Stabilization of a Copper(II) Complex by Hydrogen Bonds between the Axial Tetrafluoroborate Anion and the Ammonium Group from the Coordinated Cationic Ligand Bis(imidazol-2-yl)methyl(isopropyl)ammonium

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Keywords: Hydrogen bonds / Copper / EPR / N ligands

A new mononuclear copper complex [Cu(HIm-*i*Pr)$_2$(BF$_4$)$_2$](BF$_4$)$_2$·2CH$_3$OH {where Im-*i*Pr is [bis(imidazol-2-yl)methyl](isopropyl)amine} has been obtained by diethyl ether diffusion into a methanol solution of Im-*i*Pr and Cu(BF$_4$)$_2$. The complex has been characterized by X-ray analysis, UV/Vis, IR and EPR spectroscopy. Its crystal structure is built up by centrosymmetric [Cu(HIm-*i*Pr)$_2$(BF$_4$)$_2$]$^{2+}$ complex cations, BF$_4^-$ counterions and methanol lattice molecules. In the cation, the Cu atom exhibits a distorted octahedral CuN$_4$F$_2$ chromophore coordinated by two axial BF$_4^-$ ions and by four equatorial imidazole nitrogen atoms from two cationic HIm-*i*Pr ligands. The complex is stabilized by two intramolecular pseudo-chelate hydrogen bonds between the axial BF$_4^-$ ions and the ammonium nitrogen atoms of the HIm-*i*Pr ligand [N5···F8 = 2.761(5) Å].

Introduction

Copper ions, as centers of the active site of various metalloproteins, play an essential role in biological processes such as electron transfer, oxidation catalysis and dioxygen transport.[1] All copper proteins studied so far, except for the copper(I) metallothioneins, contain one or more imidazole residues of histidine, coordinated to the copper ions.[2] In the active site of the type-3 copper proteins, each copper ion is coordinated by three imidazole nitrogen atoms.[3]

Considerable progress in modeling the features of copper centers of type-3 copper proteins has been made, especially with the characterization of synthetic copper−dioxygen complexes.[4] In bioinorganic modeling studies frequently used ligand systems are based on pyridine, pyrazole,[5] and benzimidazole moieties.[6] Since side-chain imidazole coordination derived from histidine is very common in the active-site chemistry of copper proteins,[7] and imidazole-based ligand systems are relatively less reported,[8,9] there has recently been a great deal of interest in polyimidazole copper chemistry.

In the course of our research, [bis(imidazol-2-yl)methyl](isopropyl)amine (Im-*i*Pr, Figure 1), a bulky ligand with one amine and four imidazole nitrogen atoms, was synthesized by reaction of isopropylamine with the intermediate bis(imidazol-2-yl)nitromethane unit.[10] This potential tridentate ligand has been designed to investigate the coordination behavior and the binding properties of the bis(imidazol-2-yl) unit, which is present in most of the designed polyimidazole ligands.[11,12] Furthermore, the electronic effects of replacing aromatic rings like pyridine or imidazole with a short aliphatic chain such as isopropyl can be examined. All these studies are likely to provide important information for dioxygen binding chemistry. In this study, the crystal structure of the copper complex [Cu(HIm-*i*Pr)$_2$(BF$_4$)$_2$](BF$_4$)$_2$·2CH$_3$OH is presented. The complex is stabilized by hydrogen bonding between the axial BF$_4^-$ ions and the ammonium group from the cationic HIm-*i*Pr ligands that is thought to be the driving force for the formation of this unusual copper complex.

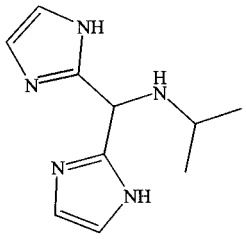

Figure 1. Molecular structure of the ligand Im-*i*Pr

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Results and Discussion

X-ray Crystal Structure Studies

The mononuclear copper complex with the formula $[Cu(HIm\text{-}iPr)_2(BF_4)_2](BF_4)_2{\cdot}2CH_3OH$ was obtained by reaction of 1 equiv. of Im-*i*Pr with 1 equiv. of $Cu(BF_4)_2$ in methanol. Diethyl ether diffusion into the methanolic solution led to the formation of blue crystals suitable for X-ray diffraction analysis. The structure formally contains two units of HBF_4. A molecular plot representing the complex, together with the atom-labeling scheme is shown in Figure 2.

