Synthesis and Characterization of Two Copper(II) Complexes with Protonated 6-Benzylaminopurine as Ligand. Crystal and Molecular Structure of [$CuCl_3$(6-benzylaminopurineH)$_2$]Cl·H_2O

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Abstract

Two new mononuclear complexes of Cu(II), [CuX_3(6-benzylaminopurineH)$_2$]X·H_2O (X = Cl, Br) have been obtained by direct reaction of CuX_2·aq and 6-benzylaminopurine in hydrochloric or hydrobromic acid. The chloro complex crystallizes in the monoclinic system, $a = 13.508(3)$, $b = 21.181(4)$, $c = 10.661(2)$ Å, $\beta = 110.644(2)°$, $Z = 4$. The crystal structure consists of mononuclear units where Cu(II) displays a distorted bpt geometry. Cu and three chlorine atoms are placed in the equatorial plane while the N atoms belonging to the imidazole ring of 6-benzylaminopurine protonated ligands are in the apical sites. The EPR spectrum at room temperature presents three g values $g_1 = 2.285$, $g_2 = 2.133$ and $g_3 = 2.035$. They clearly indicate a distortion of bpt to sp geometry according to the molecular structure.

Introduction

Purine and pyrimidine derivatives are known to be metal-binding bases in many biological processes [1]. Among these bases, adenine is of particular interest due to its known tendency to act as a monodentate, bidentate or bridging bidentate ligand with copper(II) cation [2]. This ligand presents the interesting feature of acting as a bridge even in strong acidic media (concentrated HCl or HBr) [3].

Under these conditions adenine becomes protonated and acts as a bridging ligand together with chlorine anions, forming a trinuclear copper(II) complex [3].

Our attempts to extend this behaviour to other adenine derivatives (commercial 6-benzylaminopurine, 8-azaadenine or others) were unsuccessful. Nevertheless, 6-benzylaminopurine allowed the synthesis of two new mononuclear complexes of copper(II) with the protonated N^6-benzyladenine acting only as a monodentate ligand. The results and characterization, including the crystal and molecular structure of [$CuCl_3$(6-benzylaminopurineH)$_2$]Cl·H_2O and EPR studies, are presented in this paper.

Experimental

Synthesis of [$CuX_3(C_{12}H_{10}N_5)_2$]X (X = Cl, Br)

The molar ratio between CuX_2·aq and 6-benzylaminopurine is not important in the preparation of the mononuclear complexes because polynuclear ones are never formed. The best crystals were obtained by mixing 0.7 mmol of CuX_2·aq and 0.35 mmol of 6-benzylaminopurine (Aldrich, used without further purification) in 10 ml of 2 M HCl or HBr respectively. After heating in a steam bath with constant stirring, the clear solution was left to crystallize at room temperature. The blue crystals were filtered and washed with cold concentrated acid. *Anal.* Calc. for $CuC_{24}H_{20}Cl_4N_{10}\cdot H_2O$: C, 42.90; N, 20.85; H, 3.30; Cl, 21.11; Cu, 9.46. Found: C, 42.7; N, 20.6; H, 3.3; Cl, 21.1; Cu, 9.5%. Calc. for $CuC_{24}H_{20}Br_4N_{10}$: C, 34.66; N, 16.84; H, 2.42; Br, 31.62; Cu, 7.64. Found: C, 34.6; N, 16.5; H, 2.4; Br, 31.3; Cu, 7.6%.

Crystal Structure Determination of the Chloro Complex

A tabular crystal (0.1 × 0.1 × 0.07 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4 \leq \theta \leq 12$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using the ω-scan technique, with scan width 0.8° and scan speed 0.03° s^{-1}. 2045 reflections

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TABLE 1. Crystal Data of [$CuCl_3$(6-benzylaminopurineH)$_2$]$Cl \cdot H_2O$

Formula	[$CuCl_3(C_{12}H_{10}N_5)_2$]$Cl \cdot H_2O$
Formula weight	671.9
Crystal system	monoclinic
Space group	$P2_1a$
a (Å)	13.508(3)
b (Å)	21.181(4)
c (Å)	10.661(2)
β (°)	110.64(2)
V (Å^3)	2854(1)
D_x (g cm^{-3})	1.563
Z	4
F(000)	1362
λ(Mo Kα) (Å)	0.71069
μ(Mo Kα) (cm^{-1})	12.05
Temperature (K)	288

