

Halide and Nitrite Recognizing Hexanuclear Metallacycle Copper(II) Pyrazolates

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Halide-centered hexanuclear, anionic copper(II) pyrazolate complexes [*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆X]⁻, X = Cl, Br, I are isolated in a good yield from the redox reaction of the trinuclear copper(I) pyrazolate complex [*μ*-Cu₃((3,5-CF₃)₂pz)₃] with a halide source such as PPh₃AuCl or [Bu₄N]X, X = Cl, Br, or I, in air. X-ray structures of the anion-centered hexanuclear complexes show that the six copper atoms are bridged by bis(3,5-trifluoromethyl)pyrazolate and hydroxyl ligands above and below the six copper atom plane. The anions are located at the center of the cavity and weakly bound to the six copper atoms in a *μ*₆-arrangement, Cu–X = ~3.1 Å. A nitrite-centered hexanuclear copper(II) pyrazolate complex [*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆(NO₂)⁻] was obtained when a solution of [PPN]NO₂ in CH₃CN was added dropwise to the trinuclear copper(I) pyrazolate complex [*μ*-Cu₃((3,5-CF₃)₂pz)₃] dissolved in CH₃CN, in air. Blue crystals are produced by slow evaporation of the acetonitrile solvent. The X-ray structure of [PPN][*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆(NO₂)] complex shows the nitrite anion sits in the hexanuclear cavity and is perpendicular to the copper plane with a O–N–O angle of 118.3(7)°. The ¹⁹F and ¹H NMR of the pyrazolate ring atoms are sensitive to the anion present in the ring. Anion exchange of the NO₂⁻ by Cl⁻ can be observed easily by ¹H NMR.

Introduction

Anion encapsulation by metallacycles and the relevance of this chemistry to biology, molecular magnetism, and various spectroscopies has attracted much attention.¹ Several transition metal complexes are capable of forming metallacycles

via anion template reactions. Known examples are the halide-centered complexes of silver, copper, cadmium, mercury, molybdenum, and lanthanides.² Metal based coordination polyhedra, with a halide at the center of the metal cluster; include planar, tetrahedral, octahedral, and cubic arrangements of the metal atoms.

Mercury(II) based metallacycles act as hosts for anions, and the recognition of these anions results in an extended stacked chain or a centered halide complex.³ The copper(II) pyrazolate polymer [Cu(pz)₂·H₂O]_n also shows electrophilic features, and possesses interesting properties such as the adsorption of small molecules with Lewis acid character.⁴ Several copper(II) pyrazolates are known to carry out efficient oxidation reactions.⁵ Triangular copper(II) pyrazolate complexes can accommodate *μ*³-bridging halides, and the

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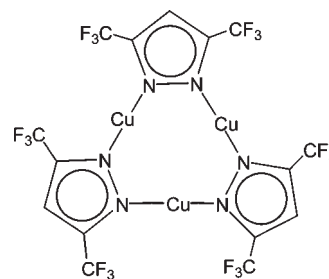
controlled interchange of these anions brings about an orderly transition from antiferromagnetic to ferromagnetic exchange among the copper centers.⁶

The chemistry of copper assemblies is reminiscent of our work on the halide- and sulfide-centered cubal copper(I) dialkyldithiophosphate ligands.⁷ A high purity synthesis of chloride- $[\{Cu_8[S_2P(O^iPr)_2]_6(\mu_8-Cl)\}]PF_6$ and bromide- $[\{Cu_8[S_2P(O^iPr)_2]_6(\mu_8-Br)\}]PF_6$ centered Cu_8 cubal clusters was achieved by the reaction of $[Cu(CH_3CN)_4]PF_6$ and $NH_4[S_2P(O^iPr)_2]$ in the presence of $[BzEt_3N]X$ ($X = Cl$ or Br) in tetrahydrofuran (THF). The nearly perfect $Cu(I)_8$ cube encapsulates the closed shell ions Cl^- or Br^- .⁷ This work has led to some elegant further studies by Liu et al.⁸

Several metal acyclic copper(II) pyrazolates have been synthesized such as $[Cu_x(OH)_x(pz)_x]$, where $x = 6, 8, 9, 12, 14$; chlorides and other anions were found sandwiched between these high nuclearity copper(II) metallacycles.⁹ Halide-centered copper(II) clusters, however, are less well-known. A cage-type hexanuclear $Cu(II)$ complex $[Cu_6(MeO)_2(pz)_9Cl]$ was reported to form via a chloride ion template reaction.¹⁰ The chloride ion is located at the center of the Cu_6 trigonal prism with a μ_6 -mode of bonding. This synthetic procedure was not successful for the synthesis of the larger bromide or iodide centered clusters.

