Synthesis and Characterization of a Novel Energetic Complex [Cd(DAT)₆](NO₃)₂ (DAT = 1,5-diamino-tetrazole) with High Nitrogen Content

Jian-Guo Zhang,^{*[a]} Jing-Yu Li,^[a] Yan Zang,^[b] Yuan-Jie Shu,^[c] Tong-Lai Zhang,^[a] Li Yang,^[a] and Philip P. Power^[d]

Keywords: Nitrogen; Cadmium; 1,5-Diamino-tetrazole (DAT); Thermochemistry; Structure elucidation

Abstract. The novel high nitrogen-containing energetic complex $[Cd(DAT)_6](NO_3)_2$ was synthesized by reaction of $Cd(NO_3)_2$ ·6H₂O with 1,5-diamino-tetrazole (DAT). It was characterized by elemental analysis, FT-IR spectroscopy and single-crystal X-ray diffraction analysis. The central Cd^{2+} ion is coordinated by six nitrogen atoms from six DAT ligand molecules to form a hexacoordinate distorted octahedral compound. The $[Cd(DAT)_6](NO_3)_2$ molecules are linked together

through two types of hydrogen bonds thus forming a stable three-dimensional net structure. The thermal decomposition mechanism of $[Cd(DAT)_6](NO_3)_2$ was investigated by DSC and TG/DTG analyses and FT-IR spectroscopy. The kinetic parameters of the exothermic process were studied by using *Kissinger*'s and *Ozawa–Doyle*'s methods.

Introduction

In recent years, increased attention has been paid to multinitrogen heterocyclic compounds [1–3], which have been recognized as a class of useful and promising structures for the design and synthesis of high-energy density materials (HEDMs) [4–6]. A large number of heterocycle-based energetic compounds were reported and used as high explosives and ingredients of propellants. Azole heterocycle compounds have aroused great interests because of their advantages, such as high nitrogen content, high positive heat of formation, high density and easier to reach oxygen balance [7–9]. Because of their unique structures and properties, they might be useful as ligands in the preparation of energetic complexes [10–18].

1,5-Diamino-tetrazole (DAT) has a high nitrogen content, positive enthalpy of formation, and good thermal stability [19–22]. It has six nitrogen atoms in its molecular structure; five of them are able to bind to metal ions. It is a promising ligand that can combine with transition metals to form energetic coordination compounds [23, 24]. In recent years, DAT-based ener-

* Dr. J.-G. Zhang Fax: +86-10-68913818 E-Mail: zhangjianguobit@yahoo.com.cn

- [a] State Key Laboratory of Explosion Science and Technology Beijing Institute of Technology
 Description 100001 P. B. Ching
- Beijing 100081, P. R. China
 [b] Department of Arming Remanufacture Engineering Academy of Armored Forces Engineering Beijing 100072, P. R. China
- [c] Institute of Chemical Materials
- Chinese Academy of Engineering Physics Mianyang, Sichuan 621900, P. R. China [d] Department of Chemistry
- University of California, Davis One Shields Avenue Davis, CA 95616, USA

getic salts have aroused great interest [25–28], and some new complexes using DAT as ligand were also reported [23, 29–32]. In order to study a new series of DAT-based azole energetic coordination compounds, the novel energetic complex $[Cd(DAT)_6](NO_3)_2$ with high nitrogen content has been synthesized and characterized by elemental analysis, FT-IR spectroscopy and X-ray single crystal diffraction analysis. Additionally, the thermal decomposition mechanism and non-isothermal kinetics of $[Cd(DAT)_6](NO_3)_2$ were investigated by using DSC and TG/DTG analyses and FT-IR spectroscopy.

Results and Discussion

Synthesis of DAT and [Cd(DAT)₆](NO₃)₂

1,5-diamino-tetrazole (DAT) has been synthesized by reaction of diamino-guanidinium chloride and sodium nitrite with the concentrated hydrochloric acid as catalyst according to the reference method [33]. DAT is precipitated by adjustment of the pH value with Na_2CO_3 . The reaction route is shown in Scheme 1. We optimized the reaction conditions and obtained pure DAT in 72 % yield.



Scheme 1. Synthesis of 1,5-Diamino-tetrazole (DAT).

