Et_3N/THF/0 °C; 3. $NaBH_4$/EtOH/0 °C; 4. MsCl/Et_3N/CH_2Cl_2/0 °C), followed by coupling (K_2CO_3/DMSO/RT) with 1-ethylthymine.

[10] The L.1-Me base pairs corresponding to **8b** and **9b** were also subjected to X-ray structure analyses; their structural characteristics were found to be very similar to those observed for **8b** and **9b**, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-114659 (**8b**) and CCDC-114660 (**9b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] For example, see: *Nucleic Acids in Chemistry and Biology,* 2nd ed. (Eds.: G. M. Blackburn, M. J. Gait), Oxford University Press, Oxford, **1996**, p. 21.

[12] For reviews on dynamic NMR spectroscopy, see: E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**, p. 502, and references therein.

[13] This transformation was carried out in six steps: 1. coupling (K_2CO_3/DMSO/RT) of **6** (R = Ac) with mesylated **5**; 2. $SnCl_2$/EtOH/RT → 70 °C; 3. AOC-OBT/py/RT; 4. NH_3/MeOH/RT; 5. DMTr-Cl/$AgNO_3$/py/THF/RT; 6. ClP(N*i*Pr$_2$)(OCH$_2$CH$_2$CN)/NE*t*iPr$_2$/CH_2Cl_2/RT. AOC = allyloxycarbonyl, BT = benzotriazole.

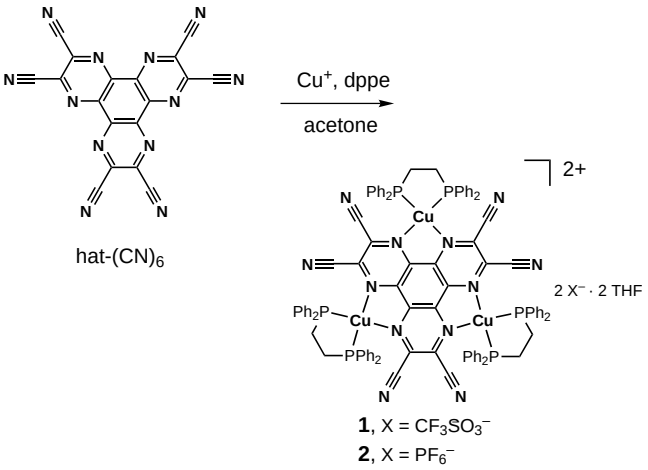
[14] The dinucleotide **11** was prepared from 5′-*O*-(*tert*-butyldimethylsilyl)thymidine 3′-*O*-(allyl-*N*,*N*-diisopropylphosphoramidite) and 3′-*O*-*tert*-butyldimethylsilyl-N^6-alloxycarbonyl-2′-deoxyadenosine in two steps: 1. 1*H*-tetrazole/MeCN/RT; 2. *t*BuCO$_2$H/CH_2Cl_2/RT, and then coupled (K_2CO_3/DMSO/RT) with mesylated **5**.

[15] Note added in proof (February 11, 1999): In the sense of primary hydrogen-bonding base pairing, only Watson–Crick and reversed Watson–Crick base pairings are possible for models **A** and **B**. However, it should be noted that Hoogsteen triplets such as T–AT and T–GC are envisioned for model **B**, but not for model **A**.

A New Anion-Trapping Radical Host, $[(Cu\text{-}dppe)_3\{hat\text{-}(CN)_6\}]^{2+}$ **

Takashi Okubo, Susumu Kitagawa,* Mitsuru Kondo, Hiroyuki Matsuzaka, and Tomohiko Ishii

Hexaazatriphenylene hexacarbonitrile, hat-$(CN)_6$, is expected to act as a unique multidentate ligand because the characteristic electron-deficient heterocyclic core has low-lying degenerate π* orbitals. To date several metal complexes containing hat derivatives have been reported;[1, 2] however, preparation of metal complexes containing the hat-$(CN)_6$ ligand is extremely difficult because the coordination ability of the aromatic nitrogen atoms in hat-$(CN)_6$ drastically decreases due to the presence of the electron-withdrawing cyano groups. The one-electron reduction of hat-$(CN)_6$ efficiently enhances its coordinating ability, and we have been able to demonstrate this by isolating the first transition metal complexes **1** and **2** (dppe = 1,2-bis(diphenylphosphanyl)ethane), which exhibit anion-trapping behavior both in the solid state and in solution (Scheme 1).