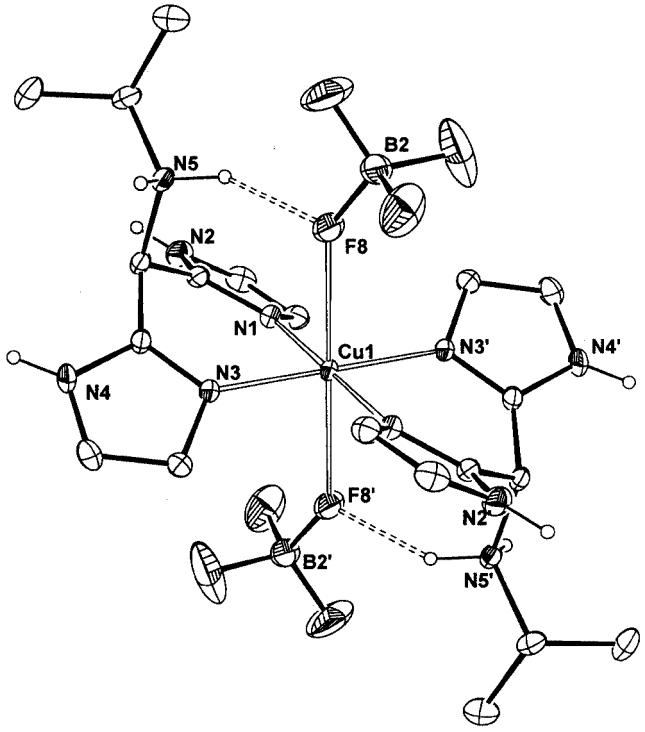

Figure 2. Thermal ellipsoid plot (20% probability level) of the mononuclear copper complex $[Cu(HIm\text{-}iPr)_2(BF_4)_2](BF_4)_2{\cdot}2CH_3OH$ showing the crystallographic numbering scheme; the hydrogen atoms at the C atoms, the non-coordinating BF_4^- ions and the methanol molecules have been omitted for clarity; selected bond lengths [Å] and angles [°]: Cu1−F8 2.493(3), Cu1−N1 2.011(3), Cu1−N3 1.995(3), N5···F8 2.761(5) (hydrogen bond); F8−Cu1−N1 91.4(1), F8−Cu1−N3 86.7(1), N1−Cu1−N3 86.4(1), N1−Cu1−N3a 93.56(11)

Its crystal structure consists of the $[Cu(HIm\text{-}iPr)_2(BF_4)_2]^{2+}$ cation (the −NH group of the Im-*i*Pr ligand is protonated in the course of the reaction to become an ammonium ion), free BF_4^- anions, and crystallization methanol molecules. The Cu^{II} ion, which in the $[Cu(HIm\text{-}iPr)_2(BF_4)_2]^{2+}$ moiety occupies the inversion center, is equatorially coordinated by four imidazole nitrogen atoms (N1, N3, N1′ and N3′) from two organic ligands [Cu1−N1 2.011(3), Cu1−N3 1.995(3) Å]. The coordination sphere is completed by coordination of two BF_4^- anions with a copper−fluoride distance of 2.493(3) Å, which is in good agreement with other values found in the literature,[13] to give a distorted octahedral environment. The complex is stabilized by two intramolecular interactions. The N5−H and N5′−H groups of the ammonium ions are in fact involved in pseudo-chelate hydrogen bonds with fluoride ions from the coordinated BF_4^- anions [N5···F8 2.761(4), H5···F8 1.94(4) Å; N5−H5···F8 144(3)°]. The cationic complexes are packed by weak intermolecular hydrogen bonds involving NH or CH groups from the cations, BF_4^- ions and methanol molecules. Also stacking interactions between the imidazole rings are present. The distance of the centroids between two least-squares imidazole planes is 3.532 Å.

