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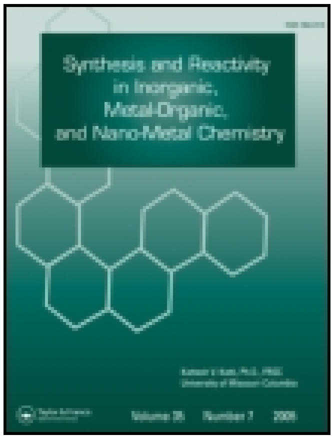

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STRUCTURES OF PENTAKIS- (IMIDAZOLE)COPPER(II) HEXAFLUOROARSENATE MONOHYDRATE AND CHLOROTETRAKIS- (IMIDAZOLE)COPPER(II) CHLORIDE

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STRUCTURES OF PENTAKIS-(IMIDAZOLE)COPPER(II) HEXAFLUOROARSENATE MONOHYDRATE AND CHLOROTETRAKIS-(IMIDAZOLE)COPPER(II) CHLORIDE

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ABSTRACT

The complexes $[Cu(imH)_5](AsF_6)_2{\cdot}H_2O$ and $[Cu(imH)_4Cl]Cl$ ($imH = $ imidazole) were prepared and characterized on the basis of elemental analyses, infrared spectroscopy, electronic spectroscopy, magnetic moment measurements and X-ray crystallography. The complex cation in each species contains a five-coordinate copper atom with a distorted square-pyramidal geometry.

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INTRODUCTION

The imidazole (imH) moiety of the histidyl residue constitutes all or part of the transition metal binding sites in a number of metalloproteins[1]. Consequently, the bonding between imidazole and transition metal ions is of considerable interest[2–5]. The copper(II)-imidazole system has been investigated by several researchers and many complexes with different ratios of imidazole to copper have been prepared and characterized[6–18]. Studies in solution by Sjöberg[19,20] indicated the existence of mononuclear complexes in which the number of imidazole ligands bound to copper(II) varies from one to six. However, only one pentakis(imidazole)copper(II) complex, $[Cu(imH)_5]$ $[P(C_6H_5O)O_3]\cdot 4H_2O$[16], and two hexakis(imidazole) complexes, $[Cu(imH)_6](NO_3)_2$[17] and $[Cu(imH)_6](HCO_2)_2$[18], have been structurally characterized by X-ray diffraction methods. We therefore undertook to make complexes containing more than four imidazole ligands per copper(II) ion by utilizing hexafluoroarsenate and hexafluorophosphate as the anions. These species have very weak ligating abilities and are commonly used as non-complexing anions[21]. In this communication we report the synthesis and characterization of $Cu(imH)_5(AsF_6)_2\cdot H_2O$ (**1**) and $[Cu(imH)_4C_l]Cl$ (**2**). The latter complex was obtained fortuitously from a solution containing $Cu(ClO_4)_2\cdot 6H_2O$, KPF_6, imH and CCl_4.

EXPERIMENTAL

Materials

$Cu(ClO_4)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 2\ 1/2\ H_2O$ and imidazole were purchased from Aldrich, $NaAsF_6$ and KPF_6 from Peninsular Chemresearch Inc., and $CuCl_2\cdot 2H_2O$ from Fisher. All reagents and solvents were used as received. Warning! Perchlorate salts are potentially explosive. They should be handled with caution and in small quantities only.

Synthesis of Pentakis(imidazole)copper(II) Hexafluoroarsenate Monohydrate, $[Cu(imH)_5](AsF_6)_2\cdot H_2O$, (1)

