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Hexaazaphenalenyl Anion Revisited: A Highly Symmetric Planar π System with Multiple-Networking Ability for Self-Assembled Metal Complexation

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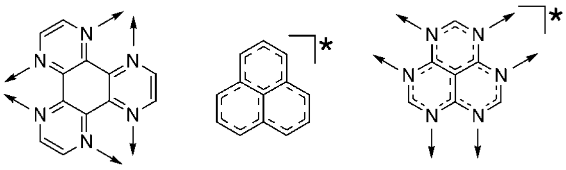
The hexaazaphenalenyl anion (HAP, $\mathbf{3}^-$), a highly symmetric heterocyclic π system, has been synthesized and characterized. The crystal structures of its potassium salt $K^+\cdot\mathbf{3}^-$ and copper complex $Cu^{2+}\cdot(NH_3)_4\cdot(\mathbf{3}^-)_2$ show π–π stacking and radially extended hydrogen bonds as well as coordination bonds constructed by the HAP anion. These in-plane and out-of-plane strong interactions demonstrate the multiple-networking ability of the HAP anion.

In the search for multifunctional metal complexes,[1,2] noncovalent interactions such as hydrogen bonding and π−π interactions have been actively used to strengthen structural and electronic communication between organic ligands. Hexaazatriphenylene (HAT, **1**), a multidentate ligand with a large π-conjugation network, has been extensively studied in supramolecular chemistry[3] and molecular magnetism.[4] Despite the virtue of the molecular symmetry and apparent bonding ability at the nitrogen sites of **1** (Figure 1), it turned out that neither hydrogen bond nor π−π stacking are seen in the metal complexes of **1** because of the dominant bidentate chelation. To enhance noncovalent interactions, it seems preferable to use ligands with a novel coordination mode and multiple-networking ability.



1 Chelating mode

2 ★ = +, •, −

3 Radially-extended mode

Figure 1. Molecular structures of **1**−**3** with their inherent directionality in coordination and hydrogen-bonding interactions.

Phenalenyl **2** is a planar π system with D_{3h} symmetry. Cationic and radical derivatives were recently isolated in the crystalline state and their physical properties characterized.[5,6] Incorporation of nitrogen atoms into the phenalenyl skeleton was found to give substantial effects on its electronic structure,[7] providing hydrogen-bonded electron-donor molecules,[7a] spin-delocalized neutral radicals,[7b,d,e] and metal complex ligands.[7c,d] Hexaazaphenalenyl (HAP, **3**) is a highly symmetric heterocycle with full nitrogen substitution in all of the α sites of phenalenyl. It is noted here that no study has been reported on **3** for nearly 40 years since the first documentation.[8] Because of the directionality of lone-pair electrons at the nitrogen sites, a radially extended mode is expected for metal-coordination and hydrogen-bonding interactions (Figure 1). This feature has encouraged us to revisit this molecule as part of our continuous efforts for phenalenyl

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chemistry.[5−7] Here we report syntheses of potassium salt $K^+\cdot\mathbf{3}^-$ and copper complex $Cu^{2+}\cdot(NH_3)_4\cdot(\mathbf{3}^-)_2$, demonstrating that **3** serves as a component of self-assembled metal complexes, with $\pi-\pi$ interactions coexisting with multiple hydrogen and coordination bonds.

The anion precursor, hexaazaphenalene ($H^+\cdot\mathbf{3}^-$), was prepared from 4,6-diamino-5-cyanopyrimidine and formamide according to the literature method[8] with some modifications. The improved purification procedure has enabled a large-scale synthesis with reliable reproducibility. We have succeeded in the synthesis of potassium salt $K^+\cdot\mathbf{3}^-$ by treatment of $H^+\cdot\mathbf{3}^-$ with an aqueous potassium hydroxide solution and recrystallized it from an ethanol−water solution to obtain colorless crystals containing two water molecules per $K^+\cdot\mathbf{3}^-$ unit.[9,10] HAP anion $\mathbf{3}^-$ was very stable in solution and the solid state under atmospheric air and water. This contrasted with the parent phenalenyl anion $\mathbf{2}^-$, which must be handled under an inert atmosphere in solution.[11] Therefore, this is the first isolation of a phenalenyl anion species that is subject to X-ray crystal structure analysis (vide infra).

Cyclic voltammetry (CV) measurement of HAP anion $\mathbf{3}^-$ gave an irreversible oxidation wave at around +1.2 (V vs Fc/Fc^+),[12] being assigned to the redox potential between $\mathbf{3}^-$ and $\mathbf{3}^\bullet$. This is much higher than the corresponding value for $\mathbf{2}^\bullet$ and $\mathbf{2}^-$ (ca. −1.3 V),[13] being consistent with a substantial decrease in the calculated highest occupied molecular orbital (HOMO) energy of $\mathbf{3}^-$ compared to $\mathbf{2}^-$.[12] Such a marked decrease in the HOMO energy was not seen in other azaphenalenyl anions, indicating the exceptionally higher stability of HAP anion $\mathbf{3}^-$ among the phenalenyl anions.

