. Waveforms were fit to an empirical function containing one exponential term $I_t = A \cdot \exp(-t/\tau) + b$; where I_t is the intensity at time t , A is a prefactor, τ is the lifetime and b is a constant to account for the detector background. The lifetimes were $0.65\text{ }\mu\text{s}$ and $0.08\text{ }\mu\text{s}$ for $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$ and $\text{Nd}(\text{NTO})_3(\text{diglyme})$, respectively, at liquid N_2 temperature. Figure 2b displays emission spectra for $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$ (black) and $\text{Nd}(\text{NTO})_3(\text{diglyme})$ (red). The spectrum consists of three main bands which broadly correspond to Nd^{3+} atomic transitions from a common upper state, the $^4\text{F}_{3/2}$, to the $^4\text{I}_{9/2}$ ground state, $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ states centered at 887.5 , 1061 , 1346.5 nm respectively. Close inspection of figure 2b reveals that these bands are split into several smaller peaks which are spaced by approximately $20\text{--}100\text{ cm}^{-1}$. This splitting is due to the electronic field of the ligands referred to as Stark splitting and splits each spin-orbit component into $J+1/2$ Stark levels [19]. The Stark levels were resolved for each band and the value for J could be unambiguously assigned for the lower electronic state. Fluorescence lifetimes of $1\text{--}10\text{ }\mu\text{s}$ are possible with lanthanide complexes, provided that the ligands do not quench the fluorescence. The lifetime of the $[\text{Nd}(\text{NTO})_6(\text{phen})_2]$ dimer approaches $1\text{ }\mu\text{s}$, but it may be possible to increase the observed fluorescence by substituting NTO with an energetic diketone ligand [14,20,21].

4. Conclusions

A new series of neodymium NTO complexes has been prepared and characterized, and evaluated for their use in explosives detection and low-collateral effects. These new complexes are not appropriate for low collateral effects applications, due to their low density and insensitivity to initiation. However, they provide a framework for future studies with inorganic coordination compounds, where structural properties may be systematically adjusted in order to improve performance.

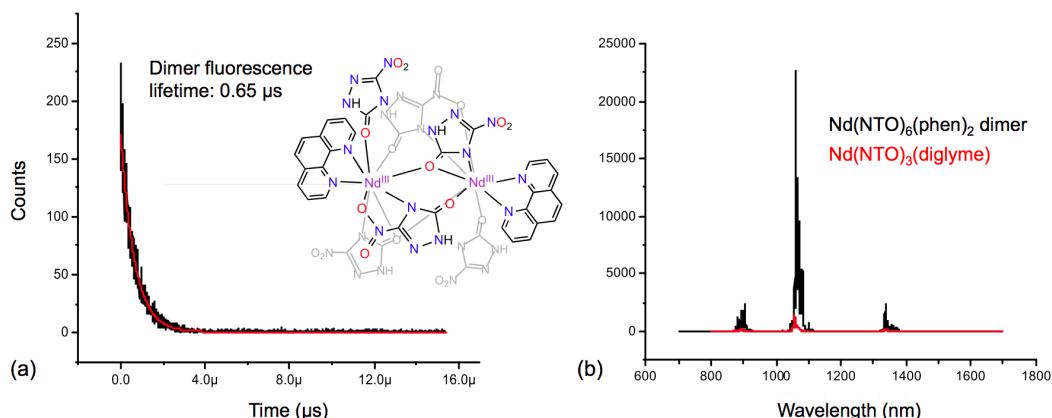


Figure 2. (a) Time-resolved waveform recorded while monitoring fluorescence from the $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$ dimer at $\sim 1063\text{ nm}$. Black trace is the experimental data and red trace is an empirical exponential function, see text for details. (b) Emission spectra for $[\text{Nd}_2(\text{NTO})_6(\text{phen})_2]$, black trace and $\text{Nd}(\text{NTO})_3(\text{diglyme})$, red trace.

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