TABLE 2. Bond Lengths for [$CuCl_3$(6-benzylaminopurineH)$_2$]$Cl \cdot H_2O$

Cl(2)–Cu	2.520(3)
Cl(3)–Cu	2.289(4)
Cl(4)–Cu	2.283(4)
N(1)–Cu	2.031(7)
N(21)–Cu	1.995(7)
C(2)–N(1)	1.368(13)
C(9)–N(1)	1.363(13)
N(3)–C(2)	1.356(11)
C(4)–N(3)	1.382(15)
C(5)–C(4)	1.396(15)
C(9)–C(4)	1.361(12)
N(6)–C(5)	1.343(16)
N(10)–C(5)	1.324(13)
C(7)–N(6)	1.343(13)
N(8)–C(7)	1.317(15)
C(9)–N(8)	1.358(15)
C(11)–N(10)	1.483(13)
C(12)–C(11)	1.503(16)
C(13)–C(12)	1.369(16)
C(17)–C(12)	1.362(14)
C(14)–C(13)	1.361(19)
C(15)–C(14)	1.340(19)
C(16)–C(15)	1.358(23)
C(17)–C(16)	1.416(19)
C(22)–N(21)	1.297(13)
C(29)–N(21)	1.298(16)
N(23)–C(22)	1.349(11)
C(24)–N(23)	1.366(15)
C(25)–C(24)	1.436(16)
C(29)–C(24)	1.396(13)
N(26)–C(25)	1.352(18)
C(29)–N(28)	1.370(16)
C(31)–N(30)	1.412(15)
C(32)–C(31)	1.509(15)
C(33)–C(32)	1.363(19)
C(37)–C(32)	1.400(14)
C(34)–C(33)	1.373(22)
C(35)–C(34)	1.311(27)
C(36)–C(35)	1.363(33)
C(37)–C(36)	1.362(22)

were measured in the range $2 \leqslant \theta \leqslant 25$, 1920 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three reflections were monitorized every two hours as orientation and intensity control. Significant intensity decay was not observed. Lorentz-polarization, but no absorption corrections, were made. The structure was solved by direct methods using the MULTAN system of computer programs [4] and refined by full-matrix least-squares using the SHELX76 program [5]. The function minimized was $w||F_o| - |F_c||^2$, where $w = (\sigma|F_o|^2 + 0.0016|F_o|^2)^{-1}$. f, f', f'', were taken from International Tables of Crystallography [6]. A disordered water molecule was observed from a difference synthesis, an occupancy factor of 0.5 was assigned to each position according to the height of peaks. The position of H atoms was calculated and refined with an overall isotropic temperature factor and the remaining atoms were refined anisotropically. The final R value was 0.052 (R_w = 0.056) for all observed reflections. Maximum peak in final difference synthesis was 0.4 e A^{-3}; maximum shift/e.s.d. was 0.3 in U_{13} of O(W2) atom. Crystallographic data, main distances and angles are given in Tables 1, 2 and 3 respectively.

Discussion

The crystal structure of the chloro complex (Fig. 1) consists of mononuclear units of [$CuCl_3$(6-benzylaminopurineH)$_2$]$^+$ (Fig. 2) with one chloride anion Cl(1) and one disordered water molecule per formula unit. The Cu(II) ion displays a distorted trigonal bipyramid geometry with the Cu and three chlorine atoms in the basal plane (largest deviation from the main plane is 0.022(3) Å in the Cu atom), while the two N atoms of organic ligands are in the apical sites. Two Cu–Cl bond lengths, Cu–Cl(3) and Cu–Cl(4), are equal (average length 2.286(3) Å (Fig. 3)) while the third Cu–Cl distance (Cu–Cl(2)) is greater than the preceding values, 2.520(3) Å. The Cl–Cu–Cl bond angles vary from 100.9(1)° to 149.4(1)° (Fig. 3). These two facts (significant differences in angles and distances) clearly indicate the distortion of the geometry with regard to the bpt structure. Effectively, taking into consideration the work of Gatteschi *et al.* [7] on the relation between angles and the distortion of bpt to square pyramidal geometry, we realize that we are in an intermediate case between bpt (α = 120) and sp (α = 90). The EPR spectra corroborate this theory (see below).