The reaction of stoichiometric amounts of $Cd(NO_3)_2 \cdot 6H_2O$ and DAT in aqueous solution afforded the title compound $[Cd(DAT)_6](NO_3)_2$ in 85 % yield. It is well soluble in water,



and slightly soluble in common organic solvents such as dichloromethane, tetrahydrofurane and toluene. After 20 days, colorless prism single crystals of the title compound suitable for X-ray analysis were obtained by slowly evaporating the saturated $[Cd(DAT)_6](NO_3)_2$ solution.

Crystal Structure Description of [Cd(DAT)₆](NO₃)₂

The molecular structure of $[Cd(DAT)_6](NO_3)_2$ is shown in Figure 1, and its packing diagrams viewed along the *a* and *c* axes are shown in Figure 2 and Figure 3, respectively. Single crystal X-ray analysis reveals that the central Cd^{2+} ion is coordinated to six nitrogen atoms from six DAT molecules, corresponding to N3, N3A, N3B, N3C, N3D, N3E (Figure 1). Notably, the Cd^{2+} ion has a hexacoordinate distorted octahedral structure, since it has peripheral d^{10} electron configuration and adopts sp³d² hybridization in theory. Because of its peripheral d^{10} electron configuration, it exhibits no d–d electronic transition and is a colorless.



Figure 1. Molecular structure of [Cd(DAT)₆](NO₃)₂.



Figure 2. Packing diagram of $[Cd(DAT)_6](NO_3)_2$, view along the *a* axis.

Selected bond lengths and angles are summarized in Table 1 and Table 2, respectively. All N–Cd bond lengths (Cd1–N3, Cd1–N3A, Cd1–N3B, Cd1–N3C, Cd1–N3D and Cd1–N3E) amount 2.368(4) Å. The atom N3D is perpendicular to the α plane formed by Cd1, N3A and N3C, the bond angles N3–Cd1–N3B and N3C–Cd1–N3D amount 90.81(13)°; The atom N3B is perpendicular to the β plane formed by Cd1, N3



Figure 3. Packing diagram of $[Cd(DAT)_6](NO_3)_2$, view along the *c* axis.

and N3E, the bond angles N3B-Cd1-N3E and N3-Cd1-N3E also amount 90.81(13)°. However, the atoms Cd1, N3, N3A, N3C and N3E are not coplanar, and the bond angle of N3B-Cd1–N3D amounts 168.56 (18)°. Thus, the α and β plane are not coplanar, and the angle between the two planes amounts 11.5°. It is obvious that the central Cd^{2+} ion can not be coplanar with the nitrogen atoms of its four surrounding DTA molecules, so the hexacoordinate configuration forms a distortion octahedral structure. The bond angles N3-Cd1-N3C, N3B-Cd1-N3D, and N3A-Cd1-N3E formed by the central Cd²⁺ ion connected to the opposite nitrogen atoms amount to 168.56(18)°. Because of the repulsive interaction among the six tetrazole rings, they are able to reach the most stable structure. The $[Cd(DAT)_6](NO_3)_2$ molecule is formed when DAT and Cd²⁺ form a coordinated cation, which combines with nitric acid through the force of electrovalence.

Table 1. Selected bond lengths for [Cd(DAT)₆](NO₃)₂.

Chemical bond	Bond length /Å	Chemical bond	Bond length /Å			
Cd1-N3#1	2.368(4)	N2-N3	1.335(6)			
Cd1-N3	2.368(4)	N3-N4	1.375(5)			
Cd1-N3#2	2.368(4)	N4-N5	1.285(6)			
Cd1-N3#3	2.368(4)	N5-C1	1.353(6)			
Cd1-N3#4	2.368(4)	N6-C1	1.389(6)			
Cd1-N3#5	2.368(4)	N6–H6A	0.898(10)			
N1-N2	1.330(6)	N6-H6B	0.898(10)			
N1-H1B	0.891(10)	O1-N7	1.233(6)			
N1-H(1A)	0.895(10)	N701#6	1.233(6)			
N2C1	1.331(6)	N701#7	1.233(6)			

Symmetry operations: #1: -x + 2, -x+y+1, -z + 1/2; #2: -x+y+2, -x + 1, z; #3: y + 1, x - 1, -z + 1/2; #4: x-y, -y, -z + 1/2; #5: -y + 1, x-y-1, z; #6: -x+y, -x + 1, z; #7: -y + 1, x-y+1, z.