The neutral ligand Im-*i*Pr has been designed to provide new information (for instance the coordinating behavior) in the field of the dioxygen binding chemistry. A general feature that is present in some imidazole-based ligands studied by our group is the [bis(imidazol-2-yl)methyl]amine unit; some examples are 1,1-bis(imidazol-2-yl)-4-(imidazol-4-yl)-2-azabutane (biib), 1,1-bis(imidazol-2-yl)-4-(pyrazol-1-yl)-2-azabutane (bipab), and 1,1-bis(imidazol-2-yl)-4-(pyridine-2-yl)-2-azabutane (bipyb).[9,11] With the potentially tetradentate ligands biib, bipab, and bipyb, dinuclear copper(II) complexes were formed by the sharing of two ligands between two Cu^{II} ions.[11] Due to steric effects, none of these tetradentate ligands can coordinate to a single Cu^{II} ion, but upon dimerization of the complexes, all four nitrogen donors of the ligands are able to coordinate to the copper atoms in a square-planar fashion. This coordination behavior, i.e. ligand sharing, is not observed with the present complex. Im-*i*Pr coordinates to the copper(II) ions in a bidentate fashion. The characteristic of the title complex $[Cu(HIm\text{-}iPr)_2(BF_4)_2](BF_4)_2{\cdot}2CH_3OH$ is that it contains a double intramolecular hydrogen-bond system, which is believed to be the driving force for the formation of the mononuclear copper complex.

Electronic Properties, EPR Spectra, ESI-MS and Conductivity Measurements

The UV/Vis spectrum of the complex in a methanol solution shows absorption bands centered at approximately 365 nm (ε = 2070 M^{-1} cm^{-1}) and 675 nm (ε = 460 M^{-1} cm^{-1}) in the range 300−800 nm. The absorption band at 365 nm is assigned to the charge-transfer transition from the imidazole nitrogen atoms to Cu^{II},[14] while the very weak absorption peak at 675 nm in the visible region of the electronic spectrum of the complex is assigned to d−d transitions of the Cu^{II} octahedral species.[15,16]

The EPR spectrum of a polycrystalline powder of the complex recorded at room temperature shows a typical axial spectrum with $g_{\|}$ = 2.22, $g_{\perp}$ = 2.07, and $A_{\|}$ = 200 G. The signals become sharper upon cooling to 77 K, but the hyperfine signals have not all been resolved.

The EPR analysis of the complex in a frozen solution of MeOH/DMSO (8:2) at 77 K shows a well-resolved axial spectrum with superhyperfine splitting superimposed on the equatorial absorption. The spectrum of the complex is redrawn in Figure 3 with $g_{\|}$ = 2.33, $g_{\perp}$ = 2.06, and $A_{\|}$ = 160 G as the dominant signals; the larger $g_{\|}$ values and the smaller $A_{\|}$ value already indicate a species different from

that in the solid state. Further, not all nine expected superhyperfine lines with $A_{N\perp}$ = 15 G are resolved, not even at high dilution; this strongly suggests that the copper complex partly dissociates in the MeOH solution. At high dilution, the characteristic EPR lines for the Cu^{2+}−MeOH species ($g_{\|}$ = 2.42, $A_{\|}$ = 115 G)[15] become visible. The fact that the $g_{\|}$ value in the solid state is lower and the $A_{\|}$ value is larger than those in solution may suggest that two axially coordinated BF_4^- anions are dissociated in the methanol solution of the complex, as further confirmed by the ESI-MS and conductivity measurements.

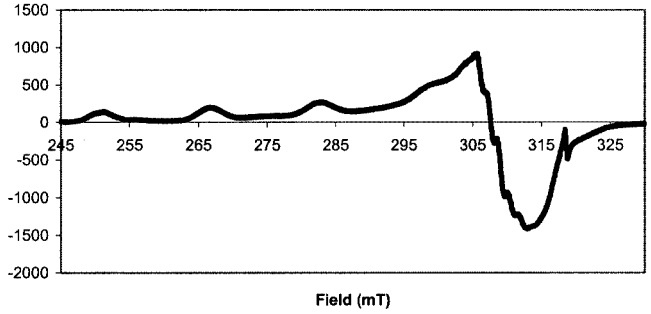

Figure 3. The EPR spectrum of the complex in a frozen solution of MeOH/DMSO (8:2) at 77 K

The conductivity measurement was performed at 25 °C on a 1 mM solution of the complex in MeOH. The value for the equivalent conductivity of the complex was found to be 275 $S{\cdot}cm^2{\cdot}mol^{-1}$, which agrees with a 3:1 type electrolyte in MeOH as the solvent.[17] The result indicates that at least one of the two axially coordinated BF_4^- anions are dissociated from the copper ion in the MeOH solution to form the 3:1 electrolyte (two non-coordinated BF_4^- anions in the crystal lattice of the complex already would have resulted in a 2:1 electrolyte).

