

# Crystal Structures of Energetic Compounds. I. Safe Small-Scale Preparation and X-Ray Structure Determination of the High-Energy Cobalt(III) Complex $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$

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**Abstract** Well-formed dark red single-crystals of the potentially explosive cobalt(III) azido complex  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$  (nitrogen content: 72.59%) have been grown using a safe small-scale preparation from  $[\text{Co}(\text{NH}_3)_5\text{N}_3]\text{Cl}_2$  and sodium azide. The complex crystallizes in the orthorhombic system, space group  $\text{Pnma}$  with unit cell parameters  $a = 12.921(3) \text{ \AA}$ ,  $b = 10.346(2) \text{ \AA}$ ,  $c = 8.0315(16) \text{ \AA}$ ,  $V = 1,073.7(4) \text{ \AA}^3$  and  $Z = 4$ . Five  $\text{NH}_3$  ligands and the azide anion surround the  $\text{Co}^{3+}$  ion in a nearly perfect octahedral geometry. Two azide anions are non-coordinating, and no water of crystallization is present in the crystal structure.

**Keywords** Energetic compounds · Cobalt(III) · Azide ligand · Crystal structure

## Introduction

Classical cobalt(III) complexes continue to receive considerable attention due to their fundamental role in the development of coordination chemistry [1–13]. Azide is a versatile ligand which exhibits a variety of coordination modes, including monodentate, end-on bridging, and end-to-end bridging [14]. The first azido complexes of cobalt(III) were reported in 1934 by Strecker and Oxenius [15]. It then took until 1950 when Linhard and Flygare prepared a series of the parent  $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$  ion [16, 17]. This was followed by the *cis*- and *trans*-tetraammin-diazido complexes [18] and the non-electrolyte  $[\text{Co}(\text{NH}_3)_3(\text{N}_3)_3]$

[19]. Typical for the  $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ -salts is their light-sensitivity and their somber coloration ranging from dark red to almost black. In their appearance these salts often resemble the color of red phosphorus [16, 17]. In contrast to the highly explosive neutral complex  $[\text{Co}(\text{NH}_3)_3(\text{N}_3)_3]$  the pentaammin-azidocobalt(III) salts are not sensitive to impact or friction and are also thermally quite stable with the exception of the title compound  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$ . With a sum formula of  $\text{H}_{15}\text{CoN}_{14}$  the diazide derivative has a nitrogen content of 72.59% and has to be considered an energetic compound. Linhard and Flygare reported that  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$  detonates with a sharp bang at temperatures above 194 °C. We report here a safe small-scale preparation of the diazide and its structural characterization by X-ray crystallography. The small-scale crystal growth employed here is an adaptation of a method frequently used by Thewalt and co-workers for obtaining dithionate salts of cobalt(III) ammine complexes [20, 21].

## Experimental

The starting material  $[\text{Co}(\text{NH}_3)_5\text{N}_3]\text{Cl}_2$  was prepared according to the original procedure [16, 17].

*Caution!* Although not encountered in our experiments, azides and azido complexes should always be considered as potentially explosive. Only small amounts of materials should be prepared and should always be handled with great care.

### Small-Scale Preparation of $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$ Single-Crystals

The total of 100 mg of  $[\text{Co}(\text{NH}_3)_5\text{N}_3]\text{Cl}_2$  were dissolved in water (7 mL) and the filtered solution was placed in a small

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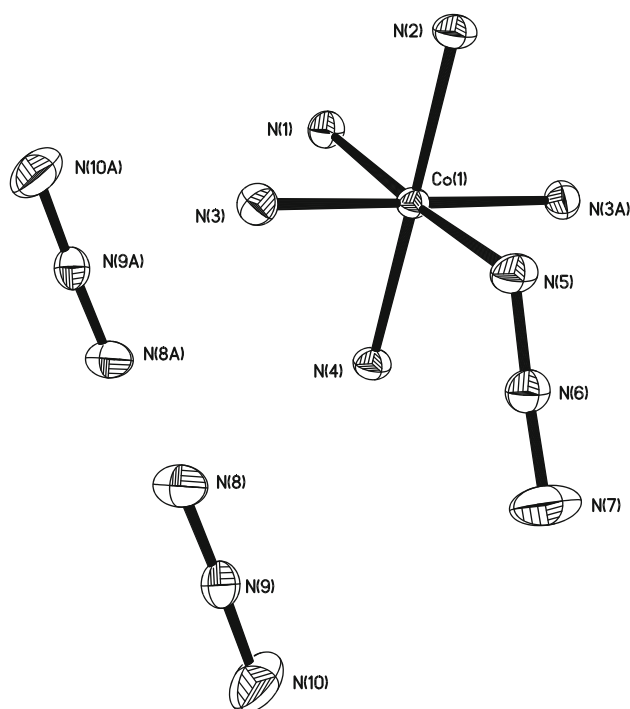
(20 mL) beaker. Three small portions of sodium azide (combined *ca.* 100 mg) were added, and the mixture was allowed to stand undisturbed at room temperature. After 24 h dark red, well-formed single-crystals of  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$  suitable for X-ray diffraction were obtained. The light red supernatant was withdrawn using a pipette, and the crystals were washed successively with dilute (50%) ethanol, anhydrous ethanol, and diethyl ether and finally dried in air. The rod-like crystals are weakly dichroitic (dark red/brown-red).