Each DAT ligand in the $[Cd(DAT)_6](NO_3)_2$ molecule has well co-planarity. The DAT molecule is a five-membered ring formed by C1, N2, N3, N4, N5, the torsion angles amount: C1–N2–N3–N4, 0.8(5)°; N2–N3–N4–N5, -0.2(5)°; N3–N4–N5–C1, -0.4 (5)°; N3–N2–C1–N5, 1.0(5)°; N4–N5–C1–N2, 0.8 (5)°. The analysis shows that the five atoms of the tetrazole molecule are coplanar, with the plane equation -2.424x



Ta	ble	2.	Sel	lected	bond	angl	es	for	[Co	l(I)A	T))6]	$(\mathbb{N}$	AC) ₃)	12.
----	-----	----	-----	--------	------	------	----	-----	-----	-----	----	----	-----	---------------	----	------------------	-----

Chemical bond	Bond angle /°	Chemical bond	Bond angle $^{\circ}$
N3#1-Cd1-N3	97.86(18)	N1-N2-C1	124.50(4)
N3#1-Cd1-N3#2	81.66(18)	N1-N2-N3	127.80(4)
N3-Cd1-N3#2	90.81(13)	C1-N2-N3	107.70(4)
N3#1-Cd1-N3#3	90.81(13)	N2-N3-N4	105.80(4)
N3-Cd1-N3#3	168.56(18)	N2-N3-Cd1	128.70(3)
N3#2-Cd1-N3#3	97.86(18)	N4-N3-Cd1	119.10(3)
N3#1-Cd1-N3#4	90.81(13)	N5-N4-N3	110.50(4)
N3-Cd1-N3#4	81.66(18)	N4-N5-C1	106.60(4)
N3#2-Cd1-N3#4	168.57(18)	C1-N6-H6A	110.00(5)
N3#3-Cd1-N3#4	90.81(13)	C1-N6-H6B	100.00(5)
N3#1-Cd1-N3#5	168.56(18)	H6A-N6-H6B	113.10(18)
N3-Cd1-N3#5	90.81(13)	N2-C1-N5	109.40(4)
N3#2-Cd1-N3#5	90.81(13)	N5-C1-N6	125.80(4)
N3#3-Cd1-N3#5	81.66(18)	O1#6-N7-O1	119.91(8)
N3#4-Cd1-N3#5	97.85(19)	O1#6-N7-O1#7	119.90(8)
N2N1H1B	120.00(3)	O1-N7-O1#7	119.91(8)

Symmetry operations: #1: -x + 2, -x+y+1, -z + 1/2; #2: -x+y+2, -x + 1, z; #3: y + 1, x - 1, -z + 1/2; #4: x-y, -y, -z + 1/2; #5: -y + 1, x-y-1, z; #6: -x+y, -x + 1, z; #7: -y + 1, x-y+1, z.

+2.094*y* +12.427*z* = -0.1957 and a deviation of 0.0033. From the torsion angle data: N1–N2–N3–N4, -177.2(4)°; N1–N2– C1–N5, 177.1(4)°, it is obvious that the amino nitrogen atom N1 is coplanar to the tetrazole ring with the plane equation – 2.384*x* +2.213*y* +12.419*z* = -0.1445 and a deviation of 0.0134. The torsion angle data N3–N2–C1–N6, -176.7(5)°; N4–N5– C1–N6, 176.5(5)° shows that the tetrazole ring and amino nitrogen atom N6 are coplanar, with the plane equation –2.238*x* +2.024*y* +12.465*z* = -0.0410 and a deviation of 0.0127. In addition, it was found that the [Cd(DAT)₆]²⁺ ion is almost centrosymmetric, so the rest of plane equations are not listed.

Six DAT ligand molecules forming tetrazole ring planes are shown: plane I [C1, N2, N3, N4, N5], plane II [C1A, N2A, N3A, N4A, N5A], plane III[C1B, N2B, N3B, N4B, N5 B], plane IV[C1C, N2C, N3C, N4C, N5C], plane V[C1D, N2D, N3D, N4D, N5D], plane VI[C1E, N2E, N3E, N4E, N5E]. From the six planes it is obvious that in the opposite angle position the DAT tetrazole ring planes (plane I and IV, plane II and VI, plane III and V) are almost parallel to each other with an angle of 3.2°; the angle between adjacent planes (plane I and V, plane II and IV, plane III and VI) amounts 23.7°; and the angle between the other adjacent planes (plane I and VI, plane II and V, plane III and IV) amounts 20.4° and the angle of the interval planes amounts 22.2°.