The two N^6-benzyladenine ligands are linked by the imidazole atoms N(1) and N(21). This fact agrees with the current behaviour on the naturally occurring purine bases: coordination is frequently made by

TABLE 3. Bond Angles for $[CuCl_3(6\text{-benzylaminopurineH})_2]Cl \cdot H_2O$

Cl(3)–Cu–Cl(2)	100.9(1)	C(13)–C(12)–C(11)	121.8(9)
Cl(4)–Cu–Cl(2)	109.6(1)	C(17)–C(12)–C(11)	119.8(10)
Cl(4)–Cu–Cl(3)	149.4(1)	C(17)–C(12)–C(13)	118.4(11)
N(1)–Cu–Cl(2)	92.5(2)	C(14)–C(13)–C(12)	122.0(10)
N(1)–Cu–Cl(3)	89.8(3)	C(15)–C(14)–C(13)	119.8(14)
N(1)–Cu–Cl(4)	90.8(3)	C(16)–C(15)–C(14)	121.0(15)
N(21)–Cu–Cl(2)	94.0(2)	C(17)–C(16)–C(15)	119.1(11)
N(21)–Cu–Cl(3)	90.0(3)	C(16)–C(17)–C(12)	119.7(12)
N(21)–Cu–Cl(4)	86.0(3)	C(22)–N(21)–Cu	127.2(6)
N(21)–Cu–N(1)	173.4(3)	C(29)–N(21)–Cu	129.1(7)
C(2)–N(1)–Cu	123.2(6)	C(29)–N(21)–C(22)	103.4(7)
C(9)–N(1)–Cu	131.3(7)	N(23)–C(22)–N(21)	114.7(10)
C(9)–N(1)–C(2)	105.3(7)	C(24)–N(23)–C(22)	105.2(3)
N(3)–C(2)–N(1)	110.4(9)	C(25)–C(24)–N(23)	134.2(9)
C(4)–N(3)–C(2)	107.1(8)	C(29)–C(24)–N(23)	103.0(9)
C(5)–C(4)–N(3)	133.9(9)	C(29)–C(24)–C(25)	122.8(11)
C(9)–C(4)–N(3)	106.7(9)	N(26)–C(25)–C(24)	115.8(9)
C(9)–C(4)–C(5)	119.3(11)	C(24)–C(29)–N(21)	113.6(10)
N(6)–C(5)–C(4)	117.6(9)	N(28)–C(29)–N(21)	131.0(9)
N(10)–C(5)–C(4)	122.7(11)	N(28)–C(29)–C(24)	115.4(11)
N(10)–C(5)–N(6)	119.6(10)	C(32)–C(31)–N(30)	110.9(10)
C(7)–N(6)–C(5)	118.7(10)	C(33)–C(32)–C(31)	119.4(9)
N(8)–C(7)–N(6)	127.4(12)	C(37)–C(32)–C(31)	121.4(11)
C(9)–N(8)–C(7)	113.7(8)	C(37)–C(32)–C(33)	119.2(11)
C(4)–C(9)–N(1)	110.5(10)	C(34)–C(33)–C(32)	119.2(13)
N(8)–C(9)–N(1)	126.1(8)	C(35)–C(34)–C(33)	122.0(20)
N(8)–C(9)–C(4)	123.2(9)	C(36)–C(35)–C(34)	120.0(18)
C(11)–N(10)–C(5)	124.7(10)	C(37)–C(36)–C(35)	120.8(16)
C(12)–C(11)–N(10)	109.9(10)	C(36)–C(37)–C(32)	118.7(14)

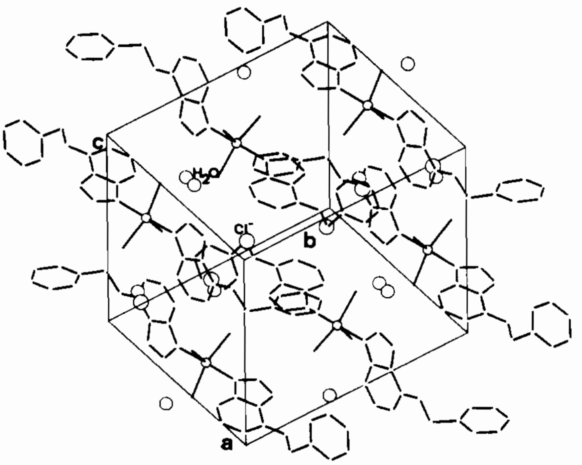

Fig. 1. Crystal structure of $[CuCl_3(6\text{-benzylaminopurineH})_2]Cl \cdot H_2O$.

using imidazole N atoms [8]. The main differences between the two organic ligands occur in the C(5)–C(10)–C(11)–C(12) and C(25)–C(30)–C(31)–C(32) torsion angles which alter from 109.5(10) in the C(10)–C(11) bond to 126.2(9) in the C(30)–C(31) bond. This difference is assumed to be due to esteric effects in the crystal packing.