Copper(II) nitrite complexes are of interest to the understanding the reaction mechanism of copper-containing nitrite reductases.¹¹ The nitrite anion $[NO_2]^-$ has been proposed as a major storage pool of bioactive nitric oxide under reduced oxygen conditions in mammals.¹² The crystal structures of the nitrite adducts of cytochrome *cd1* NiR,¹³ cytochrome *c* NiR,¹⁴ and sulfite reductase (SiR) heme protein¹⁵ clearly

Chart 1. Representation of the Trinuclear Copper(I) Pyrazolate Starting Material



reveal the *N*-nitro binding mode of the nitrite. Recently, there has been interest in nitrite-bridged polynuclear complexes associated with the study of the sign and strength of the magnetic interactions mediated by their different bridging modes.¹⁶

It appears that the synthesis of halide-centered clusters is somewhat sensitive to the electronic and steric features of the ligands (vide infra). A preliminary report of the X-ray structure and magnetic properties of the chloride-centered anionic cluster $[trans-Cu_6((3,5-CF_3)_2pz)_6(OH)_6Cl]^-$ with the cation $[Au(PPh_3)_2]^+$ was published.¹⁷ Here we report the syntheses and structures of hexanuclear, anionic copper(II) hydroxyl pyrazolate clusters with Cl^- , Br^- , and I^- centers as well as nitrite. The polyhedral coordination with the chloride at the center of the planar cavity as synthesized with $Au(PPh_3)Cl$ was the first in copper chemistry. Hence we were interested in the generality of the anionic structures produced. Our approach has utilized oxidation of the trinuclear $Cu(I)$ complex of the 3,5-bis(trifluoromethyl)pyrazolate ligand, sketch in Chart 1, with molecular oxygen to form the halide and nitrite centered copper(II) clusters.

Experimental Section

General Procedures. Solvents were purchased from Aldrich Co. and used as received. The starting complex $[Cu(3,5-(CF_3)_2pz)]_3$ was prepared as described.¹⁸ The Hewlett-Packard 1100 MSD mass spectrometer was used in all the analyses involving Atmospheric Pressure Chemical Ionization (APCI) or Electro Spray Ionization (ESI). The experimental conditions were as follows: the organic phase flow was 300 $\mu L/min$, the drying gas flow (N_2) was 10 L/min, the nebulization pressure was 30 psig, the temperature of the drying gas was 350 $^\circ C$, the capillary potential was 4000 V, the value for the fragmentor was fixed to 30, the acquisition of the data was performed by scanning in ranges from 100 to 1500 amu and from 1400 to 3000 amu. Complexes **1–5** were characterized by APCI/ESI MS by dissolving the analytical samples in HPLC grade acetonitrile. Elemental analyses were carried out with a Carlo Erba 1106 elemental microanalyzer. For the IR spectra a Perkin-Elmer Spectrum One System Instrument was used. One must cautiously interpret the NMR results since chloride exchanges with the central anions in these complexes (vide infra).

NMR Measurements. Both (pzC-H) proton and (pzCF₃) fluorine NMR measurements of **2–5** were made in acetone-*d*⁶ at room temperature. In addition a ¹H NMR study of a sample

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of **5** with added tetrabutylammonium chloride was performed. The chloride exchanges completely for the nitrite with both signals clearly observed at molar ratios below one of added chloride. This data is presented in the Supporting Information.

Synthesis of [Au(PPh₃)₂][*trans*-Cu₆((CF₃)₂pz)₆(OH)₆Cl], **1.** The corrected synthesis to the one reported in the communication¹⁷ uses the following amounts of materials: To stirred wet CH₃CN solution (4 mL) of [Cu(μ -3,5-(CF₃)₂pz)]₃ (0.1221 g), Ph₃PAuCl (0.0377 g; 0.076 mmol) and Ph₃P (0.020 g) were added.

Synthesis of [Bu₄N][*trans*-Cu₆((CF₃)₂pz)₆(OH)₆X], X = Cl (2**), Br (**3**), I (**4**).** A 30 mg portion of [Cu(3,5-CF₃)₂pz]₃ (0.0375 mmol) was stirred with [Bu₄N]Cl (5.2 mg; 0.0187 mmol), or [Bu₄N]Br (6.05 mg; 0.0187 mmol) or [Bu₄N]I (6.9 mg; 0.0187 mmol) in wet CH₃CN (4 mL) solution for 3 h. Slowly the solution became blue, and after few days blue crystals of the hexanuclear copper(II) clusters **2**, **3** and **4** were isolated.

Characterization of Compound 2. Yield 91%. Elemental analysis: Calcd for C₄₆H₄₈N₁₃F₃₆ClO₆Cu₆: C 27.91, N 9.20, H 2.44; Found: C 28.34, N 9.22, H 1.87. Mp 146.2–148.6 °C with decomposition. IR (cm⁻¹): 3653 (w), 3155 (w), 2972 (w), 2883 (w), 1609 (m), 1538 (m), 1503 (m), 1365 (m), 1255 (s), 1117 (vs), 1023 (s), 923 (m), 816 (m), 758 (m), 735 (m), 716 (m). ESI MS (acetonitrile, HPLC grade): (+) 242.4 *m/z* (100%, Bu₄N), (-) 203.1 *m/z* (100%, (CF₃)₂pz), 469.1 (18%), 648.7 (20%), 1737.2 *m/z* (100%, (Cu₆((CF₃)₂pz)₆(OH)₆Cl)). ¹H and ¹⁹F NMR (acetone-d₆, r. t.): 34.52 (s, pzC-H), -56.79 (s, pzCF₃); 3.48 (m, CH₂-N), 1.84 (m, -CH₂-), 1.45 (m, -CH₂-), 0.99 (t, CH₃-).

