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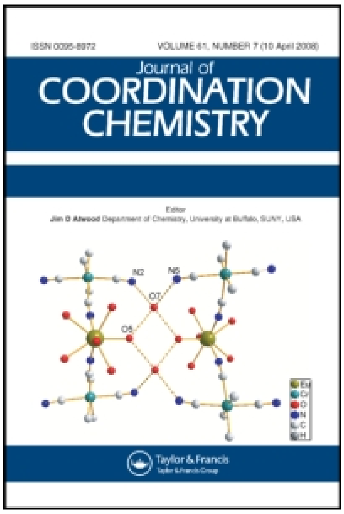

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THE CRYSTAL STRUCTURE OF TRANS-BIS(8-AMINOQUINOLINE)AQUAZINC(II) TETRACHLOROZINCATE(II)

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The crystal structure of trans-bis(8-aminoquinoline)aquazinc(II) tetrachlorozincate(II), $[Zn(C_9H_8)_2H_2O, ZnCl_4]$, monoclinic $C2/c$, $a = 11.234$, $b = 10.8527$, $c = 19.025$ Å, $\beta = 108.43°$, $Z = 4$, has been determined with X-ray (Mo$K\alpha$) diffractometer data. The structure was solved by direct methods and refined with full-matrix least-squares to $R = 0.041$. The cation and anion lie on a crystallographic dyad. The anion has the expected tetrahedral configuration. The structure of the cation is roughly halfway between the limiting trigonal bipyramid and square pyramid five-coordinate geometries. The structure is rationalized on the basis of the bite of the 8-aminoquinoline, and the electronegativities of the two nitrogen atoms and water oxygen atom.

INTRODUCTION

The 8-aminoquinolines form an important class of antimalarial drugs, the most effective of which is probably primaquine, 6-methoxy-8-(1′-methyl-4′-aminobutyl)aminoquinoline. As a model for demonstrating the coordination geometry of this class of antimalarials with inorganic cations, we have prepared a complex from 8-aminoquinoline and zinc(II) chloride, and herein describe the results of an X-ray structure determination of the title compound. To our knowledge, this is the first report of zinc(II) complex with an 8-aminoquinoline.[2]

EXPERIMENTAL

The complex was prepared by mixing 1.44 g (0.01 mol) of 8-aminoquinoline in methanol with 100 ml of 0.1 M zinc(II) chloride, following the procedure of Fanning and Taylor.[5] Elemental analysis was consistent with the formula $C_9H_8N_2ZnCl_2{\cdot}\frac{1}{2}H_2O$. Colorless, prism-shaped crystals were obtained by the slow evaporation of an aqueous methanol solution. Although preliminary X-ray work was done with the samples contained in protective glass capillaries to prevent possible dehydration, it subsequently was found that the crystals were quite stable and the final X-ray data were collected with an unenclosed specimen.

A 0.4 × 0.2 × 0.15 mm crystal, mounted parallel to the long axis (c), was used for preliminary X-ray photography. Oscillation and Weissenberg photographs (Cu radiation) revealed the symmetry and systematic absences appropriate for the monoclinic space groups Cc and $C2/c$, and provided initial cell parameter data. The final lattice parameter and all intensity measurements were made with a crystal of similar dimensions on a Picker FACS-I diffractometer with Mo radiation (graphite monochromator, $K\alpha$ $\lambda = 0.71069$ Å). The crystal was aligned to place c^* parallel to the instrument's ϕ axis. The unit cell dimensions, obtained by least-squares from the Bragg angles of seventeen reflections manually centered at $\pm 2\theta$ (average of $|2\theta_o - 2\theta_c| = 0.004°$) were $a = 11.234$ (1), $b = 10.8527$ (8), $c = 19.025$ (2) Å, $\beta = 108.43$ (1)°. The crystal density, measured by the neutral bouyancy method in *sym*-$C_2H_2Br_4/CCl_4$, was 1.72 g cm^{-3}; the X-ray density assuming eight $C_8H_8N_2ZnCl_2{\cdot}\frac{1}{2}H_2O$ units per cell was 1.73 g cm^{-3}.