A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.830 g, 2.24 mmol) in 5 mL of ethanol containing 10% v/v 2,2-dimethoxypropane was added to $NaAsF_6$ (1.063 g, 5.02 mmol) dissolved in 25 mL of the same solvent. The mixture was stirred for 0.25 h and filtered. To the filtrate was added more $NaAsF_6$ (0.521 g, 2.46 mmol) and the mixture once again stirred for 0.25 h and filtered into a solution of imidazole (1.037 g, 15.2 mmol) in 4 mL of the above solvent. The mixture was stirred for 0.5 h and then the solvent pumped off under vacuum. The blue solid product was recrystallized from methanol. Blue crystals were obtained in about 2 days. Crystals for X-ray analysis were removed directly from the supernatant liquid and mounted on glass fibers. The rest of the product was isolated by decantation, washed with small amounts of methanol, and air-dried. Yield, 0.685 g (38%). Anal. Calculated for $C_{15}H_{22}N_{10}As_2CuF_{12}O$ (799.78): C, 22.53; H, 2.77; N, 17.51. Found: C, 22.20; H, 2.87; N, 17.07. IR bands (cm^{-1}): 3293 m, 3174 s, 3119 s, 3059 m, 2950 w, 2843 w, 1535 s, 1492 m, 1424 m, 1330 m, 1261 m, 1138 m, 1109 m, 1095 m, 1068 vs, 943 w, 921 w, 875 m, 856 m, 831 w, 781 s, 750 s, 707 vs, 662 s, 621 m, 609 s, 412 s. μ_{eff} (B.M.) = 1.84. VIS: $_{\max}$ (methanol) = 594 nm, = 50 L mol^{-1} cm^{-1}.

Synthesis of Chlorotetrakis(imidazole)copper(II) Chloride, $[Cu(imH)_4Cl]Cl$, (2)

A purple solution was prepared following the procedure outlined above using $Cu(ClO_4)_2{\cdot}6H_2O$ (0.830 g, 2.24 mmol), KPF_6 (0.832 g, 4.47 mmol, which only partially dissolves), additional KPF_6 (0.461 g, 2.50 mmol), and imidazole (1.099 g, 16.14 mmol). The volume of the solution was reduced to about 5 mL by pumping off the solvent under vacuum. To the above solution was added 5 mL of carbon tetrachloride and the mixture stirred thoroughly for one minute at room temperature. The reaction vessel was covered with parafilm onto which pinholes were made to allow for slow solvent evaporation. Blue crystals formed overnight. Crystals for X-ray analysis were removed directly from the supernatant liquid. The rest of the product was isolated by decantation, washed with small amounts of methanol, and air-dried. Yield, 0.50 g (55%). Anal. Calculated for $C_{12}H_{16}N_8Cl_2Cu$ (406.76): C, 35.43; H, 3.96; N, 27.55. Found: C, 35.63; H, 3.90; N, 27.12. IR bands (cm^{-1}): 3298 w, 3121 vs, 3061 m, 2953 w, 2849 w, 1536 s, 1494 m, 1431 m, 1338 m, 1329 m, 1263 m, 1246 w, 1175 w, 1165 w, 1141 m, 1128 w, 1110 w, 1095 m, 1070 vs, 954 w, 943 w, 921 w, 874 m, 861 m, 846 w, 803 m, 775 s, 757 s, 747 s, 730 m, 665 vs, 623 m, 611 m. μ_{eff} = 1.88 B.M. VIS: $_{\max}$ (methanol) = 649 nm, = 60 L mol^{-1} cm^{-1}.

Physical Methods

Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana. Infrared spectra were recorded as KBr pellets on a

Bio-Rad Model FTS3000 FT-IR spectrometer. Visible spectra of samples dissolved in methanol were recorded on a Cary 1C UV-Visible spectrophotometer. Magnetic measurements were made at room temperature on a Johnson Matthey Model MKI magnetic susceptibility balance.

X-Ray Structure Analysis

X-ray crystallographic data were collected at room temperature (**1**) and at 173 K (**2**) on a Nonius KappaCCD diffractometer. Reflections were indexed and scaled using the Denzo-SMN software package[22]. The structures were solved with SHELXTL-PC[23] and refined with SHELXL-93/7[24]. All N-H hydrogen atoms were found from difference maps and refined isotropically, while all C-Hs were placed in calculated positions. Crystals of **2** were monoclinic with $\sim 90^\circ$ and exhibited pseudo orthorhombic twinning that mapped $hkl \rightarrow \bar{h}\bar{k}l$.