Characterization of Compound 3. Yield 95.6%. Elemental analysis: Calcd for C₄₆H₄₈N₁₃BrF₃₆O₆Cu₆: C, 27.30%; H, 2.39%; N, 9.00%. Found: C, 27.28%, H, 2.37%, N, 8.99%. Mp 183.4–185.6 °C with decomposition. IR (cm⁻¹): 3654 (w), 3162 (w), 2970 (w), 2880 (w), 1539 (m), 1503 (m), 1466 (w), 1366 (m), 1255 (s), 1119 (vs), 1022 (s), 928 (m), 819 (m), 760 (m), 735 (m), 718 (m). ESI MS (acetonitrile, HPLC grade): (+) 242.4 *m/z* (100%, Bu₄N), (-) 157.1 *m/z* (80%), 426 (22%), 469.0 (12%), 603.3 (100%), 1237.4 *m/z* (23%), 1737.2 *m/z* (32%, (Cu₆((CF₃)₂pz)₆(OH)₆Cl)), 1781.3 *m/z* (100%, (Cu₆((CF₃)₂pz)₆(OH)₆Br)). ¹H and ¹⁹F NMR (acetone-d₆, r. t.): 34.45 (s, pzC-H), -56.45 (s, pzCF₃); 3.47 (m, CH₂-N); 1.84 (m, -CH₂-); 1.43 (m, -CH₂-); 0.98 (t, CH₃-). UV-vis (CH₃CN, 1.5 × 10⁻⁴ M): λ_{max} 279 and 584 nm.

Characterization of Compound 4. Yield 92.4%. Elemental analysis: Calcd for C₄₆H₄₈N₁₃IF₃₆O₆Cu₆: C 26.68%, H, 2.34%, N, 8.79%. Found: C, 26.89%, H, 2.47%, N, 8.05%. Mp 145.2–146.4 °C. IR (cm⁻¹): 3650 (w), 3154 (w), 2969 (w), 2880 (w), 1538 (m), 1504 (m), 1484 (w), 1466 (w), 1366 (m), 1256 (vs), 1233 (s), 1115 (vs), 1022 (s), 929 (m), 819 (m), 759 (m), 735 (m), 716 (m). ESI MS (acetonitrile, HPLC grade): (+) 242.4 *m/z* (100%, Bu₄N), (-) 203.1 *m/z* (100%, ((CF₃)₂pz)), 648.6 (22%), 1737.2 *m/z* (100%, (Cu₆((CF₃)₂pz)₆(OH)₆Cl)), 1829.3 *m/z* (43%, (Cu₆((CF₃)₂pz)₆(OH)₆I)). UV-vis (CH₃CN, 1 × 10⁻⁴ M): λ_{max} 340 and 597 nm. ¹H and ¹⁹F NMR (acetone-d₆, r. t.): 34.39 (s, pzC-H), -55.56 (s, pzCF₃); 3.48 (m, CH₂-N); 1.84 (m, -CH₂-); 1.46 (m, -CH₂-); 0.98 (t, CH₃-).

Synthesis of PPN[*trans*-Cu₆(μ -OH)₆{ μ -(3,5-CF₃)₂pz}₆(NO₂)], **5.** The trinuclear complex [Cu(μ -3,5-(CF₃)₂pz)]₃ (0.040 g, 0.05 mmol) was dissolved in 4.5 mL of CH₃CN (HPLC grade) in air, then a solution of [PPN]NO₂ (0.030 g, 0.05 mmol in 3 mL of CH₃CN) was added dropwise. The solution became dark green. Blue crystals grew by slow evaporation of the solvent. Yield 92%. Elemental analysis: Calcd for C₆₆H₄₂N₁₄F₃₆O₈Cu₆P₂: C, 34.67%, H, 1.85%, N, 8.58%. Found: C, 35.39%, H, 1.75%, N, 8.07%. Mp 207–209 °C with decomposition. IR (cm⁻¹): 3654 (w), 3140 (w), 1591 (w), 1542 (m), 1503 (m), 1484 (w), 1442 (m), 1364 (m), 1255 (vs), 1233 (s), 1178 (m), 1163 (s), 1126 (vs), 1021 (vs), 927 (s, br), 829 (m), 821 (m), 806 (m), 759 (m), 748 (m), 724 (s), 691 (s). ESI MS (acetonitrile, HPLC grade): (+) 538.5 *m/z* (100%, PPN), (-) 203.1 *m/z* (93%, ((CF₃)₂pz)), 469.2 (100%), 735.3 (21%), 1003.3 (13%), 1535.2 (8%), 1664.3 (10%), 1737.2 *m/z* (100%,

(Cu₆((CF₃)₂pz)₆(OH)₆Cl)). UV-vis (CH₃CN, 1 × 10⁻⁴ M): λ_{max} 307 and 584 nm. ¹H and ¹⁹F NMR (acetone-d₆, r. t.): 31.46 (s, pzC-H), -57.69 (s, pzCF₃); 7.72 (m), 7.58 (m).