The X-ray intensities were measured by the θ–2θ scan method with a 2θ rate of 2.0° min^{-1} and with 40 s backgrounds. Three standard reflections were counted at 100 reflection intervals. A total of 3040 intensities, measured to a 2θ maximum of 55°, yielded 2539 unique reflections (excluding systematically absent data); 259 of these were less than 3σ above background. The distribution of the quasi-normalized structure factors (E) suggested that the

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space group was the centric $C2/c$, but initial attempts to solve the structure from the Patterson function with this in mind were unsuccessful. The structure was finally solved by direct methods in Cc to reveal two unique zinc atoms, one tetrahedrally coordinated to four chlorines atoms and the other linked to two 8-aminoquinoline molecules plus a molecule of water. After initial structure refinement in Cc, the two-fold symmetry about the two zinc atoms was recognized and the calculations were completed in $C2/c$. The structure refinement was by full-matrix least-squares minimizing the function $\Sigma w(F_o - F_c)^2$, where $w = (1/\sigma(F_o))^2$. The calculations used anisotropic temperature factors for C, N, O, Cl and Zn and isotropic terms for H (these atoms were located initially in a difference electron density map), and included corrections for secondary extinction[6] and dispersion for Zn and Cl.[7] Of the two hydrogen atoms on N(2), H(2a) behaved improperly during refinement. It was subsequently fixed 1 Å from N(2) in a tetrahedral geometry defined by C(8)–N(2)–Zn(1); only its temperature factor was allowed to vary. The final R $(\Sigma \mid F_o - F_c \mid / \Sigma F_o)$ and weighted R $((\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2})$ are 0.04 and 0.042, respectively. The atomic parameters are listed in Table I.

Atomic scattering factors for H were interpolated from tabulated values;[8] values for C, N, O, Cl and Zn were generated from the analytical expressions of Cromer and Mann.[9] All calculations were performed with the X-ray System[10] of programs on a UNIVAC 1108 computer at the University of Maryland's Computer Science Center.

RESULTS AND DISCUSSION

The structure (see Figure 1) contains two zinc atoms alternately surrounded by tetrahedra of chlorine atoms forming the tetrachlorozincate anion, $[ZnCl_4]^=$, and a water and two 8-aminoquinoline (AQ) molecules arranged in a five-coordinated cationic complex, $[Zn(AQ)_2H_2O]^{++}$. Both cation and anion have exact C_2 symmetry by virtue of their intersection with and utilization of a crystallographic dyad.

The Zn—Cl distances and Cl—Zn—Cl angles in the $[ZnCl_4]^=$ anion are similar to previously reported values[11] for the species.

TABLE I

Fractional atomic coordinates, temperature factors and estimated standard deviations in parentheses.