Scheme 1. Synthesis of **1** and **2**.

Complexes **1** and **2** were prepared in a one-pot reaction of a copper(I) source ($[\{Cu(CF_3SO_3)\}_2(benzene)]$ (**1**) or $[Cu(CH_3CN)_4]PF_6$ (**2**)), hat-$(CN)_6$, and dppe in acetone. The hat-$(CN)_6$ ligand is reduced by the copper(I) ion in the solution, affording the corresponding $[hat\text{-}(CN)_6]^-$ ion. This anion can also be prepared electrolytically. The crystal structures of **1** and **2** have been determined by X-ray crystallography.[3]

The cation in **1** has a trinuclear structure in which the unique sixdentate anion radical ligand $[hat\text{-}(CN)_6]^{\bullet-}$ coordinates to three Cu-dppe fragments (Figure 1). A similar

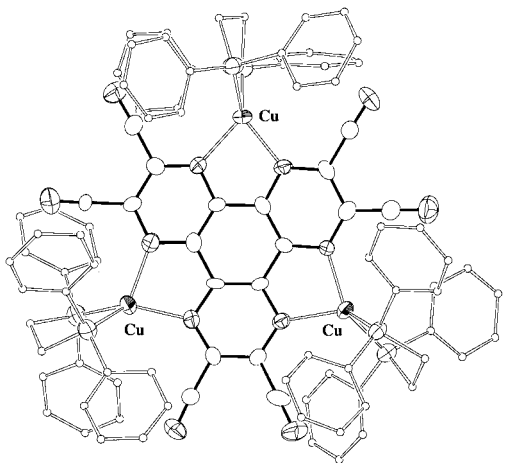


Figure 1. ORTEP view of the cationic moiety of **1** with thermal ellipsoids at 50 % level for Cu, P, C, and N atoms. All the hydrogen atoms are omitted for clarity. Ellipsoids of the carbon atoms in phenyl groups have been arbitrarily reduced for clarity.

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trinuclear structure is found in **2**. Although the molecular structures for **1** and **2** slightly deviate from D_{3h} symmetry, all the copper(I) ions have intrinsically a similar distorted tetrahedral environment with a N_2P_2 chromophore. The ESR spectra for both complexes at 77 K show one similar resonance due to a typical organic radical. The obtained g value of 1.998 is less than that of a free electron (2.002). A similar feature has been observed for metal complexes containing anion radical ligands.[4] Anisotropic spectra at low temperature display features characteristic of the axial symmetry; the $g_{\parallel}$ and $g_{\perp}$ values estimated from the spectrum at 5.4 K are 1.970 and 2.002, respectively. The UV spectrum of **2** in acetone shows an intense absorption (dark green; 712 nm ($\varepsilon = 19600$)) with a shoulder at about 770 nm derived from the radical $[hat\text{-}(CN)_6]^{\bullet -}$. The thin-layer cyclic voltammogram[5] of **2** in THF shows multiredox couples at $E_{1/2} = +0.47$, $+0.18$, -0.16, and -0.91 V (vs. SCE), which are assigned to $[hat\text{-}(CN)_6]^0/[hat\text{-}(CN)_6]^-$, $[hat\text{-}(CN)_6]^-/[hat\text{-}(CN)_6]^{2-}$, $[hat\text{-}(CN)_6]^{2-}/[hat\text{-}(CN)_6]^{3-}$, and $[hat\text{-}(CN)_6]^{3-}/[hat\text{-}(CN)_6]^{4-}$, respectively. Thus, the compound hat-$(CN)_6$ is in the one-electron-reduced $[hat\text{-}(CN)_6]^{\bullet -}$ state at the resting potential ($+0.27$ V). Notably the coordination of the copper(I) ions induces the positive shift of the redox waves, which results in the formation of a stable radical complex.