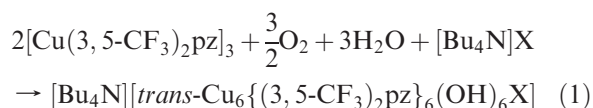
Data Collection. Data for **2** and **5** were collected using a Siemens (Bruker) SMART 1K CCD (charge coupled device) area detector based diffractometer equipped with an LT-2 low-temperature apparatus operating at 110 K for complex **2** and 213 K for **5**. Data for complexes **3** and **4** were collected using a Bruker D8 tricycles diffractometer with APEX II detector CCD based equipped with an LT-2 low-temperature apparatus operating at 110 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Cell parameters for **2** and **5** were retrieved using the SMART software and refined using SAINT on all observed reflections;¹⁹ for **3** and **4** the cell parameters were determined and refined using APEX II software on all observed reflections. For **2** and **5** data reduction was performed using the SAINT, and for **3** and **4** using APEX II software, which correct for Lp and decay.²⁰ Absorption corrections were applied using SADABS supplied by G. Sheldrick.²¹ In compounds **3** and **4**, additional face absorption corrections were done. The structures are solved by the direct method using the SHELXS-97 program and refined by least-squares method on *F*², SHELXL-97, incorporated in SHELXTL-PC V 5.03.^{22,23}

The structures of **2**, **3**, **4**, and **5** were solved by analysis of systematic absences. Hydrogen atoms were calculated by geometrical methods and refined as a riding model. The crystallographic details are listed in Table 1, and bond distances and angles are listed in Tables 2–5.

Results and Discussion

Synthesis. Several attempts have been made to synthesize high nuclearity copper pyrazolate complexes. The reaction of Cu(OH)₂ with pyrazole in presence of NaOH and a chloride source formed the chloride-centered cluster [Bu₄N][{[Cu(OH)(pz)]₆₊₁₂}₂Cl].⁹ The polymeric copper(I) complex [Cu(3,5-CH₃)₂pz]_n formed the blue octanuclear copper(II)-hydroxo cluster [Cu₈{3,5-(CH₃)₂pz}₈(OH)₈] in quantitative yield in presence of molecular oxygen.⁵ Other trials such as mixing the Cu(II) salt with pyrazole in methanol formed the chloride-centered prismatic cluster [Cu₆(CH₃O)₂(pz)₉Cl] with one methoxy group on the apex of each of the two prisms.¹⁰

By starting with a wet and aerated acetonitrile solution of the copper(I) complex [Cu(3,5-CF₃)₂pz]₃, sketch in Chart 1, and using a halide source such as Ph₃PAuCl or [Bu₄N]Cl for complexes **1** and **2**, [Bu₄N]Br and [Bu₄N]I for complexes **3** and **4**, the corresponding halide centered copper(II) complexes [*trans*-Cu₆{(3,5-CF₃)₂pz}₆(OH)₆(X)] were obtained, eq 1.



(19) SMART Software for the CCD Detector System, V 4.043; Bruker Analytical X-ray Systems: Madison, WI, 1995.

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Table 1. Crystallographic Data for [Bu₄N][*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆Cl], **2**, [Bu₄N][*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆Br], **3**, [Bu₄N][*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆I], **4**, and [PPN][*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆(NO₂)], **5**

	2	3	4	5
formula	C ₄₆ H ₄₂ ClCu ₆ F ₃₆ N ₁₃ O ₆	C ₃₀ H ₁₂ BrCu ₆ F ₃₆ N ₁₂ O ₆ C ₁₆ H ₃₆ N	C ₃₀ H ₁₂ ICu ₆ F ₃₆ N ₁₂ O ₆ C ₁₆ H ₃₆ N	C ₆₆ H ₄₂ Cu ₆ F ₃₆ N ₁₄ O ₈ P ₂
Fw	1973.62	2196.48	2240.49	2280.33
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	12.5942(17)	12.6182(17)	12.5997(16)	22.366(7)
<i>b</i> , Å	12.7607(18)	12.7454(17)	12.7588(16)	13.967(7)
<i>c</i> , Å	25.769(4)	25.807(4)	25.747(3)	29.090(12)
α , deg	93.835(2)	93.053(2)	93.777(2)	90.00
β , deg	98.987(3)	99.173(2)	98.994(2)	112.246(11)
γ , deg	91.077(2)	91.543(2)	91.077(2)	90.00
cell vol, Å ³	4079.5(10)	4088.8(10)	4077.4(9)	8411(6)
<i>Z</i>	2	2	2	4
<i>D</i> _{calc} , g cm ⁻³	1.607	1.784	1.825	1.801
wavelength	0.71073	0.71073	0.71073	0.71073
temp, K	110	110	110	213
GOF	1.015	1.035	1.068	0.989
parameters	992	1118	1076	618
R1	0.0436	0.0435	0.0682	0.0502
wR2	0.1063	0.0966	0.1380	0.1163

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex [Bu₄N][*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆Cl], **2**

Cu(1)–O(1)	1.918(2)	Cu(1)–O(2)	1.919(2)
Cu(1)–N(2)	2.005(3)	Cu(1)–N(1)	2.007(3)
O(1)–Cu(1)–O(2)	168.61(10)	O(2)–Cu(2)–O(3)	165.29(11)
N(2)–Cu(1)–O(2)	86.09(10)	N(2)–Cu(1)–O(1)	97.00(11)
N(1)–Cu(1)–O(2)	95.72(11)	N(1)–Cu(1)–O(1)	84.55(11)
N(2)–Cu(1)–N(1)	162.95(12)	Cu(1)–O(2)–Cu(2)	107.53(11)