RESULTS AND DISCUSSION

Synthesis and Magnetic and Spectroscopic Studies

The synthesis of the complexes may be represented by the following general equations in which M is Na^+ or K^+ and E is As or P.

$$Cu(ClO_4)_2{\cdot}6H_2O + 2\ MEF_6 \xrightarrow{\text{ethanol}} [Cu(EF_6)_2] + 2\ MClO_4$$

$$[Cu(EF_6)_2] + \text{excess imH} \xrightarrow{\text{ethanol}} Cu(imH)_n(EF_6)_2$$

The products are soluble and remain in solution. Compound (**1**) was isolated in solid form by pumping-off the solvent, and then recrystallized from methanol. In the case of (**2**) the same procedure yielded an oil rather than a solid. Upon addition of CCl_4 to the reaction mixture, however, blue crystals formed overnight. The product was shown to have the composition $[Cu(imH)_4Cl]Cl$ by elemental analysis and X-ray crystallography. The chloride ions in this compound originated from carbon tetrachloride used for crystallization. The other chlorine containing reagent used, $Cu(ClO_4)_2{\cdot}6H_2O$, is eliminated because (**2**) can also be obtained when $Cu(NO_3)_2{\cdot}2\frac{1}{2}H_2O$ is used instead of the perchlorate salt. Reactions involving the transfer of chlorine atoms from CCl_4 to metal ions are well documented[25–28]. Examples involving copper(II) include the conversion of

Cu(phen)DBcat (phen = 1, 10-phenanthroline and DbcatH_2 = 3,5-di-*tert*-butylcatechol) to Cu(phen)Cl_2[26], Cu(Et_2dtc) $_2$ (Et_2dtcH = diethyldithiocarbamate) to Cu(Et_2dtc)Cl and $CuCl_2$[27], and [Cu(Et_2dtc)](NO_3) to Cu(Et_2dtc)Cl[28]. As in the formation of (**2**), these reactions result in no net change in oxidation state of copper. It has, however, been suggested that copper(I) species are formed as intermediates and it is these species that react with CCl_4[26–28].

Compound (**2**) can also be prepared by the direct reaction of $CuCl_2$ with excess imidazole and our spectroscopic and magnetic data for this compound (presented in the experimental section) are in good agreement with those reported previously[7,8]. The infrared bands for the AsF_6^- moiety in (**1**) are assigned on the basis of data from previously characterized metal(II) hexafluoroarsenate complexes[29,30]. The v_3 and v_4 bands of the AsF_6^- group are observed at 707 and 412 cm^{-1}, respectively, and show no splitting. These data are characteristic of non-coordinated AsF_6^- moieties[29,30]. Thus, the spectroscopic and magnetic data for both (**1**) and (**2**) are characteristic of magnetically dilute copper(II) ion and consistent with the structures of the compounds as determined by X-ray crystallography.

Structure of [Cu(imH)$_5$](AsF_6)$_2$·H_2O, (1)

X-ray crystallographic data for compounds (**1**) and (**2**) are listed in Table I. Selected bond lengths and bond angles are listed in Tables II and III for (**1**) and (**2**), respectively. The structure of (**1**) consists of the $[Cu(imH)_5]^{2+}$ cation, AsF_6^- counterions and lattice water. The coordination sphere around copper in (**1**) with the atom numbering scheme is shown in Figure 1. The copper(II) ion has a distorted square-pyramidal geometry. The Cu-N bond lengths involving the basal imidazole ligands are in the range 2.014(3) to 2.031(2) Å and are consistent with previously published values[9,12–16]. The apical Cu-N bond length is considerably longer, being 2.273(3) Å. This value is intermediate between the values of 2.141(1) Å and 2.593(3) Å observed for axial imidazole ligands in bis(dimethylglyoximato)(imidazole) copper(II)[6] and hexakis(imidazole) copper(II) nitrate[17], respectively, and comparable to the value of 2.230(5) Å observed in the only other structurally characterized pentakis(imidazole) copper(II) complex, [Cu(imH) $_5$] [P(C_6H_5O)O_3]·4H_2O[16]. The *trans* N-Cu-N bond angles show significant deviations from linearity. The N(2)-Cu(1)-N(4) and N(3)-Cu(1)-N(5) bond angles are 167.80(10)° and 166.95(10)°, respectively. The *cis* N-Cu-N bond angles involving adjacent basal ligands range from 88.72(10)° to 89.89(10)°, whereas those involving the apical ligand and the basal ligands lie between 95.43(10)° and