The trapping of molecules by synthetic receptors[1, 6, 7] is one of the most attractive areas of study in the field of host–guest chemistry, and the complexation of anions has recently been recognized and developed as a new area of coordination chemistry.[1, 7] The anion trapping behavior of the cationic moiety $[(Cu\text{-}dppe)_3\{hat\text{-}(CN)_6\}]^{2+}$ in the complexes **1** and **2** is well-illustrated by CPK representations such as that shown for **1** in Figure 2. Six phenyl groups of the three dppe ligands

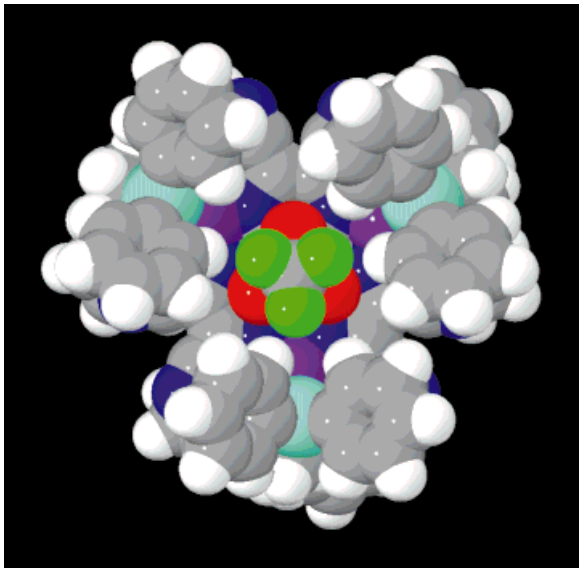

Figure 2. The anion trap structure **1** depicted as a CPK representation (top view). Color code: C: gray, H: white, N: blue, Cu: purple, F: green, O: red, P: sky blue.

create concave cavities on each side of the planar $[hat\text{-}(CN)_6]^-$ unit, into which the $CF_3SO_3^-$ ions are effectively trapped. The inclusion occurs on both sides of the cation. Compound **2** has essentially the same anion trapping structure in the solid state.

The anion radical ligand $[hat\text{-}(CN)_6]^{\bullet -}$ in **2** facilitates the evaluation of the host–guest interaction in solution by conventional NMR techniques. The ^{31}P NMR resonance for the PF_6^- ion of $(n\text{Bu}_4\text{N})PF_6$ and **2** in $CDCl_3$ at room temperature is given in Figures 3a and 3b, respectively. Figure 3b

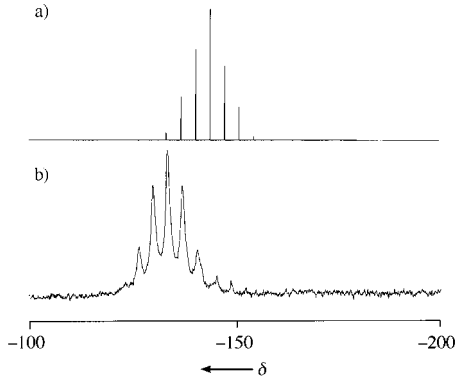

Figure 3. ^{31}P NMR spectra at room temperature for $(n\text{Bu}_4\text{N})PF_6$ (a) and **2** (b) in $CDCl_3$ solution.