The ESI mass spectrum of the complex was measured in MeOH. The most intensive peak at m/z = 206 corresponds to the free ligand Im-*i*Pr. Other major peaks observed at m/z = 450, 419, 391, and 325 correspond to the $[Cu(Im\text{-}iPr)(BF_4)(MeOH)_3]^+$, $[Cu(Im\text{-}iPr)(BF_4)(MeOH)_2]^+$, $[Cu(Im\text{-}iPr)(BF_4)(H_2O)_2]^+$, and $[Cu(HIm\text{-}iPr)_2(BF_4)_2]^{2+}$ cations, respectively; in fact the experimentally observed isotopic pattern is in very good agreement with the theoretical result of the isotope pattern calculation. The ESI mass spectrum of a mixture of the free ligand and $Cu(BF_4)_2$ gave very similar results. It seems that several species are present in the methanolic solution, which may arise from the electrochemical reduction of the copper complex during the electrospray process. Due to the very low solubility of the complex in non-coordinating solvents such as CH_2Cl_2, no information could be obtained with our experimental setup. Extensive studies would be needed to give more detailed information about the solution chemistry of the complex.

Conclusion

In summary, a new mononuclear copper complex has been obtained from the ligand Im-*i*Pr and $Cu(BF_4)_2$. The protonated cationic ligands HIm-*i*Pr coordinate to the copper(II) ion in a bidentate fashion, while two BF_4^- groups complete the distorted octahedral geometry around the metal atom. The complex is stabilized by intramolecular hydrogen bonds formed between the axially coordinated BF_4^- anions and the ammonium group of the ligand HIm-*i*Pr. The frozen-solution EPR spectrum of the complex in MeOH shows dissociation of the tetrafluoroborate anions. The higher $g_{\|}$ value in the solid state than in solution agrees with at least partial dissociation of the BF_4^- anions from the copper ion of the complex in MeOH, which is supported by solution conductivity data. Further studies on the dioxygen binding properties of the corresponding Cu^I complex are currently being carried out in our laboratories.

Experimental Section

General Remarks: All reagents and solvents were purchased from commercial sources and used as received. C, H, N analyses were carried out with a Perkin−Elmer 2400 series II analyzer. IR spectra were recorded with a Perkin−Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate Diamond ATR device, using the diffuse reflectance technique. X-band EPR spectra were recorded at room temperature and at 77 K with a Jeol RE2X ESR spectrometer with DPPH (g = 2.0036) as a standard. The UV/Vis spectrum of the compound was recorded in the 250−800 nm range with a Cary 50 Varian UV/Vis/NIR spectrometer. Electrospray ionization mass spectra (ESI-MS, positive ion) in a methanol solution was recorded with a Thermo Finnigan AQA apparatus. The conductivity measurement was performed with a Philips PW 9526 digital conductivity meter and PW 9551/60 measuring cell with a 1 mM solution of the complex in methanol.

Synthesis of [Bis(imidazol-2-yl)methyl](isopropyl)amine (Im-*i*Pr): Isopropylamine (0.26 g, 4.36 mmol) was added to a solution of the hydrochloride salt of bis(imidazol-2-yl)nitromethane[10] (1.0 g, 4.36 mmol) in sodium hydroxide (10 mL of a 2.0 M of solution). The solution was stirred at 80 °C for more than 2 h and then cooled to room temperature. A white product precipitated from the solution. The precipitate was filtered, and the desired product was washed with small amounts of ethanol and diethyl ether. Yield: 40% (0.36 g). ^1H NMR (200 MHz, CD_3OD, 25 °C, 0−10 ppm): δ = 7.10 (s, 4 H, Im-H), 5.28 (s, 1 H, CH), 2.66 (m, 1 H, CH), 1.10 (d, 6 H, CH_3) ppm. ESI-MS: m/z = 206.1 $[M + H]^+$.