Table I. Crystallographic Data for $[Cu(imH)_5](AsF_6)_2 \cdot H_2O$ (**1**) and $[Cu(imH)_4Cl]Cl$ (**2**)

Compound	$[Cu(imH)_5](AsF_6)_2 \cdot H_2O$	$[Cu(imH)_4Cl]Cl$
Formula	$C_{15}H_{22}As_2CuF_{12}N_{10}O$	$C_{12}H_{16}Cl_2CuN_8$
Formula weight	799.81	406.77
Crystal system	Triclinic	monoclinic
Space group	P-1 (No. 2)	$P2_1/n$ (No. 14)
A (Å)	10.802(2)	8.8430(18)
B (Å)	12.168(2)	13.209(3)
C (Å)	12.990(3)	13.866(3)
α (deg)	116.53(3)	90.00
(deg)	91.93(3)	90.000(10)
γ (deg)	110.83(3)	90.00
V (Å^3)	1389.4(5)	1619.6(6)
T (K)	298	173
Z	2	4
ρ_{calcd} (Mg m^{-3})	1.912	1.668
μ (mm^{-1})	3.261	1.689
Measured reflections	6294	9231
Unique data	6294	2948
Data with $I > 2\sigma(I)$	5286	2669
$R^a(I > 2\sigma(I))$	0.0386	0.0293
$R_w^b(I > 2\sigma(I))$	0.0954	0.0660
gof	1.030	1.039

$^a R = \sum \|F_o| - |F_c\| / \sum |F_o|$.

$^b Rw = \left[\sum w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)^2]\right]^{1/2}$.

96.78(10)°. The copper(II) ion lies 0.222(1) Å above the plane defined by the four coordinated nitrogen atoms of the basal ligands.

All of the imidazole rings are planar within experimental error. The C-N bond lengths range from 1.294(4) Å to 1.372(4) Å. In each ring, the shortest bond length corresponds to the classical C=N double bond. The C-C bond lengths of the rings range from 1.330(5) Å to 1.353(4) Å and have an average value of 1.340(5) Å. There is an extensive network of hydrogen bonding interactions in (**1**), which probably plays a role in stabilizing the complex. Some of these interactions involve the oxygen atom of the water molecule and the N-H hydrogen atoms of the imidazole ligands, whereas others involve the fluorine atoms of the AsF_6^- moieties and the water hydrogen atoms.

Table II. Selected Bond Lengths (Å) and Angles (°) for $[Cu(imH)_5](AsF_6)_2 \cdot H_2O$ (**1**)

	Bonds		
Cu(1)-N(2)	2.014(3)	Cu(1)-N(4)	2.018(3)
Cu(1)-N(3)	2.021(2)	Cu(1)-N(5)	2.031(2)
Cu(1)-N(1)	2.273(3)		
	Angles		
N(2)-Cu(1)-N(4)	167.80(10)	N(2)-Cu(1)-N(3)	89.73(10)
N(4)-Cu(1)-N(3)	88.90(10)	N(2)-Cu(1)-N(5)	88.72(10)
N(4)-Cu(1)-N(5)	89.89(10)	N(3)-Cu(1)-N(5)	166.95(10)
N(2)-Cu(1)-N(1)	96.78(10)	N(4)-Cu(1)-N(1)	95.43(10)
N(3)-Cu(1)-N(1)	96.74(10)	N(5)-Cu(1)-N(1)	96.31(10)

Structure of $[Cu(imH)_4Cl]Cl$, (2)