shows an extremely broad signal at $\delta = -134.1$ (septet $J(^{19}F,^{31}P) = 713 \pm 10$ Hz), which is shifted downfield relative to that for the free PF_6^- ion (Figure 3a). Due to the absence of a direct bonding interaction between the radical center and the counteranion PF_6^-, the temperature-dependence of the chemical shift is simply accounted for by the paramagnetic effect (pseudo-contact term; $\delta_{pseudo\text{-}con}$).[8] On the basis of Equation (1),[9] the separation between the hat-$(CN)_6$ center and the observed nucleus was estimated to be 3.3 Å. The separation is quite similar to the distance (3.9 Å) estimated from the crystal structure analysis, which clearly indicates that the anion sits in a position so close to the hat-$(CN)_6$ ligand that the electronic-nuclear spin magnetic interaction operates effectively. Thus, the PF_6^- ion is well-trapped in the positively charged concave cavities, even in solution.[10]

Experimental Section

All operations were carried out under an argon atmosphere by using standard Schlenk techniques. $(n\text{Bu}_4\text{N})BF_4$ was used as a supporting electrolyte with a saturated calomel electrode (SCE) as the reference electrode. H_3PO_4/D_2O (85:15) at 23 °C was used as an external shift reference for the ^{31}P NMR spectroscopy.

The compound hat-$(CN)_6$ was prepared according to literature procedures[11] from diaminomaleonitrile and hexaoxocyclohexane.

A solution of dppe (1.168 g, 2.93 mmol) in acetone (10 mL) was added to a solution of $[\{Cu(CF_3SO_3)\}_2(benzene)]$[12] (0.740 g, 1.47 mmol) in acetone, and the mixture was then added to a solution of hat-$(CN)_6$ (0.282 g, 0.73 mmol) in acetone (20 mL). The reaction mixture immediately turned dark green, the color attributed to the formation of $[hat\text{-}(CN)_6]^-$ ion. This indicated that hat-$(CN)_6$ was reduced by the copper(I) ion. Addition of MeOH (150 mL) to the resultant dark green solution precipitated microcrystals, which were recrystallized from THF/hexane to give dark green crystals (52%). Elemental analysis calcd for $C_{98}H_{72}Cu_3F_6N_{12}O_6P_6S_2$ (%): C 56.91, H 3.51, N 8.13; found: C 55.92, H 3.64, N 7.93.

Compound **2** was prepared in a similar way to compound **1**, except that $[Cu(CH_3CN)_4](PF_6)$[13] was used as the starting material. All other operations for this species were carried out using the same method as for compound **1**. Elemental analysis calcd for $C_{96}H_{72}Cu_3F_{12}N_{12}P_8$ (%): C 55.97, H 3.52, N 8.16; found: C 55.91, H 3.57, N 7.92.

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The complex **2** was also synthesized electrolytically. The compound hat-$(CN)_6$ was reduced in acetone at -0.3 V (vs. SCE) in a 100 mL electrolysis cell, in which $(n\mathrm{Bu}_4\mathrm{N})\mathrm{PF}_6$ was used as the supporting electrolyte. The resultant green solution was added to a solution of $[\mathrm{Cu}(\mathrm{CH}_3\mathrm{CN})_4]\mathrm{PF}_6$ and dppe in acetone. The product corresponded to that obtained from the direct mixing of hat-$(CN)_6$, $[\mathrm{Cu}(\mathrm{CH}_3\mathrm{CN})_4]\mathrm{PF}_6$, and dppe.