X-ray crystal structure analysis showed that HAP anion $\mathbf{3}^-$ possessed high planarity and nearly D_{3h} symmetry (Figure 2a).[14] The atoms of the phenalenyl skeleton deviated by only ±0.015(2) Å from the least-squares plane. The bond equalization observed in the carbon−nitrogen bonds [1.333(3)−1.350(2) Å] in the phenalenyl skeleton is experimental evidence of charge delocalization (Figure 2b). The HAP anions $\mathbf{3}^-$ were uniformly stacked along the *c* axis with an interplanar distance of about 3.4 Å, nearly equal to the van der Waals contact of the two HAP planes. Such a $\pi-\pi$ stacking has never been reported for the metal complexes of **1**,[3,4] except for its analogues with substantial modifications in the structure and π network.[15] The neighboring HAP

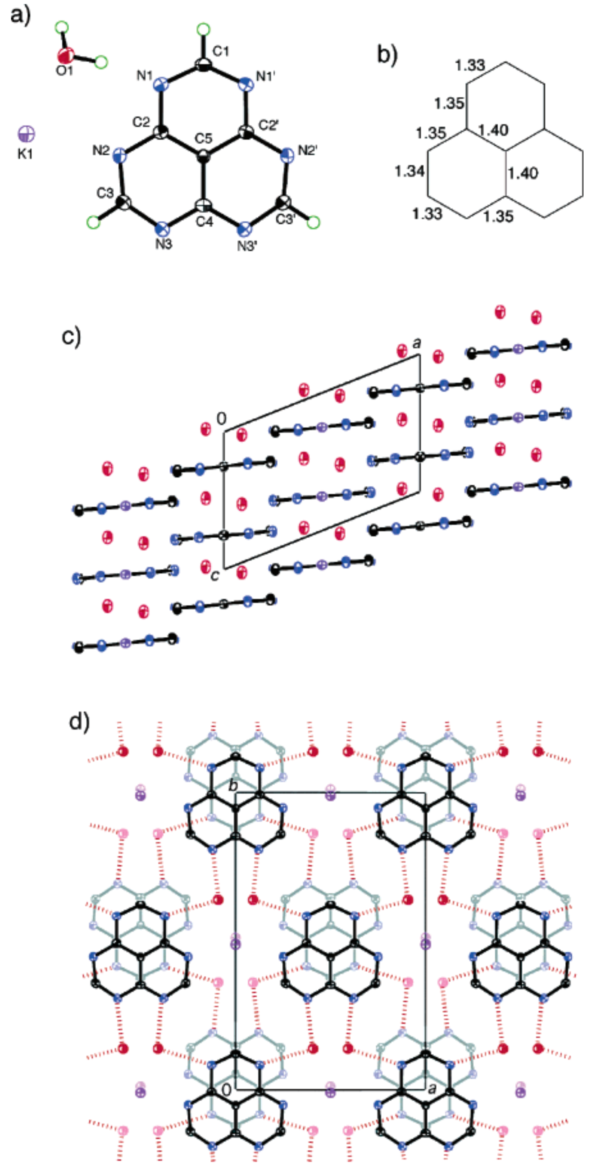

Figure 2. ORTEP representations for $K^+\cdot\mathbf{3}^-$: (a) top view; (b) selected bond length (Å). Packing diagrams in (c) the *ac* plane and (d) the *ab* plane: C, gray; N, blue; O, red; K, purple; hydrogen bond, orange dashed line. The light-colored molecular framework belongs in the next sheet of the forefront network. The hydrogen atoms are omitted for clarity.

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(9) Selected physical data: $K^+\cdot\mathbf{3}^-$: mp >300 °C; ^1H NMR (D_2O, 270 MHz) δ 8.67 ppm (s, 3H); ^{13}C NMR (D_2O, 270 MHz) δ 108.5, 165.0, 166.2 ppm; IR (KBr) 1599, 1519, 1310, 1241 cm^{-1}; UV (KBr) 306, 220 nm. Anal. Calcd for $K\cdot C_7H_3N_6\cdot 2H_2O$: C, 34.14; H, 2.87; N, 34.13. Found: C, 34.27; H, 2.81; N, 34.04.

(10) The synthetic method of $K^+\cdot\mathbf{3}^-$ was also reported in Tomlin's Ph.D. Thesis; see ref 8. However, the data of the product (especially IR spectral data) were significantly different from our data of $K^+\cdot\mathbf{3}^-$.