In the crystal structure of $[Cd(DAT)_6](NO_3)_2$, two types of hydrogen bonds were observed. One occurs between the nitrogen atom of the tetrazole ring and a hydrogen atom of the amino group of an adjacent tetrazole ring, N1–H1A···N4. This type of hydrogen bonding combines the DAT molecules together to stabilze the inner $[Cd(DAT)_6](NO_3)_2$ structure. Another type of hydrogen bonding occurs between the hydrogen atoms of the amino groups of the tetrazole rings and the oxygen atoms of the nitrate ions, N6–H6A···O1 and N1–H1B···O1, which bridge $[Cd(DAT)_6](NO_3)_2$ molecules together to form a stable three-dimensional net structure. Selected hydrogen bonds of $[Cd(DAT)_6](NO_3)_2$ are listed in Table 3.

Table 3. Selected hydrogen bonds for [Cd(DAT)₆](NO₃)₂.

D–H•••A	D–H /Å	H•••A /Å	D····A /Å	D–H•••A /°
N1–H1B····O1 #1	0.891	2.137	2.989	159.67
N1-H1B····O1 #2	0.891	2.607	3.147	119.86
N1-H1A····N4	0.895	2.125	2.993	163.05
N6–H6A•••O1 #3	0.898	2.367	3.248	166.92

Symmetry operations: #1: x, y - 1, z; #2: -x+y, -x, z; #3: -y + 1, x-y-1, z.

Thermal Decomposition Mechanism of $[Cd(DAT)_6](NO_3)_2$

In order to investigate the thermal decomposition of $[Cd(DAT)_6](NO_3)_2$, the DSC and TG/DTG experiments were carried out with a linear heating rate of 10 °C·min⁻¹ under nitrogen. The DSC curve of $[Cd(DAT)_6](NO_3)_2$ shown in Figure 4 exhibits two sharp peaks, the first is a sharp endothermic peak, caused by melting. The melting peak starts at 203.2 °C with a peak temperature of 215.9 °C; afterwards the melting product immediately decomposes to form an exothermic process, with a peak temperature of 242.4 °C, and ends at 266.0 °C.



Figure 4. DSC curve of $[Cd(DAT)_6](NO_3)_2$ with a heating rate of 10 °C·min⁻¹.

As we can see from the TG/DTG diagram (Figure 5), three main thermal decomposition processes can be observed for $[Cd(DAT)_6](NO_3)_2$. The first mass loss happens in the range 178.3–265.7 °C and amounts to 58.9 %, the maximum mass loss rate shows up at 231.1 °C, with a rate of 18.1 %·min⁻¹; the second mass loss happens in the range 265.7–401.1 °C with a value of 17.7 %; the third mass loss happens in the range 401.1–531.6 °C, the final residual quantity is 13.9 %. FT-IR spectroscopy shows that no obvious characteristic peaks exist in the range 400–4000 cm⁻¹. Combined with the element analysis, the residue is CdO. However, there is a certain deviation of 15.4 % of the theoretical residua amount. It may occur because $[Cd(DAT)_6](NO_3)_2$ decomposes and exothermic so rapidly.

Non-isothermal Kinetic Analysis of the Main Exothermic Peak of [Cd(DAT)₆](NO₃)₂

From the DSC and TG/DTG analyses of $[Cd(DAT)_6](NO_3)_2$, we can infer that the exothermic process has a dominant effect on the decomposition of the title compound. *Kissinger*'s and



Figure 5. TG/DTG curves of $[Cd(DAT)_6](NO_3)_2$ with a heating rate of 10 °C·min⁻¹.

Ozawa–Doyle's methods were applied to study the kinetic parameters of the exothermic process of the title compound, based on the DSC curve obtained under the condition of static air at heating rates of 2, 5, 10, 15 and 20 °C \cdot min⁻¹. The Kissinger and Ozawa–Doyle equations are shown in Scheme 2.

$$\frac{d \ln \frac{\beta}{T_p^2}}{d \frac{1}{T_p}} = -\frac{E}{R}$$
$$\log \beta + \frac{0.4567 E}{RT_p} = C$$

Scheme 2. The Kissinger and Ozawa–Doyle equations. T_p : peak temperature /K; *R*: gas constant, 8.314 J·mol⁻¹·K⁻¹; β : linear heating rate / K·min⁻¹; *C*: constant.