Table 3. Selected Bond Lengths (Å) and Angles (deg) of Complex [Bu₄N][*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆Br], **3**

Cu(1)–O(1)	1.909(3)	Cu(1)–O(2)	1.913(3)
Cu(1)–N(2)	1.985(3)	Cu(1)–N(3)	2.004(3)
O(1)–Cu(1)–O(2)	167.20(11)	O(2)–Cu(2)–O(3)	166.35(12)
N(2)–Cu(1)–O(2)	95.59(13)	N(2)–Cu(1)–O(1)	85.00(13)
N(2)–Cu(1)–O(1)	85.23(12)	N(3)–Cu(1)–O(1)	97.83(12)
Cu(1)–O(2)–Cu(2)	106.46(13)	N(2)–Cu(1)–N(3)	163.54(14)

Table 4. Selected Bond Lengths (Å) and Angles (deg) of Complex [Bu₄N][*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆I], **4**

Cu(1)–O(1)	1.923(6)	Cu(1)–O(5)	1.913(6)
Cu(1)–N(1)	1.996(7)	Cu(1)–N(6)	1.998(7)
O(1)–Cu(1)–O(5)	167.3(3)	O(1)–Cu(2)–O(2)	165.1(3)
N(1)–Cu(1)–O(5)	98.2(3)	N(1)–Cu(1)–O(1)	84.6(3)
Cu(1)–O(1)–Cu(2)	106.9(3)	N(1)–Cu(1)–N(6)	163.8(3)

Table 5. Selected Bond Lengths (Å) and Angles (deg) of Complex [PPN][*trans*-Cu₆((3,5-CF₃)₂pz)₆(OH)₆(NO₂)], **5**

Cu(1)–O(1)	1.937(3)	Cu(1)–O(3)	1.927(3)
Cu(1)–N(1)	2.007(3)	Cu(1)–N(6)	2.026(3)
N(7)–O(4)	1.011(10)	N(7)–O(5)	0.991(12)
O(1)–Cu(1)–O(3)	164.35(12)	N(1)–Cu(1)–O(1)	97.90(12)
N(1)–Cu(1)–O(3)	84.66(12)	N(6)–Cu(1)–O(3)	97.90(12)
N(6)–Cu(1)–O(1)	84.74(12)	N(1)–Cu(1)–N(6)	160.99(13)
Cu(1)–O(1)–Cu(2)	108.50(12)	O(4)–N(7)–O(5)	118.3(7)

Complexes **1**, **2**, **3**, and **4** have been obtained in high yields. Blue crystals of complexes **2**, **3**, and **4** were grown at room temperature from the reaction solution in a few days. These crystals show moderate solubility in most of the organic solvents. By reacting [Cu(3,5-CF₃)₂pz]₃ complex with PPN[NO₂] (PPN = bis (triphenylphosphoranylidene)ammonium) in CH₃CN solution, blue

crystals of complex **5** were collected in 92% yield. Complexes **2–5** were characterized by elemental analysis, ESI mass spectrometry (ESI MS), ¹H NMR, UV–vis, and IR spectroscopy's. The ESI MS parent ion (Cl[−] present in ESI technique used) could be observed in each case except for **5**. Partial chloride exchange was observed for **3** and **4** while complete Cl[−] exchange apparently takes place in the ESI MS for **5**.

Molecular Structures

Crystal structures of compounds **2**, **3**, and **4** are isomorphous, Figures 1 and 2 (Tables 1–5). The structure of the anion of **1** was communicated previously, and it is virtually identical with that of **2**.¹⁷ In all compounds each unit has a core containing a hexanuclear copper(II) ring bridged by six hydroxyl groups and six pyrazolate ligands. The copper atoms exist in a distorted hexagonal planar geometry. The Cu–Cu distance in the complexes **1–5** is 3.0591(7)–3.1497(13) Å. The plane of the molecules is twisted 74.64 (1)° in compound **2**, 74.73 (1)° in compound **3**, and 74.55 (2)° in compound **4**.

In the hexanuclear copper complexes with halide in the cavity, the average Cu–X–Cu bond angle is ~60°. The average Cu–X bond distance is 3.069 Å in compound **1** (X = Cl), 3.0717 Å in **2** (X = Cl), 3.074 Å in **3** (X = Br), and 3.096 Å in **4** (X = I). These bond distances are significantly longer than the covalent ones of 2.38, 2.43, and 2.77 Å, reflecting the primarily ionic interactions between the halide and copper ions.¹ The best description of the structures is that of a halide ion encapsulated in the Cu₆ cavity. To the best of our knowledge, this is the first example of planar μ₆-halide reported in copper chemistry. It appears that halide ions place no direct constraints upon the copper geometry. The guest ions are large enough that ligand–ligand repulsion effects are to be taken as a factor in the geometry control.

