High-Nitrogen Compounds

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A Symmetric $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$ High-Nitrogen Compound Formed by Cobalt(II) Cation Trapping of a Cyclo-N_5^- Anion

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Abstract: *The reactions of $(N_5)_6(H_3O)_3(NH_4)_4Cl$ with $Co(NO_3)_2{\cdot}6\,H_2O$ at room temperature yielded $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$ as an air-stable orange metal complex. The structure, as determined by single-crystal X-ray diffraction, has two planar cyclo-N_5^- rings and four bound water molecules symmetrically positioned around the central metal ion. Thermal analysis demonstrated the explosive properties of the material.*

Polynitrogen and nitrogen-rich compounds have received attention in the search for novel high energy density materials because of their excellent explosive performance and environmentally friendly characteristics.[1] Pentazole (HN_5) and its anion (cyclo-N_5^-) have been controversial since the pioneering work of Hurzeler, Huisgen, and Ugi;[2] partially because of the uncertainty over whether a stable form of pentazolate species can be isolated and/or trapped in metal complexes.[3] Recently, we reported a major breakthrough that focused on the synthesis of a stable pentazolate salt with the chemical formula $(N_5)_6(H_3O)_3(NH_4)_4Cl$.[4] However, the 1.340 $g\,cm^{-3}$ density of the material, and dilution with non-energetic components, did not meet the demands of high energy density materials. To produce pentazolate compounds with higher performance while maintaining thermal stability, metal ions and/or high-nitrogen-containing cations were thus investigated as cyclo-N_5^- traps.

Although no experimental procedure for preparing metal pentazole-based species has been published prior to this work, a large body of literature on classes of compounds such as sandwich complexes $Fe(\eta^5\text{-}N_5)_2$ and *N*-σ structure analogues $[M(N_5)_n]^x$ ($M = Li^+, Na^+, Mg^{2+}, Ca^{2+}, B^{3+}, Si^{4+}, Cr^{6+}, Mo^{6+}$; $n = 1, 2, 4, 6, 8$; $x = 0, -1, -2$), have been investigated with density functional theory (DFT) calculations.[5] These metal pentazole materials were predicted to be energy-rich but kinetically stable compounds. Thus, herein we adopt Co^{2+} to capture cyclo-N_5^- from $(N_5)_6(H_3O)_3(NH_4)_4Cl$, forming stable and symmetric $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$. The structure of the compound was determined by single-crystal X-ray diffraction, in which the cobalt ion acts as a shared center linking two pentagonal N_5^- rings through two σ-bonds and binding four H_2O molecules.

The synthesis of $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$ was performed by salt metathesis by reacting $(N_5)_6(H_3O)_3(NH_4)_4Cl$ with $Co(NO_3)_2{\cdot}6\,H_2O$ in a methanol/H_2O solution at room temperature, followed by removal of the volatile products at 30 °C (Supporting Information, Figures S1 and S2). Suitable crystals of $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$ were obtained by slow evaporation of an acetone solution at 15 °C, which crystallizes in the orthorhombic space group *Fmmm* with four molecules in the unit cell with a calculated density of 1.694 $g\,cm^{-3}$ at 173 K. As seen in the structure of the $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$ (Figure 1; Supporting Information, Figure S7), the principal building element of the structure consists of two planes. One of the planes contains Co^{2+} centers, each of which are surrounded by four H_2O (O1) molecules on the 16*n* positions with completely equal Co–O bonds. The valence state of the cobalt ion was determined by X-ray photoelectron spectroscopy (XPS), which presents only one type of oxidation state and the main peak is associated with photoelectrons emitted from cobalt atoms in the Co^{2+} state (Supporting Information, Figure S4).[6] The other plane consists of two pentagonal N_5^- rings and a shared Co^{2+} center, which exhibits a perfectly

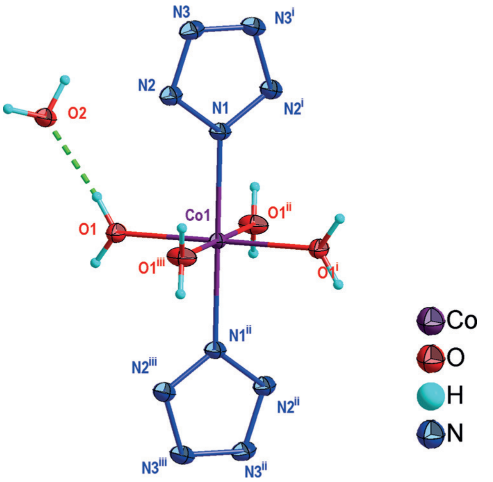

Figure 1. Ellipsoid plot of $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$ at the 50% probability level. Hydrogen bonds are indicated by green dotted lines. Symmetry codes: (i) $1-x, y, 1-z$; (ii) $1-x, 1-y, z$; (iii) $x, 1-y, 1-z$.