### Crystal Structure Determination and Refinement

The single crystal X-ray diffraction study of the title compound was performed on a Stoe IPDS 2T diffractometer with  $\text{MoK}_\alpha$  radiation. The data were collected with the Stoe XAREA program using  $\omega$ -scans. No absorption correction was applied. The space group was determined with XPREP program, and the structure was solved by direct methods (SHELXS-97) [22] and refined with all data by full-matrix least-squares methods on  $F^2$  using SHELXL-97 [23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically fixed at calculated positions.

### Results and Discussion

By using the small-scale preparation as described in the Experimental section well-formed, rod-like single crystals



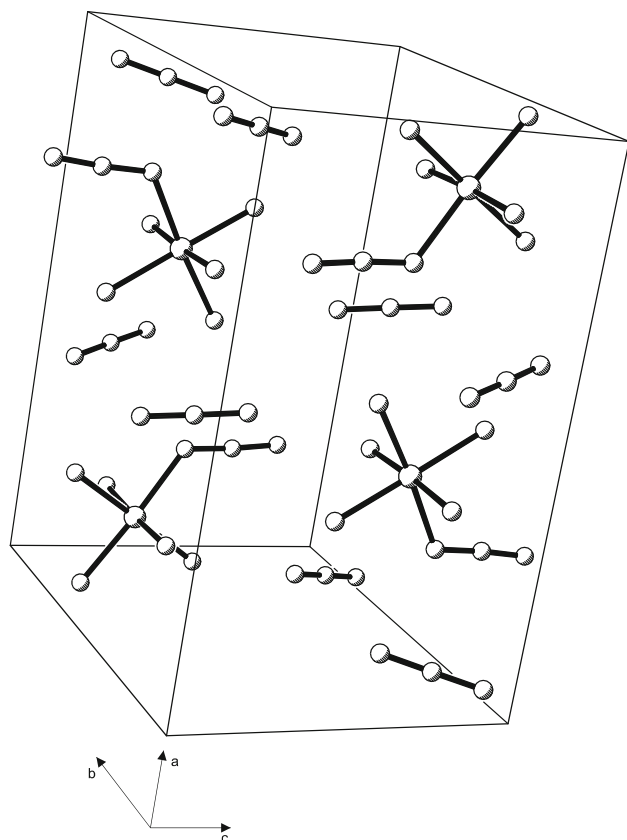
**Fig. 1** Structure of  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$ . The displacement ellipsoids are drawn at 50% probability level

of  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$  suitable for X-ray diffraction are readily obtained in a safe manner. The crystals resemble red phosphorus in color and show weak dichroism (dark red/brown-red). Prepared in this manner the sample consists almost entirely of individual single crystals. The structure is illustrated in Fig. 1. Significant bond parameters are listed in Table 1.

The pentaammin-azidocobalt(III) cation represents a prototypical hexacoordinated classical cobalt complex. The coordination geometry around the central  $\text{Co}^{3+}$  ion is nearly ideally octahedral with N–Co–N angles ranging from  $86.90(6)^\circ$  to  $94.06(6)^\circ$ . With an average of  $1.9533(14)$  Å the Co–N( $\text{NH}_3$ ) bond lengths are virtually identical with the Co–N( $\text{N}_3$ ) distance [ $1.9591(14)$ ]. The overall structural parameters of the  $\text{CoN}_6$  octahedron are in good agreement with previous reports [24–28]. The coordinated azide ligand is nearly linear [N(5)–N(6)–N(7)  $176.23(19)^\circ$ ]. It is coordinated to the central  $\text{Co}^{3+}$  ion with a Co(1)–N(5)–N(6) angle of  $121.98(12)^\circ$ , which is favorably comparable with corresponding Co–N–N angles reported earlier [29]. A closer inspection of the unit cell packing diagram