The average of internal diameter inside the cavities is 6.141 Å in compound **2**, 6.147 Å in **3**, 6.191 Å in **4**, and 6.247 Å in **5**. The average height of the cavity is 7.346 Å in **2**, 7.954 Å in **3**, 7.856 Å in **4**, and 8.182 Å in **5**. Although the direction of the hydrogen atoms on the hydroxyl groups are not assigned with certainty, apparently, the anions are held in the cavity by a weak interaction with the six copper atoms and also by

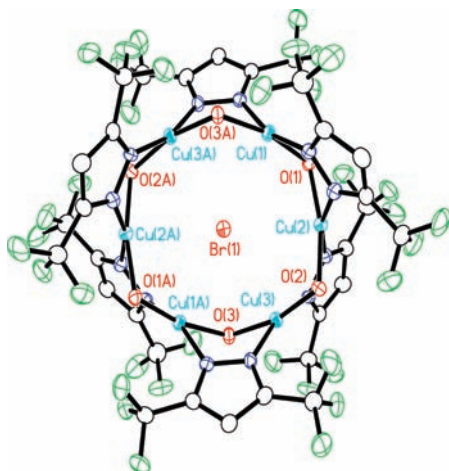


Figure 1. Top view of **3** showing the bromide anion in the center of the cavity.

weak hydrogen bonds to the hydroxyls, $X \cdots OH$ average is 3.4149 Å in compound **2** ($X = Cl$), 3.439 Å in compound **3** ($X = Br$), 3.454 Å in compound **4** ($X = I$) and 2.888 Å in compound **5** ($X = O$ from NO_2), Figure 3 and Table 5. In compounds **2**, **3**, and **4**, the cation $[Bu_4N]^+$ is partially disordered and located between the two molecules in the unit cell. Compounds **3** and **4** have two disordered hexane solvent molecules (hexane solvent was used in the crystallization of the trinuclear copper starting material) between the two molecules in the unit cell. Compound **2** also contains a disordered solvent molecule but in this case the Squeeze tool from Platon software was applied to complete the refinement. In compound **5**, the nitrogen atom of the $[NO_2]^-$ anion is at the center of the cavity and coplanar with the copper atoms. The oxygen atoms are pointing above and below the copper plane. The nitrite anion lies on special position and is disordered around the inversion center of the molecule, Figure 3.

The elasticity of the cavity allows different sizes of trapped molecules. This fact makes the copper compounds a good choice to trap various spherical and bent anions. The promotion to a higher ensemble from the $[Cu(\mu-3,5-(CF_3)_2pz)]_3$ complex in the presence of anions and air gives rise to the formation of these hexanuclear copper structures. The size and nature of the guest in the cavity determine the dimensions of the molecule, Table 6. It is observed that the cavity diameter average increases with the increase in the size of the anion; 6.141 Å (Cl^-), 6.147 Å (Br^-), 6.191 Å (I^-) and 6.247 Å (NO_2^-). Similarly, the host–guest distance also increases with the size of the anion; $Cu-Cl = 3.027$ Å, $Cu-Br = 3.073$ Å and $Cu-I = 3.095$ Å.

The nitrite anion is reported in several crystal structures bound to a metal as bidentate,²⁴ bridged,²⁵ or as terminal monodentate.²⁶ In the crystal structures of nitrite linked to a

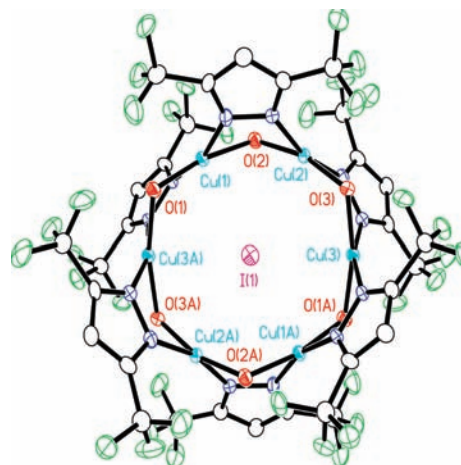


Figure 2. Top view of **4** showing the iodide anion in the center of the cavity.