Based on spectroscopic data, a tetragonally distorted octahedral structure was previously proposed for (**2**)[7]. However, results reported here show unambiguously that the copper ion in this compound is five-coordinate. The structure of (**2**) consists of the $[Cu(imH)_4Cl]^+$ cation and Cl^- counterion. The coordination sphere around copper in (**2**) with the atom numbering scheme is shown in Figure 2. Like in (**1**), the copper(II) ion in (**2**) has a distorted square-pyramidal geometry. The nitrogen atoms of the imidazole ligands form the square base with an average Cu-N bond length of 2.005(2) Å and an average *cis* N-Cu-N bond angle of 89.53(12) Å. The *trans* N-Cu-N bond angles show significant deviations from linearity [N(7)-Cu-N(3) = 174.88(9)°, N(1)-Cu-N(5) = 158.48(9)°]. The copper(II) ion lies 0.232(1) Å above the plane defined by the four coordinated nitrogen atoms of the imidazole ligands. The coordinated chloride occupies the apical

Table III. Selected Bond Lengths (Å) and Angles (°) for $[Cu(imH)_4Cl]Cl$ (**2**)

	Bonds		
Cu-N(7)	1.997(2)	Cu-N(3)	1.999(3)
Cu-N(1)	2.009(2)	Cu-N(5)	2.013(2)
Cu-Cl(1)	2.6146(8)		
	Angles		
N(7)-Cu-N(3)	174.88(9)	N(7)-Cu-N(1)	89.60(11)
N(3)-Cu-N(1)	90.04(11)	N(7)-Cu-N(5)	89.23(13)
N(3)-Cu-N(5)	89.24(12)	N(1)-Cu-N(5)	158.48(9)
N(7)-Cu-Cl(1)	92.86(9)	N(3)-Cu-Cl(1)	92.25(9)
N(1)-Cu-Cl(1)	97.91(7)	N(5)-Cu-Cl(1)	103.61(7)

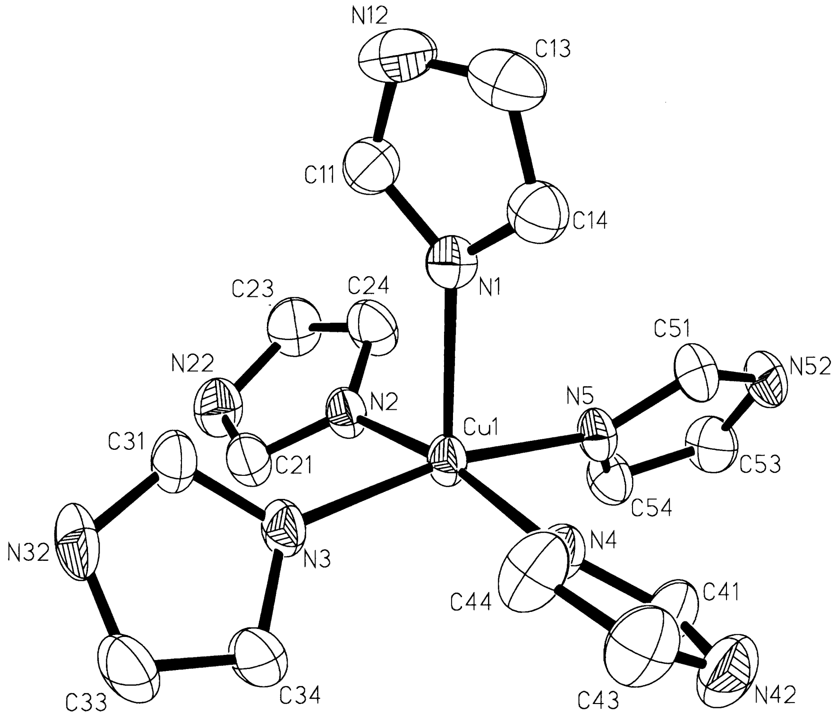

Figure 1. ORTEP diagram of cation in (**1**) with thermal ellipsoids drawn at the 30% probability level. Counterions, water and hydrogen atoms are omitted for clarity.