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[1] J.-M. Lehn *Supramoleculer Chemistry*, VCH, Weinheim, **1995**.
[2] a) P. Baxter, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem.* **1993**, *105*, 92; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 69 – 71; b) V. J. Catalano, W. E. Larson, M. M. Olmstead, H. B. Gray, *Inorg. Chem.* **1994**, *33*, 4502 – 4509; c) T. J. Rutherford, O. Van Gijte, A. Kirsch-De Mesmaeker, F. R. Keene, *Inorg. Chem.* **1997**, *36*, 4465 – 4474; d) C. Moucheron, A. Kirsch-De Mesmaeker, *J. Am. Chem. Soc.* **1996**, *118*, 12834 – 12835; e) F. R. Keene, *Chem. Soc. Rev.* **1998**, *27*, 185 – 193.
[3] The data collections for **1** and **2** were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromatic $\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation. The data for **1** and **2** were collected at a temperature of $-30\,^{\circ}\mathrm{C}$ to a maximum 2θ value of 51.4 and 51.3°, respectively. A total of 12 and 14 oscillation images (6.00°) were collected, each being exposed for 8.0 and 18.0 min, respectively. A total of 9858 and 9073 reflections, respectively, were collected. The linear absorption coefficients, μ, for $\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation are 7.4 and 8.0 cm^{-1}, respectively. The data were corrected for Lorentz and polarization effects. Crystal data for **1**: $\mathrm{C}_{106}\mathrm{H}_{88}\mathrm{N}_{12}\mathrm{Cu}_3\mathrm{S}_2\mathrm{O}_8\mathrm{F}_6\mathrm{P}_6$, M_{r}=2212.53, orthorhombic, space group $P2_12_12_1$, $a=24.545(3)$, $b=26.687(1)$, $c=16.0793(8)$ Å, $V=10532(1)$ Å^3, $Z=4$, $\rho_{\mathrm{calcd}}=1.395$ g cm^{-3}, $T=-30\,^{\circ}\mathrm{C}$, $2\theta_{\mathrm{max}}=51.4^{\circ}$, $R=0.073$, $R_{\mathrm{w}}=0.071$. Crystal data for **2**: $\mathrm{C}_{104}\mathrm{H}_{88}\mathrm{N}_{12}\mathrm{Cu}_3\mathrm{F}_{12}\mathrm{O}_2\mathrm{P}_8$, $M_{\mathrm{r}}=2204.33$, monoclinic, space group $C2/c$, $a=28.552(2)$, $b=15.777(4)$, $c=25.298(2)$ Å, $\beta=95.006(7)^{\circ}$, $V=11352(1)$ Å^3, $Z=4$, $\rho_{\mathrm{calcd}}=1.290$ g cm^{-3}, $T=-30\,^{\circ}\mathrm{C}$, $2\theta_{\mathrm{max}}=51.3^{\circ}$, $R=0.093$, $R_{\mathrm{w}}=0.135$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-107042 (**1**) and 107044 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[4] a) S. Ernst, P. Hänel, J. Jordanov, W. Kaim, V. Kasack, E. Roth, *J. Am. Chem. Soc.* **1989**, *111*, 1733 – 1738; b) W. Kaim, S. Kohlmann, *Inorg. Chem.* **1986**, *25*, 3442 – 3448; c) W. Kaim, S. Ernst, S. Kohlmann, P. Welkerling, *Chem. Phys. Lett.* **1985**, *118*, 431 – 434.
[5] K. Unoura, A. Iwase, H. Ogino, *J. Electroanal. Chem.* **1990**, *295*, 385 – 392.
[6] D. L. Caulder, R. E. Powers, T. N. Parac, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1940 – 1943; *Angew. Chem. Int. Ed.* **1998**, *37*, 1840 – 1843.
[7] a) A. Bianchi, K. Bowman-James, A. Garcia-España, *Supramolecular Chemistry of Anions*, VCH, New York, **1997**; b) P. D. Beer, D. Hesek, J. E. Kingston, D. K. Smith, S. E. Stokes, M. G. B. Drew, *Organometallics* **1995**, *14*, 3288; c) P. D. Beer, A. R. Graydon, A. O. M. Johnson, D. K. Smith, *Inorg. Chem.* **1997**, *36*, 2112 – 2118; d) K. T. Holman, M. M. Halihan, S. S. Jurisson, J. L. Atwood, R. S. Burkhalter, A. R. Mitchell, J. W. Steed, *J. Am. Chem. Soc.* **1996**, *118*, 9567 – 9576; e) S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa, M. Munakata, *Inorg. Chem.* **1995**, *34*, 1455 – 1465; f) J. S. Fleming, K. L. V. Mann, C.-A. Carraz, E. Psillakis, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Angew. Chem.* **1998**, *110*, 1315 – 1318; *Angew. Chem. Int. Ed.* **1998**, *37*, 1279 – 1281.
[8] a) G. N. LaMar, J. W. D. Horrocks, R. H. Holm, *NMR of Paramagnetic Molecules*, Academic Press, New York, **1973**; b) I. Bertini, C. Luchinat, *NMR of Paramagnetic Molecules in Biological Systems*, The Benjamin/Cummings Publishing Company, Menlo Park, **1986**.
[9] The pseudo-contact term; $\delta_{\mathrm{pseudo\text{-}con}}$ is represented by Equation (1), where β, k, and S have the usual meaning, while R is a distance between a paramagnetic center and the observed nucleus, and θ is an angle between the molecular principal axis and the R vector. The R value was calculated to be 3.31 Å by using the slope of a linear plot of the observed chemical shift for PF_6^- against T^{-1}, and the anisotropic g values obtained from the ESR spectrum at 5.4 K.