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(12) The CV measurement also suggested that HAP radical $\mathbf{3}^\bullet$ was an unstable species, giving irreversible oxidation waves. For details, see the Supporting Information.

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(14) X-ray structure analysis for $K^+\cdot\mathbf{3}^-$ was performed at 200 K: $K\cdot C_7H_3N_6\cdot 2H_2O$, crystal dimensions 0.20 × 0.35 × 0.10 mm, colorless, Rigaku RAXIS−RAPID imaging plate diffractometer, Mo Kα radiation, monoclinic, space group *C*2/*c* (No. 15), $a = 10.2649(6)$ Å, $b = 14.924(1)$ Å, $c = 6.6971(3)$ Å, $\beta = 111.818(2)°$, $V = 952.5(1)$ Å^3, $Z = 4$, $\rho_{calc} = 1.717$ $g\cdot cm^{-3}$, 4104 reflections collected, 1129 unique intensity reflections observed [$I > 2.00\sigma(I)$], $2\theta_{max} = 55.0°$, structure solution with direct methods (SHELXS-86) and refinement on *F* with 75 parameters, R1 (wR2) = 0.041 (0.131), *S* (GOF) = 1.17.

columns were linked with each other by hydrogen bonds through water molecules [N−O distances: 2.823(2) and 2.911(2) Å], constructing a three-dimensional structure (Figure 2c,d). The potassium ions were located in a vacant channel surrounded by water molecules and formed a one-dimensional chain structure along the *c* axis with a potassium−potassium distance of about 3.4 Å (Figure 2d).[16]

The characteristic feature of the highly stable HAP anion $\mathbf{3}^-$ with the ability of hydrogen bonding and $\pi-\pi$ interaction meets the design criteria of a building block for a self-assembled metal complex with cooperative multiple-networking structure. A copper(II) complex of HAP anion $\mathbf{3}^-$ was synthesized by mixing a methanol−aqueous ammonia solution of $H^+\cdot\mathbf{3}^-$ with a methanol solution of $Cu(OAc)_2$. We obtained the complex $Cu^{2+}\cdot(NH_3)_4\cdot(\mathbf{3}^-)_2$ as purplish-blue crystals (Figure 3).[17,18] X-ray structure analysis showed that two HAP anions $\mathbf{3}^-$ are coordinated by a copper atom and are located at the trans position (Figure 3a). The Cu−N1 bond distance was 2.894(2) Å with the N1−Cu−N7 angle of 70.98(5)°. The molecular plane of HAP was perpendicular to the plane consisting of the copper and ammonia molecules. The HAP anions $\mathbf{3}^-$ were uniformly stacked along the *a* axis to form a one-dimensional columnar structure with a face-to-face distance of about 3.4 Å (Figure 3b,c). Furthermore, the neighboring columns were tightly connected with each other by multiple hydrogen bonds through the ammonia molecules coordinated to copper (N−N distances: 3.14−3.31 Å). Coexistence of all of the intermolecular bonding interactions around the HAP anion resulted in a three-dimensional network with a highly ordered structure (Figure 3b,c).[19] These results indicate that the HAP anion works as an adhesive ligand, which is suitable for in-plane networking as well as out-of-plane π stacking.

In summary, HAP anion $\mathbf{3}^-$, a rigidly planar π system with high molecular symmetry, has turned out to form uniform columnar structures with $\pi-\pi$ interactions in the crystals of the alkali-metal salt, $K^+\cdot\mathbf{3}^-$, and the copper complex, $Cu^{2+}\cdot(NH_3)_4\cdot(\mathbf{3}^-)_2$. The unique directionality of the lone-pair electrons at the six nitrogen sites gives rise to the radially extended mode in multiple hydrogen and metal-coordination bonds.[20] Now that the synthetic accessibility and potential applicability of the HAP anion have been demonstrated, the ligand can serve as a testing ground for various self-assembled metal complexes with highly integrated organic−inorganic composites.