position 2.6146(8) Å from the copper. The chloride counterion is 4.118(1) Å away from the nearest copper atom in a direction opposite the bonded chlorine (Cl(1)-Cu . . . Cl(2) = 176.61(2)°). While the bonded Cu-Cl distance is a little longer than the sum of the ionic radii of the chloride and five-coordinate copper(II) ions (r_{Cl^-} = 1.67 Å, $r_{Cu^{2+}}$ = 0.79 Å)[31], it is comparable to Cu-Cl bond lengths found in other complexes with similar geometry. For instance, Cu-Cl bond lengths of 2.559(2) Å and 2.751(6) Å have been observed for $Cu(im)(imH)_2Cl$[9] and $Cu(imH)_2Cl_2$[11], respectively. In fact, the geometrical features exhibited by (**2**) are comparable to those observed for the analogous N-methylimidazole complex, $[Cu(N\text{-}MeimH)_4Cl]Cl$, in which the average Cu-N = 2.015 (Å), Cu-Cl = 2.542(2) Å, Cu · · · Cl = 3.843 Å, Cl-Cu · · · Cl = 177.9° and the copper atom is displaced by 0.257 Å from the basal plane[32].

The N(2), N(3), N(4), N(5) imidazole ligand planes in (**1**) have orientations of 34.9(2)°, 126.8(2)°, 149.1(2)° and 116.4(2)°, respectively,

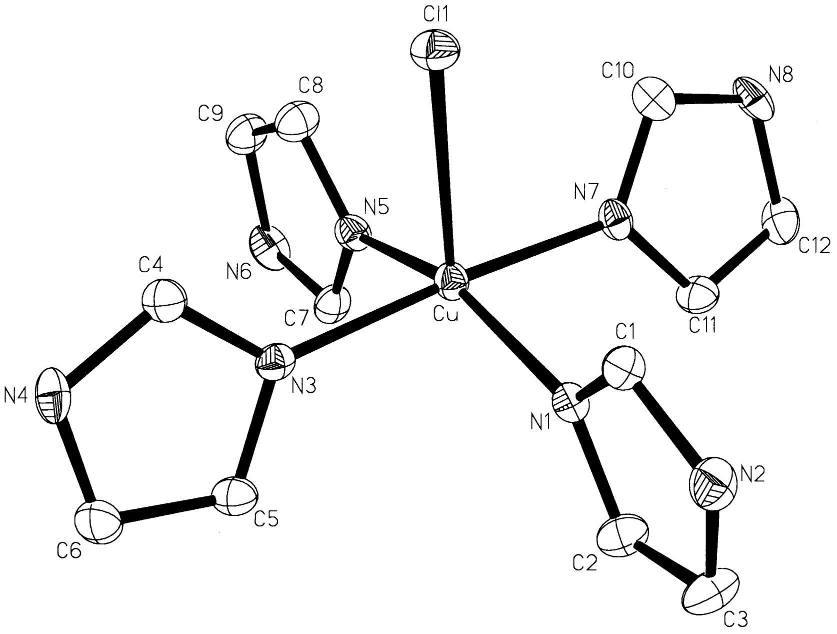

Figure 2. ORTEP diagram of cation in (**2**) with thermal ellipsoids drawn at the 50% probability level. Counterion and hydrogen atoms are omitted for clarity.

relative to the N_4 coordination square. The corresponding values in (**2**) are spread over a narrower range: 87.61(16)°, 77.45(8)°, 87.41(17)° and 70.00(8)° for N(1), N(3), N(5), and N(7) imidazoles, respectively. These data are consistent with previous observation that orientations of imidazole rings relative to the basal plane in five-coordinate copper(II) complexes vary significantly but do not follow any trend[16,32]. The angles range from 10.5(6)° to 110.0(6)° in $[Cu(imH)_5][P(C_6H_5O)O_3]{\cdot}4H_2O$[16] and from 59.6° to 84.9° in $[Cu(N\text{-}MeimH)_4Cl]Cl$[30]. In absolute terms, the planes of the basal imidazoles in the pentakis(imidazole) complexes deviate less from the N_4 coordination square than in the tetrakis(imidazole) derivatives. This is probably a consequence of steric crowding resulting from the fifth imidazole ligand in the apical position.

Supporting Information Available

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data

Centre as supplementary publication nos. CCDC 167734 for (**1**) and CCDC 167735 for (**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 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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