$$\delta_{\mathrm{pseudo\text{-}con}}=\beta^2S(S+1)/9kTR^3(1-3\cos^2\theta)\,(g_{\parallel}^2-g_{\perp}^2) \qquad (1)$$

[10] Similar trapping behavior ($\delta=-133.3$ at room temperature) for the PF_6^- ion was observed in benzene, while the anion release occurs in acetone, in which relatively sharp signals centered at $\delta=-143.6$, close to that of free PF_6^-, were observed.
[11] a) J. T. Rademacher, K. Kanakarajan, A. W. Czarnik, *Synthesis* **1994**, 378 – 379; b) K. Kanakarajan, A. W. Czarnik, *J. Heterocycl. Chem.* **1988**, *25*, 1869 – 1870; c) J. C. Beeson, L. J. Fitzgerald, J. C. Gallucci, R. E. Gerkin, J. T. Rademacher, A. W. Czarnik, *J. Am. Chem. Soc.* **1994**, *116*, 4621 – 4622.
[12] This reagent was purchased from Aldrich Chemical Co.
[13] a) P. Hemmerich, C. Sigwart, *Experientia* **1963**, *15*, 448; b) G. Kubas, *Inorg. Synth.* **1979**, *19*, 90.

Noncovalent Assembly of a Fifteen-Component Hydrogen-Bonded Nanostructure

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The design and synthesis of molecules that contain all the necessary information to organize themselves spontaneously into well-defined finite nanostructures provides one of the most important challenges in supramolecular chemistry.[1, 2] Strong coordinative and much weaker hydrogen bonds are possible interactions that can drive the assembly process. The reversible formation of helicates,[3, 4] grids,[5] cages,[6, 7] metallodendrimers,[8] or hydrogen-bonded rosettes,[9, 10] capsules,[11] spheres,[12] dendrimers,[13, 14] polymers,[15] and other architectures[16, 17] has been realized over the past decade. The major difficulty in this area is to control the assembly process whilst increasing the structural complexity of the assembly.[18–20]

We have previously reported the formation of assembly $\mathbf{1}_3\cdot(\mathrm{DEB})_6$ (DEB = 5,5-diethylbarbituric acid) that is held together by 36 hydrogen bonds.[21] We are currently investigating the formation of supramolecular libraries of noncovalent assemblies,[22] with the long-term objective of this work being to develop self-assembled nanostructures with binding properties that mimic those of natural antibodies.[23] Therefore, we have now investigated the assembly of tetramelamine derivatives **2**, in which two calix[4]arene units are covalently connected through a flexible linker X, with four equivalents of DEB. Variation of the size and chemical nature of the connector unit X creates chemical diversity in the resulting

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