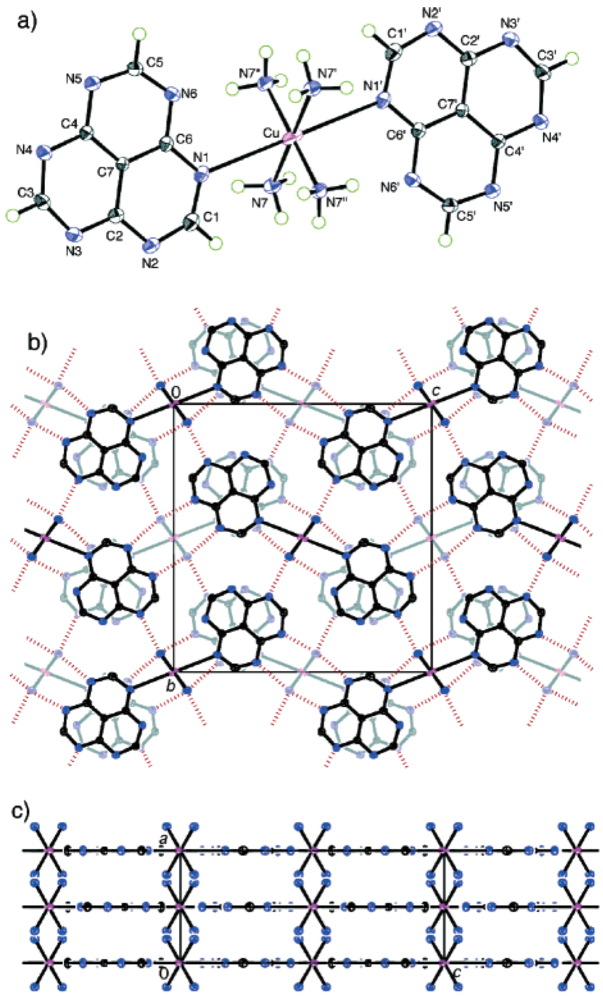

Figure 3. ORTEP representation of $Cu^{2+}\cdot(NH_3)_4\cdot(\mathbf{3}^-)_2$: (a) molecular structure. Packing diagrams in (b) the *bc* plane and (c) the *ac* plane: C, gray; N, blue; Cu, purple; hydrogen bond, orange dashed line. The light-colored molecular framework belongs in the next sheet of the forefront network. The hydrogen atoms are omitted for clarity.

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Supporting Information Available: Synthetic procedures of $H^+\cdot\mathbf{3}^-$, $K^+\cdot\mathbf{3}^-$, and $Cu^{2+}\cdot(NH_3)_4\cdot(\mathbf{3}^-)_2$ and X-ray data in CIF format for $K^+\cdot\mathbf{3}^-$ and $Cu^{2+}\cdot(NH_3)_4\cdot(\mathbf{3}^-)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) We have also succeeded in isolation and crystal structure determination of $Li^+\cdot\mathbf{3}^-$, $Na^+\cdot\mathbf{3}^-$, $Cs^+\cdot\mathbf{3}^-$, and $NH_4{}^+\cdot\mathbf{3}^-$, which will be reported elsewhere.

(17) The copper crystal $Cu^{2+}\cdot(NH_3)_4\cdot(\mathbf{3}^-)_2$ immediately changed to a vivid greenish-blue solid at room temperature when we separated it from the mother liquid. Elemental analysis data suggested that the two ammonia molecules were released. Thus, it is difficult to clarify the physical properties of the copper crystal $Cu^{2+}\cdot(NH_3)_4\cdot(\mathbf{3}^-)_2$. Anal. Calcd for $Cu\cdot(NH_3)_2\cdot(C_7H_3N_6)_2$: C, 38.23; H, 2.75; N, 44.58. Found: C, 38.01; H, 2.75; N, 44.30.

(18) X-ray structure analysis for $Cu^{2+}\cdot(NH_3)_4\cdot(\mathbf{3}^-)_2$ was performed at 150 K: $Cu\cdot(NH_3)_4\cdot(C_7H_3N_6)_2$, crystal dimensions 0.80 × 0.10 × 0.05 mm, colorless, Rigaku MSC mercury CCD diffractometer, Mo Kα radiation, orthorhombic, space group *Cmca* (No. 64), $a = 6.818(1)$ Å, $b = 16.535(3)$ Å, $c = 15.868(3)$ Å, $V = 1789.0(6)$ Å^3, $Z = 4$, $\rho_{calc} = 1.76$ g·cm^{-3}, 8981 reflections collected, 1113 unique intensity reflections observed [$I > 2.00\sigma(I)$], $2\theta_{max} = 55.0°$, structure solution with direct methods (SIR92) and refinement on *F* with 971 parameters, R1 (wR2) = 0.036 (0.095), *S* (GOF) = 1.18.

(19) We have also succeeded in isolation and determination of the crystal structure of the Ni(II) complex of $\mathbf{3}^-$. The hexaazaphenalenyl anion acts as a spacer and counteranion of the $Ni^{2+}\cdot(NH_3)_4\cdot(H_2O)_2$ ion and forms a columnar structure. The details will be reported elsewhere.

(20) We have clarified the pK_a values for $H^+\cdot\mathbf{3}^-$ in terms of pH-dependent electronic spectra. See the Supporting Information.