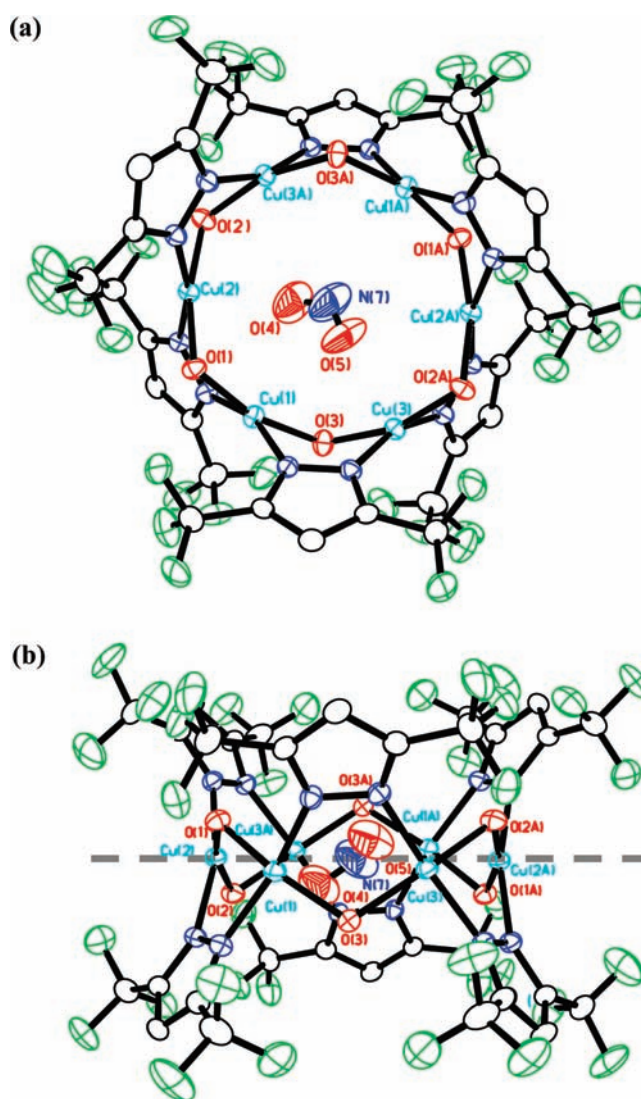


Figure 3. (a) Top and (b) side view of **5** showing the nitrite anion in the center of the cavity.

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copper atom,²⁷ the O–N–O bond angles are less than 115° as in $[Cu(dpyam)_2(ONO)]SO_4 \cdot 0.5H_2O$ ($111.7(6)^\circ$)²⁸, dpyam = 2-pyridylamine or in $[Zn(\mu-4,4'-bipy)(NO_2)_2]_n$

Table 6. Comparison of Non-Bonding Distances (Ranges) and Host–Guest Interaction in the Copper Complexes 2–5

measurements	2	3	4	5
Cu–Cu distance	3.0905(7)–3.0591(7)	3.0624(8)–3.0887(7)	3.1089(14)–3.0880(15)	3.1497(13)–3.0942(11)
diameter inside the cavity	5.9531(10)–6.3398(11)	6.3321(12)–5.9968(11)	6.3283(21)–6.0764(22)	6.1241(19)–6.3390(19)
Cu–X	2.9765(5)–3.1699(5)	3.1660(6)–2.9984(6)	3.1641(11)–3.0382(11)	<i>b</i> ^c
X–O	3.3380(25)–3.4942(24)	3.3798(26)–3.4844(26)	3.5018(57)–3.4159(59)	2.738(11)–2.965(13)
height of the cavity ^a	6.6661(37) and 8.0274(33)	8.0800(26) and 7.8298(26)	8.0629(52) and 7.6514(44)	8.1828(53)

^a Measurements for two molecules in the unit cell. ^b Disorder in the NO₂[−] anion prevents describing a meaningful Cu–X distance.

(113.8(4)°, 113.9(4)° and 113.3(4)°).²⁹ Less frequently as in **5**, the O–N–O bond angle is greater than 115° as in [L^{Py}Cu(ONO)]O₃SCF₃ (L^{Py} = 1,4-diisopropyl-7-2-pyridylmethyl-1,4,7-triazacyclononane) (115.455°)³⁰ or in [Ru(salen)(ONO)(NO)] (118.564°).³¹ These structures correspond to nitrite terminally bound or where steric and electronic effects allow greater angles. Generally, the N–O bond distance is longer than 1.1 Å. There are very few crystal structures where the N–O distance lies in the range 0.8–1.1 Å, similar to the bond distances in compound **5** (1.011(10) and 0.991(12) Å), as in compound [Cu(NO₂)₂(tpmbz)] [tpmbz = (C₅H₄N)₃CN=C(CHC₆H₅)] (0.843 Å).³²

Compound **5** is the first example of the nitrite anion at the center of the cavity of a metallacycle. Nitrite is “located within the stacks, between consecutive {Co₁₀} molecules” of a polynuclear Co(III)-pyrazolate.³³ This structure of **5** not only has relevance in the field of coordination chemistry but also has significance in biology. Nitrite has been found to act as a source of nitric oxide in biological systems.³⁴ In some copper-enzymes such as ceruloplasmin, cytochrome c oxidase, dopamine β-hydroxylase and laccase, it has been suggested that Cu(II)-NO interaction plays an important role in controlling the activity.³⁵ The laccase enzyme has four copper centers, three of them behave as a cluster binding to nitric oxide, and studies have shown that under anaerobic conditions nitrite acts as nitric oxide donor by interaction with metalloproteins.³⁶ As the nature of the intermediates in the reduction from nitrite to nitric oxide is still unknown and the presence of copper(II) is crucial, these findings indicate that the structural and chemical study of compound **5** may relate to copper nitrite bonding chemistry in biological systems.

Although the communication¹⁷ reporting the encapsulated chloride anion also presented the existence of strong antiferromagnetic coupling between the copper(II) centers,

further magnetic measurements of these new halide and nitrite clusters seemed likely to show similar magnetic results and was not performed. Magnetic influences of the essentially planar paramagnetic copper ring on the ¹H and ¹⁹F NMR chemical shifts cannot be quantified in this study. However, the chemical shifts are sensitive to the different anions present in the center of the cluster: for ¹H NMR, Cl[−], 34.52; Br[−], 34.45; I[−], 34.39; NO₂[−], 31.46 ppm; for ¹⁹F NMR, Cl[−], −56.79; Br[−], −56.45; I[−], −55.56; NO₂[−], −57.69 ppm. Bulk magnetic measurements related to the antiferromagnetic coupling between copper(II) atoms requires avoiding the presence of small amounts of chloride in the syntheses. Correlations which may exist between these proton and fluorine chemical shifts and structural and bulk magnetic properties of the complexes are not apparent from the data obtained here. However, the NMR results clearly establish the fact that anion exchange occurs (see Supporting Information). Further study should be able to examine the solution thermodynamics of the exchange process.