The peak temperatures T_p /°C of the exothermic process at different heating rates, the apparent activation energy E_k and E_o /kJ·mol⁻¹, the pre-exponential factor A_k /s⁻¹ and the linear coefficient R_k and R_o were determined and are listed in Table 4. The calculated results using both methods are similar and they are all in the normal range of kinetic parameters for the thermal decomposition reaction of solid materials [34].

Table 4. Peak temperatures of the first main exothermic stage at different heating rates and kinetic parameters for [Cd(DAT)₆](NO₃)₂.

2	5	10	15	20
215.8	234.1	242.4	250.1	253.8
121.7	/ 10.28	/ -0.9	937	
123.7	/ -0.99	44		
	2 215.8 121.7 123.7	2 5 215.8 234.1 121.7 / 10.28 123.7 / -0.99	2 5 10 215.8 234.1 242.4 121.7 / 10.28 / -0.99 123.7 / -0.9944	2 5 10 15 215.8 234.1 242.4 250.1 121.7 10.28 -0.9937 123.7 -0.9944

The Arrhenius equations can be expressed by using the calculated E_a (the average of E_k and E_o) and $\ln A_k$ (Table 4) values, as follows: $\ln k = 10.28 - 121.7 \times 10^3/RT$ for the exothermic decomposition. The Arrhenius equation can be used to estimate the rate constants of the initial thermal decomposition process of $[Cd(DAT)_6](NO_3)_2$.

Conclusions

The novel energetic coordination compound $[Cd(DAT)_6](NO_3)_2$ with high nitrogen content was synthesized by reaction of 1,5-diamino-tetrazole(DAT) and Cd(NO_3)_2· 6H_2O. It displays a hexacoordinate, distorted octahedral configuration; the central Cd²⁺ ion coordinates with six nitrogen atoms of six DAT molecules. The $[Cd(DAT)_6](NO_3)_2$ molecules are connected by hydrogen bonds forming a stable three-dimensional net structure. Additionally, it has an exothermic activation energy of 121.7 kJ·mol⁻¹.

Experimental Section

Caution

1,5-Diamino-tetrazole and $[Cd(DAT)_6](NO_3)_2$ are both energetic materials and tend to explode under certain stimuli. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, shoes, gloves and ear plugs) should be taken, especially when the compound is prepared on a larger scale.

Materials and General Methods

Diamino-guanidinium chloride (industrial grade) and all chemical reagents and solvents used to prepare DAT and $[Cd(DAT)_6](NO_3)_2$ were of analytical grade and purchased commercially.

Elemental analysis was performed with a Flash EA 1112 fully-automated trace element analyzer. The FT-IR spectrum was recorded on a Bruker Equinox 55 infrared spectrometer (KBr pellets) in the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹. DSC measurement was carried out with a Pyris-1 differential scanning calorimeter in static air. Thermogravimetric (TG) analysis was carried out with a Pyris-1 thermogravimetric analyzer under dry oxygen-free nitrogen with a flowing rate of 20 mL· min⁻¹. A sample of about 0.5 mg was sealed in aluminum pans for DSC and held in platinum pans for TG in the temperature range 30–600 °C.

Synthesis of the Title Compound

Cd(NO₃)₂·6H₂O (1.7 g, 5 mmol) was dissolved in distilled water (20 mL) afterwards it was added dropwise to a solution of DAT (1.2 g, 12mmol) in distilled water (30 mL) at 70 °C. The mixture was stirred at the same temperature for another hour. Afterwards it was slowly cooled to room temperature. The precipitate was collected by filtration, washed with ethanol, and dried in a vacuum drier. The title compound [Cd(DAT)₆](NO₃)₂ was obtained in 65 % yield. Elemental analysis: Anal. Calcd.(%) for [Cd(DAT)₆](NO₃)₂ :C, 8.61; H, 2.87; N, 63.60. Found: C, 8.58; H, 2.92; N, 63.64. **IR** (KBr): $\tilde{v} = 3365 \text{cm}^{-1}$ (s), 3162(s), 1675(s), 1626(s), 1358(s), 1118(s), 994 (w), 834(w), 695(s), 572(m) cm⁻¹.