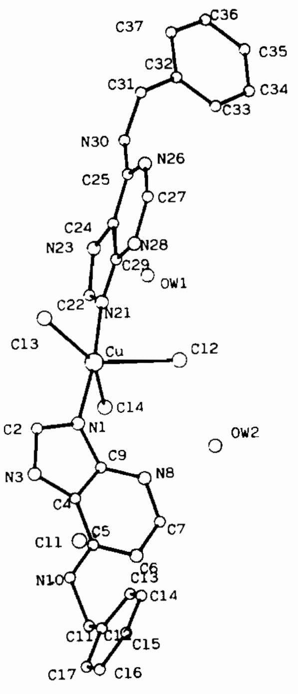

Fig. 2. Molecular structure of the $[CuCl_3(6\text{-benzylaminopurineH})_2]^+$ cation.

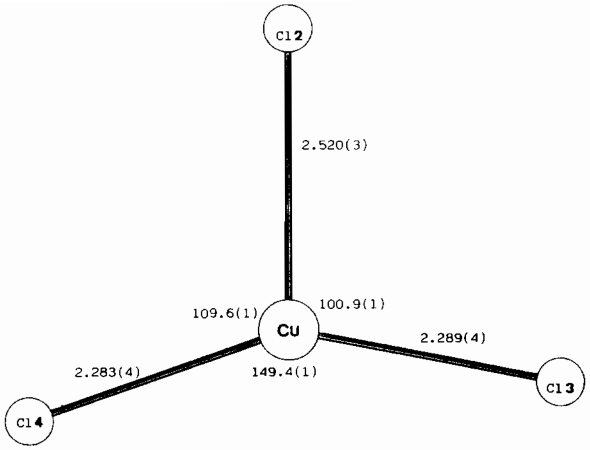

Fig. 3. Lengths and angles of the equatorial plane of the $[CuCl_3(6\text{-benzylaminopurineH})_2]^+$ cation.

The non-coordinated chlorine Cl(1) atom is hydrogen bonded to N(23) [N(23)...Cl(1)i = 3.102(6) Å; H(23)...Cl(1)i = 2.15(6) Å] and N(3) atoms [N(3)...Cl(1)ii = 3.134(6) Å; H(3)...Cl(1)ii = 2.19(6) Å]; symmetry code $i = x, y, z$; $ii = \frac{1}{2} + x, \frac{1}{2} - y, z$). The distance between Cu(II) and Cl(1) is 5.348 Å, indicating no interaction between them. Finally, the disordered water molecule is hydrogen bonded to a cation [O(W1)....N(26)iii = 3.17(1) Å; O(W1)...N(8)i = 2.90(1) Å; O(W2)...Cl(2)iv = 3.109(8) Å and O(W2)...N(28)v = 2.69(1) Å; symmetry code $iii = x - \frac{1}{2}, \frac{1}{2} - y, -z$; $iv = 1 - x, -y, -z$ and $v = \frac{1}{2} + x, \frac{1}{2} - y, 1 + z$. Distances between these water molecules and the Cu(II) ion are very long (4.292 and 4.155 Å) indicating no interaction.

The EPR powder spectra show three g values: $g_1 = 2.285$, $g_2 = 2.133$ and $g_3 = 2.035$. This pattern corresponds to a considerable distortion from the bpt geometry to sp [7, 9]. Nevertheless, Extended Hückel calculations [10] over the structure gives the unpaired electronic distribution principally along the axial direction (bpt geometry). According to Gatteschi *et al.* [7], we should expect a higher g_2 value similar to g_1 and a lower g_3 value. This disagreement indicates that the EPR spectrum with the powder sample can reflect crystal rather than molecular data. Unfortunately, our attempts to obtain frozen solutions useful for EPR yield product decomposition.

The bromo derivative shows an EPR powder pattern corresponding to an sp geometry, with $g_{\parallel} = 2.21$ and $g_{\perp} = 2.02$. It was not possible to obtain suitable crystals for X-ray structural determination to confirm its geometry.

Supplementary Material

Observed and calculated structure factors (8 pages); anisotropic thermal parameters; final atomic coordinates and final hydrogen coordinates are available from the authors on request.

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