Preparation of the Copper Complex $[Cu(HIm\text{-}iPr)_2(BF_4)_2]\cdot(BF_4)_2\cdot 2CH_3OH$: A solution of the ligand Im-*i*Pr (16.4 mg, 0.08 mmol) in MeOH (5 mL) was added to a solution of $Cu(BF_4)_2\cdot 6H_2O$ (27.6 mg, 0.08 mmol) in MeOH (5 mL). The reaction mixture was stirred for 15 min until the solution was completely clear, then it was filtered. Slow diethyl ether diffusion into the filtrate for several days led to the formation of blue crystals suitable for X-ray analysis. Yield: 30% (10.6 mg). $C_{22}H_{40}B_4CuF_{16}N_{10}O_2$ (887.42): calcd. C 29.8, H 4.5, N 15.8; found

C 30.2, H 4.9, N 15.3. IR (solid): $\tilde{\nu}$ = 3339.9, 1569.5, 1471.3, 1393.7, 1009.6, 764.3, 697.1, 519.8, 442.2 cm^{-1}.

X-ray Crystallographic Study: The molecular structure of $[Cu(HIm\text{-}iPr)_2(BF_4)_2](BF_4)_2\cdot 2CH_3OH$ was determined by single-crystal X-ray diffraction methods. Crystallographic and experimental details for the structure are summarized in Table 1. Intensity data and cell parameters were recorded at room temperature (25 °C) with a Philips PW 1100 single-crystal diffractometer using graphite-monochromated Mo-K_α radiation and the θ/2θ scan technique. A correction for absorption was made (maximum and minimum value for the transmission coefficient was 1.000 and 0.5472).[18] The structure was solved by Direct Methods using the SIR97 program[19] and refined on F_o^2 by full-matrix least-squares procedures, with the SHELXL-97 program.[20] All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealized geometry (C−H 0.95 Å) and refined "riding" on the corresponding parent atoms, with the exception of H4, H5NA, H5NB, H8, and H1S, which were located in the difference Fourier map. The weighting scheme used in the last cycle of refinement was $w = 1/[\sigma^2F_o^2 + (0.1758P)^2]$ [where $P = (F_o^2 + 2F_c^2)/3$]. Molecular geometry calculations were carried out with the PARST97 program[21]. Drawings were obtained by ORTEP3 in the WinGX suite.[22] All calculations were carried out with a DIGITAL Alpha Station 255 computer. CCDC-235117 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for $[Cu(HIm\text{-}iPr)_2(BF_4)_2](BF_4)_2\cdot 2CH_3OH$

	$[C_{20}H_{32}Cu_1N_{10}B_2F_8](BF_4)_2\cdot 2CH_3OH$
Formula mass	887.42
Crystal system	monoclinic
Space group	$P21/n$
a [Å]	8.583(5)
b [Å]	13.832(5)
c [Å]	15.573(5)
β [°]	91.133(5)
V [Å^3]	1848.5(14)
Z	2
$D_{calcd.}$ [g·cm^{-3}]	1.594
Linear absorption coeff. [mm^{-1}]	0.711
$F(000)$	902
Crystal size [mm]	0.15 × 0.20 × 0.24
Index ranges	$-12 \le h \le 12$, $0 \le k \le 19$, $0 \le l \le 21$
θ range for data collection[°]	3.06−30.00
Reflections collected	5530
Independent reflections	5364 (R_{int} = 0.0852)
Observed reflections [$I > 2\sigma(I)$]	3551
Data/restraints/parameters	5364/0/276
Goodness-of-fit on F^2 [a]	1.002
Final R indices (obsd. data)[b]	R_1 = 0.0848, wR_2 = 0.2304
R indices (all data)[b]	R_1 = 0.1167, wR_2 = 0.2495
Largest diff. peak/hole [e/Å^{-3}]	1.011/−1.941

[a] Goodness-of-fit $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflections and p the number of parameters. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Acknowledgments

The work described here has been supported by the Leiden University Study group WFMO (Werkgroep Fundamenteel Materialen-Onderzoek). Support from the NRSC Catalysis (a Research School Combination of HRSMC and NIOK) is kindly acknowledged. The project is financially supported by the Dutch Economy, Ecology, Technology (EET) program, a joint program of the Ministry of Economic Affairs, the Ministry of Education, Culture and Science, and the Ministry of Housing, Spatial Planning and the Environment.

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Received April 7, 2004