X-ray Crystallography

The crystal data of $[Cd(DAT)_6](NO_3)_2$ were collected with a Bruker Smart CCD diffractometer with graphite monochromatic Mo- K_α radiation ($\lambda = 0.71073$ Å) at 294 (2) K using φ and ω scan modes. The structure was determined and refined by using direct methods SHELXS-97 [35] and SHELXL-97 [36] program. All hydrogen atoms were located from difference Fourier electron-density maps and refined isotropically, while all non-hydrogen atoms were obtained from the difference Fourier map and refined anisotropically. Detailed informa-



tion concerning crystallographic data collection and structure refinement is summarized in Table 5. CCDC-749571 contain the supplementary crystallographic data for this paper, these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-Mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 5. Crystal data and structure refinement for [Cd(DAT)₆](NO₃)₂.

Empirical formula	$C_6H_{24}CdN_{38}O_6$
Formula weight	837.03
Crystal dimension /mm	$0.24 \times 0.18 \times 0.16$
Crystal system	Trigonal
Space group	$P\bar{3}c1$
a /Å	11.8249(8)
b /Å	11.8249(8)
c /Å	12.7457(16)
β /°	90
V /Å ³	1543.4(2)
Z	2
$\rho /g \cdot cm^{-3}$	1.801
<i>F</i> (000)	844
λ/Å	0.71073
Absorption coefficient	0.175
θ /°	1.99–24.99
Reflections collected	7389
Independent reflections (R_{int})	912(0.0317)
R_1 , w $R_2 [I > 2\sigma(I)]^{a}$	0.0433, 0.1285
R_1 , wR_2 (all data) ^{a)}	0.0466, 0.1321
h/k/l	-14-13/-11-14/-15-12
Data/restraints/parameters	912/6/91
S	1.115
$\Delta \rho_{\rm max}, \ \Delta \rho_{\rm min} \ / e \cdot {\rm \AA}^{-3}$	0.876, -0.594

Note: a) $w = 1 / [\sigma^2 (F_o^2) + (0.0720P)^2 + 5.5156 P]$, of which $P = (F_o^2 + 2 F_c^2) / 3$

Acknowledgement

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 10776002, 20911120033), the project of State Key Laboratory of Science and Technology (No. ZDKT08-01), the 111 project (B07012) and the Program for New Century Excellent Talents in University.

References

- a) R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, Angew. Chem. Int. Ed. 2006, 45, 3584; b) G. Steinhauser, T. M. Klapötke, Angew. Chem. Int. Ed. 2008, 47, 3330; c) T. M. Klapötke, High Energy Density Materials, Springer, Berlin, 2007, p. 35.
- [2] U. Teipel, Energetic Materials, VCH, Weinheim, 2005, p. 1.
- [3] N. Kubota, Propellants and Explosives, VCH, Weinheim, 2007, p. 3.
- [4] R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, Angew. Chem. Int. Ed. 2006, 45, 3584.
- [5] a) J. P. Agrawal, Prog. Energy Combust. Sci. 1998, 24, 1; b) D. E. Chavez, M. A. Hiskey, R. D. Gilardi, Angew. Chem. Int. Ed. 2000, 39, 1791; c) M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud, R. D. Gilardi, J. Am. Chem. Soc. 2005, 127, 12537; d) M. Smiglak, A. Metlen, R. D. Rogers, Acc. Chem. Res. 2007,

40, 1182; e) R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, Angew. Chem. Int. Ed. 2006, 45, 3584.