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planar arrangement, as evident from the torsion angles (Co(1)-N(1)-N(2)-N(3), 180°; N(2)^i-N(1)-N(2)-N(3), 0°; N(1)-N(2)-N(3)-N(3)^i, 0°). Because of site symmetry, there are two symmetry-related pentagonal N_5^- rings around Co^{2+} and the Co−N bonds exhibit linear and symmetrical arrangements (N1-Co-N1, 180°; Co(1)−N(1), Co(1)−N(1)^{ii} 2.136 Å). In particular, the Co−N bond distance is in agreement with the metal–nitrogen distance of 2.139 Å in $\{[Co(bpm)_2(N_3)_2][Co(bpm)_2(H_2O)_2]\}(ClO_4)_2$,[7] while slightly shorter than the single Co^{2+}−N length (2.241 Å) [8] and longer than that observed in the ligand bond lengths of $[Co_6(O_2CMe)_4(hmp)_8](ClO_4)_2{\cdot}MeOH$ (1.914 Å).[9] The observed Co−N bond, together with the planarity, indicates the presence of a strongly delocalized π-electron system. In combination with the computed results for metal pentazole complexes,[10] we conclude that $Co(N_5)_2(H_2O)_4{\cdot}4H_2O$ is a σ-bonded molecule. However, in contrast to the structure of $(N_5)_6(H_3O)_3(NH_4)_4Cl$, where coordinated H_3O^+ and NH_4^+ exist, the bond lengths and angles of cyclo-N_5^- are nearly the same for both compounds.

Considering the stability of both cyclo-N_5^- and metal pentazole-based species, it is worth mentioning that, besides the Co^{2+} contribution to the excellent stability of $Co(N_5)_2(H_2O)_4{\cdot}4H_2O$, two forms of H_2O (bound water H_2O (O1) and free water H_2O (O2)) play a critical role in stabilizing the pentazolate anion. As shown in Figure 2 and Figure S10 (Supporting Information), the H_2O (O2) molecule located near the cobalt core is considered imperative for the construction of well-defined hierarchical hydrogen bond networks. In view of spatial hierarchy, the whole hydrogen bond network can be segmented into one-dimensional chains and two-dimensional nets. A one-dimensional chain shown in Figure S8 (Supporting Information) was formed through the hydrogen bond of O1−H1···O2 with a R_4^2 (8) motif along the *c* axis. The distance between two adjacent Co^{2+} ions was 6.4578(2) Å. A two-dimensional net (Supporting Information, Figure S9) was expanded through [110] and [1-10] directions by hydrogen bonds O2−H2A···N2^i and O2−H2B···N3^{ii} with a R_4^2 (10) motif. Each cyclo-N_5^- is in close contact with four H_2O (O2) molecules. Apparently, the two-dimensional net is capable of extending through the 1D-chain into a complicated hydrogen bond network. Although there are many pentagonal N_5^- rings in space packing, no π–π interactions were found between adjacent rings.

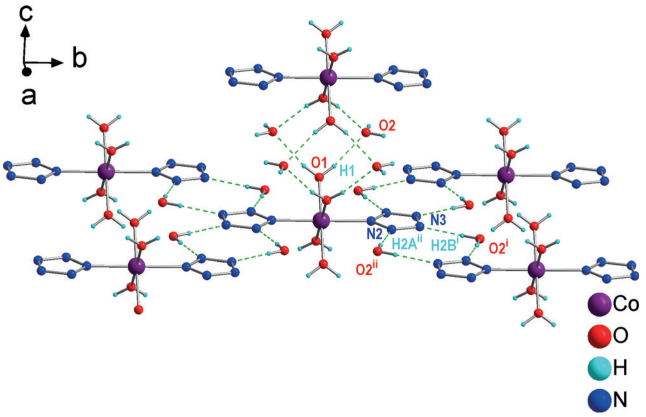

Figure 2. Representation of the hydrogen-bonded motifs in the crystal structure. Hydrogen bonds are indicated by green dotted lines. Symmetry codes: (i) *x*, 3/2−*y*, 3/2−*z*; (ii) 3/2−*x*, *y*, 3/2−*z*.