In the supramolecular assemblies of copper(II) complexes capable of anion encapsulation, the shortest host–guest distance is between the hydroxyl oxygen from the crown to the guest molecule.⁹ In the hexa-copper fluoro metallacycle cavities which contain ammonia derivatives and amino acids as guest molecules, the shortest host–guest distance is between the fluorine and the guest molecule.^{37,38} For assemblies with other metals the host–guest interaction also takes place independently of the nature of the metal, such as in the crown hexakis(μ₂-N-formylsalicylhydrazidato)-methanol-manganese(III) methanol solvate where the methanol molecules are trapped in the cavity by strong hydrogen bonds with oxygen atoms from the crown.³⁹

The stereochemistry of halide guests and the variations in coordination geometry that arise deserve comment. The neutral and ionic host–guest chemistry field has been developing for several years. Host molecules with a wide variety of metal crowns have been studied. The cyclic pentameric [(CF₃)₂CHg]₅ complex coordinates two halides, above and below the cavity with pentagonal pyramidal geometry at the halide anion. The infinite bent polyanionic chain {[(*o*-C₆F₄Hg)₃I]_{*n*}}^{*n*−} produced a trimeric complex [(*o*-C₆F₄Hg)₃] which coordinates the halide anions in a distorted octahedral geometry with a stoichiometric ratio of 1:1.^{3a–e}

There are a few reports of halide centered structures with planar coordination to six metal atoms held by the rigid ligand [η⁶-cyclo(PhSiO₂)₆] that bridge all the metals above and below the coordination plane. The diameter at the ligand plane is equal to or shorter than at the metal plane (for instance 5.334 Å at the top and 5.696 Å at the metal plane).⁴⁰

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The complex $\text{Na}\{\eta^6\text{-cyclo}(\text{PhSiO}_2)_6\}_2[\text{Fe}(\text{OR})_2]_2\text{Ni}_4(\mu_6\text{-Cl})$ ($\text{R} = \text{H}, \text{Me}$) has a chloride ion coordinated to two Fe(III) and four Ni(II) centers in *trans* arrangement.⁴¹ The Fe–Cl bond distances are 2.978 Å, and the Ni–Cl bond distances are 2.836 and 2.882 Å. The $\text{Na}[(\text{PhSiO}_2)_6\text{Cu}_3\text{Ni}_3(\mu_6\text{-Cl})\text{-}(\text{PhSiO}_2)_6]$ complex has the chloride coordinated to three Cu(II) and three Ni(II) centers in *trans* arrangement. The Ni–Cl bond distances are 3.126, 3.053, and 2.878 Å, and the Cu–Cl bond distances are 2.846, 2.581, and 2.529 Å.⁴² Complex $\text{Na}\{[\text{PhSiO}_2]_6\text{M}_6(\mu_6\text{-Cl})[\text{O}_2\text{SiPh}]_6\}$, $\text{M} = \text{Mn}, \text{Co}$, presents the Mn–Cl bond with distances which range 3.245–2.914 Å, and the Co–Cl bond distances range from 2.779 to 3.000 Å.⁴³ In $\text{Na}\{\eta^6\text{-cyclo}(\text{PhSiO}_2)_6\}_2\text{Co}_2\text{Ni}_4(\mu_6\text{-Cl})$ complex, the Ni–Cl bond distances range is from 2.813 to 2.942 Å.⁴⁰

There are several factors that control host–guest interactions, such as hydrogen bonding interactions between the halide guest ions and other charged counterions or neutral solvent species in the lattice, electrostatic interactions between the halide ions and their environment such as counterions, and bonding interactions with metal ions. These effects reduce the effective charge on the halide guest ions and minimize the ligand–ligand repulsion.⁴⁴

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Conclusions

A series of Cu_6 metallacycle host–guest compounds have been prepared. The compounds are produced by the reaction of $[\text{Cu}(\mu\text{-}3,5\text{-}(\text{CF}_3)_2\text{pz})_3]$ in the presence of a halide or nitrite source and oxygen. Planar halide-centered copper metallacycles of Cl^- , Br^- , and I^- anions⁴⁵ have been synthesized for the first time. The crystal structures reveal a correlation between the size and nature of the anionic guest with the dimensions of the Cu_6 metallacycle host, making remarkable the elasticity of the copper crown self-assembly. Self-assembly of this system is related not only to halides but also to larger anions such as nitrite, which for the first time plays the role of guest in copper cluster chemistry. The exchange of the nitrite anion by chloride in acetone- d^6 can be observed by ^1H NMR.

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Supporting Information Available: Plots of the proton and fluorine NMR chemical shifts as well as a titration of the nitrite complex, **5**, with chloride. X-ray crystallographic files for **2**, **3**, **4**, and **5** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(45) We have preliminary structural data for the fluoride encapsulated complexes but disorder is a problem. One geometry is similar to the structures observed with the Cl^- , Br^- , and I^- moieties but a second geometry with F^- encapsulated in a Cu_6 prism also is observed in the same unit cell.