- [6] a) L. E. Fried, M. R. Manaa, P. F. Pagoria, R. L. Simpson, *Annu. Rev. Mater. Res.* 2001, *31*, 291; b) M. W. Schmidt, M. S. Gordon, J. A. Boatz, *J. Phys. Chem. A* 2005, *109*, 7285; c) C. B. Jones, R. Haiges, T. Schroer, K. O. Christe, *Angew. Chem. Int. Ed.* 2006, *45*, 4981.
- [7] Y. Gao, H. Xue, B. Twamley, J. M. Shreeve, *Inorg. Chem.* 2005, 44, 5068.
- [8] Y. Gao, H. Xue, B. Twamley, J. M. Shreeve, *Chem. Mater.* 2005, 17, 191.
- [9] S. W. Arritt, H. Xue, B. Twamley, J. M. Shreeve, *Inorg. Chem.* 2004, 43, 7972.
- [10] T. Wu, B. H. Yi, D. Li, Inorg. Chem. 2005, 44, 4130.
- [11] X. J. Mo, E. Q. Gao, Z. He, W. J. Li, C. H. Yan, Inorg. Chem. Commun. 2004, 7, 353.
- [12] M. Friedrich, J. C. Gálvez-Ruiz, T. M. Klapötke, P. Mayer, B. Weber, J. J. Weigand, *Inorg. Chem.* 2005, 44, 8044.
- [13] M. Wehlan, R. Thiel, J. Fuchs, W. Beck, W. P. Fehlhammer, J. Organomet. Chem. 2000, 613, , ,159.
- [14] R. G. Xiong, X. Xue, H. Zhao, X. Z. You, B. F. Abrahams, Z. Xue, Angew. Chem. Int. Ed. 2002, 41, 3800.
- [15] M. S. Hill, P. B. Hitchcock, N. Smith, *Polyhedron* **2004**, *23*, 801.
- [16] X. S. Wang, Y. Z. Tang, X. F. Huang, Z. R. Qu, C. M. Che, P. W. H. Chan, R. G. Xiong, *Inorg. Chem.* **2005**, *44*, 5278.
- [17] M. Muttenthaler, M. Bartel, P. Weinberger, G. Hilscher, W. Linert, J. Mol. Struct. 2005, 741, 159.
- [18] C. M. Grunert, P. Weinberger, J. Schweifer, C. Hampel, A. F. Stassen, K. Mereiter, W. Linert, J. Mol. Struct. 2005, 733, 41.
- [19] O. A. Ivashkevich, S. V. Levchik, A. I. Balabanovich, A. I. Lesnikovich, *Thermochim. Acta* 1992, 207, 115.
- [20] A. I. Balabanovich, S. V. Levchik, O. A. Ivashkevich, A. I. Lesnikovich, *Thermochim. Acta* 1993, 225, 53.
- [21] A. I. Balabanovich, S. V. Levchik, O. A. Ivashkevich, P. N. Gaponik, *Polym. Degrad. Stability* 1995, 47, 333.
- [22] O. A. Ivashkevich, A. I. Lesnikovich, S. V. Levchik, A. I. Balabanovich, *Thermochim. Acta* 2002, 338, 233.
- [23] A. V. Smirnov, M. A. Ilyushin, I. V. Tselinskii, Russ. J. Appl. Chem. 2004, 77, , 794.
- [24] A. Y. Zhilin, M. A. Ilyushin, I. V. Tselinskii, A. S. Kozlov, I. S. Lisker, *Russ. J. Appl. Chem.* 2003, 76, 572.
- [25] J. C. Gálvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapötke, Inorg. Chem. 2005, 44, 4237.
- [26] G. Fischer, G. Holl, T. M. Klapötke, J. W. Jan, *Thermochim. Acta* 2005, 437, 168.
- [27] G. W. Drake, T. W. Hawkins, J. Boatz, H. Leslie, V. Ashwani, Propellants Explos. Pyrot. 2005, 30, 156.
- [28] V. E. Matulis, A. S. Lyakhov, P. N. Gaponik, V. V. Sergei, A. I. Oleg, J. Mol. Struct. 2003, 649, 309.
- [29] P. N. Gaponik, S. V. Voitekhovich, A. S. Lyakhov, V. E. Matulis, O. A. Ivashkevich, M. Quesada, J. Reedijk, *Inorg. Chim. Acta* 2005, 358, 2549.
- [30] Y. Cui, T. L. Zhang, J. G. Zhang, L. Yang, X. C. Hu, J. Zhang, J. Mol. Struct. 2008, 889, 177.
- [31] Y. Cui, J. G. Zhang, T. L. Zhang, L. Yang, J. Zhang, X. C. Hu, J. Hazard. Mater. 2008, 160, 45.
- [32] Y. Cui, J. G. Zhang, T. L. Zhang, L. Yang, Y. Zang, Y. J. Shu, *Chin. J. Chem.* 2008, 26, 2029.
- [33] J. C. Galvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapötke, K. Loehnwitz, P. Mayer, H. Noeth, K. Polborn, C. J. Rohbogner, M. Suter, J. J. Weigand, *Inorg. Chem.* 2005, 44, 4237.
- [34] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure, University of Gottingen, Germany, 1997.
- [35] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure, University of Gottingen, Germany, 1997.
- [36] R. Z. Hu, Z. Q. Yang, Y. J. Liang, Thermochim. Acta 1988, 123, 135.

Received: October 24, 2009 Published Online: February 11, 2010