**Table 1** Selected bond lengths (Å) and bond angles ( $^\circ$ )

Co(1)–N(2)	1.9491(14)
Co(1)–N(5)	1.9591(14)
Co(1)–N(3)#1	1.9622(12)
Co(1)–N(3)	1.9622(12)
Co(1)–N(1)	1.9701(14)
Co(1)–N(4)	1.9803(13)
N(5)–N(6)	1.1978(19)
N(6)–N(7)	1.156(2)
N(8)–N(9)	1.1706(15)
N(9)–N(10)	1.1748(15)
N(2)–Co(1)–N(5)	86.90(6)
N(2)–Co(1)–N(3)#1	89.02(3)
N(5)–Co(1)–N(3)#1	88.46(3)
N(2)–Co(1)–N(3)	89.02(3)
N(5)–Co(1)–N(3)	88.46(3)
N(3)#1–Co(1)–N(3)	176.44(6)
N(2)–Co(1)–N(1)	89.15(6)
N(5)–Co(1)–N(1)	176.06(6)
N(3)#1–Co(1)–N(1)	91.48(3)
N(3)–Co(1)–N(1)	91.48(3)
N(2)–Co(1)–N(4)	179.04(6)
N(5)–Co(1)–N(4)	94.06(6)
N(3)#1–Co(1)–N(4)	91.00(3)
N(3)–Co(1)–N(4)	91.00(3)
N(1)–Co(1)–N(4)	89.89(6)
N(6)–N(5)–Co(1)	121.98(12)
N(7)–N(6)–N(5)	176.23(19)
N(8)–N(9)–N(10)	178.08(13)



**Fig. 2** Unit cell packing diagram of  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$

(Fig. 2) revealed no short contacts or hydrogen bridges between the separated ions in the crystal structure of  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$ .

As mentioned above, with a sum formula of  $\text{H}_{15}\text{CoN}_{14}$  the title compound has a nitrogen content 72.59%. This is comparable with that of the recently developed high-nitrogen high-energy material hydrazinium azotetrazolate,  $[\text{N}_2\text{H}_5]^{2+}[\text{N}_4\text{C}=\text{N}=\text{N}=\text{CN}_4]^{2-} \cdot 2\text{H}_2\text{O}$  (N-content 73.3%) [30]. Hydrazinium azotetrazolate, just like  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{N}_3)_2$ , is almost insensitive to friction and impact, but detonates violently when the explosion is initiated (e.g., by rapid heating over the decomposition temperature or by using an initiator) [30]. The small-scale method as reported here allows the safe crystal growth of high-energy compounds for X-ray structural investigations. In our lab it has also been successfully employed in the preparation of single-crystals of novel azotetrazolates and dipicrylamides. These results will be reported in due course.

### Supplementary Material

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666;

**Table 2** Crystal data and experimental parameters

CSD No	CSD-418204
Empirical formula	$\text{H}_{15}\text{CoN}_{14}$
Formula weight	270.19
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pnma
Unit cell dimensions	
<i>a</i> (Å)	12.921(3)
<i>b</i> (Å)	10.346(2)
<i>c</i> (Å)	8.0315(16)
Volume	1,073.7(4) Å <sup>3</sup>
<i>Z</i>	4
Density (calculated)	1.672 Mg/m <sup>3</sup>
Absorption coefficient	1.600 mm <sup>-1</sup>
<i>F</i> (000)	560
Crystal size	0.40 mm × 0.30 mm × 0.15 mm
$\theta$ range for data collection	5.67–29.23°
Limiting indices	$-17 \leq h \leq 16$ , $-14 \leq k \leq 14$ , $-11 \leq l \leq 10$
Reflections collected/unique	10,119/1,487 [ <i>R</i> (int) = 0.0446]
Completeness to $\theta = 29.23$	97.1%
Absorption correction	None
Maximum and minimum transmission	0.7954 and 0.5671
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	1,487/0/117
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.052
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0232, w <i>R</i> <sub>2</sub> = 0.0563
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0276, w <i>R</i> <sub>2</sub> = 0.0581
Largest diff. peak and hole	0.455 and -0.523 eÅ <sup>-3</sup>

e-mail: crysdata@fiz-karlsruhe.de, [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html)) on quoting the appropriate CSD number (Table 2).

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