The Raman spectrum of $Co(N_5)_2(H_2O)_4{\cdot}4H_2O$ in the 500–4000 cm^{-1} range is shown in Figure 3. As a comparison, three cyclo-N_5^- bands at 1199 (A_1'), 1128 (E_2'), and 1031 cm^{-1} (E_2') are in excellent agreement with the frequencies observed in $(N_5)_6(H_3O)_3(NH_4)_4Cl$. The minor discrepancies (10–15 cm^{-1} red-shift) between the two compounds can be attributed to the strongest orbital interactions between Co^{2+} and cyclo-N_5^-. The spectrum also shows two new characteristic bands at 3273 and 3433 cm^{-1}, which are apparently from the bending and stretching modes of H_2O.[11] The IR spectrum of $Co(N_5)_2(H_2O)_4{\cdot}4H_2O$ was also recorded for comparison (Supporting Information, Figure S3). The distinct absorption band in the 700–3668 cm^{-1} region confirmed the presence of the cyclo-N_5^- and H_2O in the crystal structure and was assigned to the vibration of O−H···O groups and the cyclo-N_5^- plane.[12] Notably, bands in the 500–600 cm^{-1} region correspond to the stretching frequencies of the Co−N/O bonds,[13] which cannot be distinguished because of their broadness.

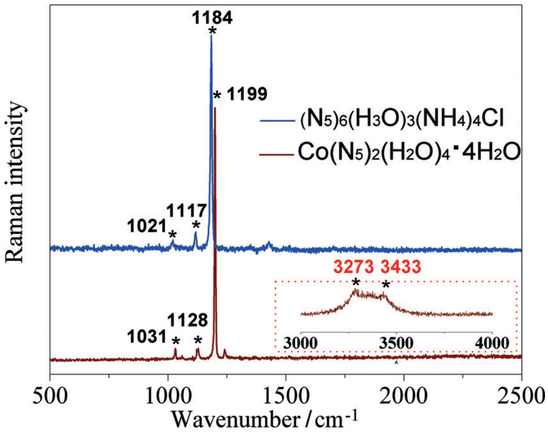

Figure 3. Raman spectra of $Co(N_5)_2(H_2O)_4{\cdot}4H_2O$ and $(N_5)_6(H_3O)_3(NH_4)_4Cl$.

Thermal analysis of $Co(N_5)_2(H_2O)_4{\cdot}4H_2O$ was performed under a N_2 atmosphere by thermogravimetric differential scanning calorimetry (TG-DSC). The data in Figure 4 reveal that the decomposition takes place in two independent steps. In the first step, lattice water is lost at 50 °C, which indicates weak hydrogen bonding between these species. Rapid weight loss follows and reaches 65 % between 60 and 145 °C, corresponding to a theoretical mass loss of 58 % for eight coordinated water molecules and two nitrogen molecules. The corresponding detailed decomposition path is proposed in Figure S5 (Supporting Information). Once the water is released, cyclo-N_5^- begins to decompose into N_2 gas and cobalt azide $[Co(N_3)_2]$. This is a reflection of the strong water–cyclo-N_5^- interaction observed in the crystal structure. One main endothermic peak at 80 °C is observed in the heating DSC curve. As expected from high energy density

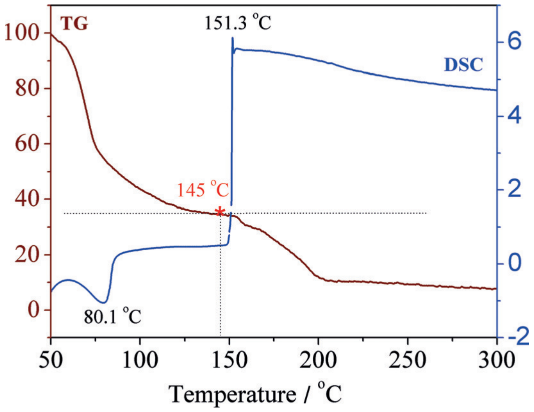

Figure 4. TG-DSC curves of $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$ under N_2 at 5 K min^{-1}.

material considerations, the decomposition of a polynitrogen compound will result in the release of a large amount of energy.[14] At the second significant decomposition step from 145 to 200 °C, an abrupt exothermic peak at about 150 °C appeared and the DSC curve suddenly rose. We concluded that the decomposition residues from the first stage exploded and much energy was released, producing an unusual DSC curve. Direct evidence can be found in Figure S6 (Supporting Information). The first thermal analysis of $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$ (using a weight of 3.0 mg) exploded when the DSC temperature reached 145 °C, and the alumina crucible exploded into small pieces (Supporting Information, Figure S6). Clearly, the pentazole-based metal species $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$ contains more energy and produced a stronger explosion than $(N_5)_6(H_3O)_3(NH_4)_4Cl$.

In conclusion, we have demonstrated that a cobalt ion can effectively capture cyclo-N_5^-, forming the stable and energy-rich compound $Co(N_5)_2(H_2O)_4{\cdot}4\,H_2O$. The structure of this complex is linear and highly symmetric, unlike sandwich complexes. Our results show promise for making a wide variety of transition-metal complexes and high-nitrogen explosives.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: explosives · high energetic density materials · metal pentazolate anion complex · pentazole · polynitrogen compounds

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