Atom	X	Y	Z	U_{11}(or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(2)	−0.2316(6)	0.4950(6)	0.6075(3)	0.047(4)	0.064(4)	0.045(4)	−0.004(3)	0.017(3)	−0.003(3)
C(3)	−0.2977(6)	0.5210(7)	0.5333(4)	0.041(4)	0.082(5)	0.053(4)	−0.001(4)	0.008(3)	−0.008(4)
C(4)	−0.2399(6)	0.5815(6)	0.4908(3)	0.060(4)	0.064(4)	0.034(4)	0.012(3)	0.008(3)	0.000(3)
C(4A)	−0.1124(5)	0.6166(5)	0.5204(3)	0.047(3)	0.039(3)	0.037(3)	0.007(3)	0.013(3)	−0.001(2)
C(5)	−0.0479(6)	0.6803(5)	0.4802(3)	0.068(4)	0.049(3)	0.042(4)	0.006(3)	0.025(3)	0.004(3)
C(6)	0.0757(7)	0.7088(5)	0.5139(3)	0.079(5)	0.055(4)	0.050(4)	−0.007(4)	0.034(4)	0.006(3)
C(7)	0.1403(6)	0.6774(5)	0.5893(3)	0.059(4)	0.052(4)	0.049(4)	−0.009(3)	0.021(3)	−0.001(3)
C(8)	0.0751(5)	0.6164(4)	0.6288(3)	0.049(3)	0.035(3)	0.029(3)	−0.003(2)	0.009(2)	−0.001(2)
C(8A)	−0.0504(5)	0.5868(4)	0.5962(3)	0.049(3)	0.031(3)	0.037(3)	0.002(2)	0.019(3)	−0.004(2)
N(1)	−0.1112(4)	0.5258(4)	0.6380(2)	0.051(3)	0.042(3)	0.032(2)	−0.002(2)	0.016(2)	−0.004(2)
N(2)	0.1327(5)	0.5825(5)	0.7050(3)	0.053(3)	0.050(3)	0.041(3)	−0.014(3)	0.012(3)	−0.001(2)
O	0	0.3224(6)	0.75	0.130(8)	0.041(4)	0.060(4)	0	0.047(5)	0
Zn(1)	0	0.50783(8)	0.75	0.0534(6)	0.0405(5)	0.0331(5)	0	0.0149(4)	0
Zn(2)	0	−0.03024(8)	0.75	0.0485(6)	0.0418(5)	0.0361(5)	0	0.0133(4)	0
Cl(1)	0.1752(1)	−0.1492(1)	0.78645(9)	0.060(1)	0.0529(9)	0.061(1)	0.0118(8)	0.0101(8)	−0.0071(8)
Cl(2)	0.0058(2)	0.0929(1)	0.65435(8)	0.087(1)	0.0521(9)	0.0427(8)	−0.0011(8)	0.0310(8)	0.0040(7)
H(2)	−0.271(5)	0.449(5)	0.637(3)	0.06(2)					
H(2a)	0.200	0.519	0.708	0.25(6)					
H(2b)	0.169(5)	0.627(5)	0.726(3)	0.06(2)					
H(3)	−0.385(5)	0.506(5)	0.518(3)	0.07(2)					
H(4)	−0.261(6)	0.596(6)	0.443(3)	0.10(3)					
H(5)	−0.110(4)	0.718(4)	0.417(3)	0.04(1)					
H(6)	0.158(6)	0.767(7)	0.503(4)	0.14(3)					
H(7)	0.239(4)	0.707(4)	0.615(2)	0.04(1)					
H	−0.053(7)	0.291(6)	0.766(4)	0.12(3)					

The forms of the isotropic and anisotropic temperature factors are $T = \exp(-8\pi^{-2} U \sin^2 \theta/\lambda^2)$ and $T = \exp(-2\pi^{-2} \Sigma U_{ij}h^2a^{*2} + \ldots 2U_{23}klb^*c^*)$.

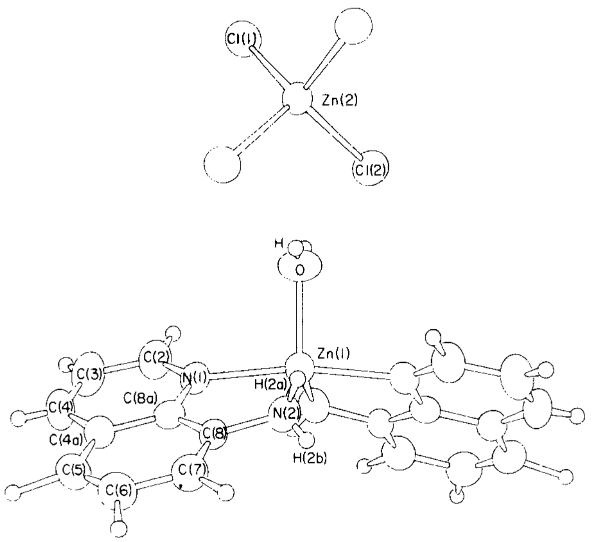

FIGURE 1 An ORTEP drawing of the molecule. The C_2 axis is vertical. The C, N, O, Zn and Cl atoms are drawn as 50% ellipses, the H atoms as 0.1 Å radius spheres.

Although there are no structures of 8-aminoquinolines known outside of transition metal complexes, the AQ fragment is structurally close to what would be expected in the free base. The quinoline is accurately planar, the average and maximum deviation of the 10 atoms from their least-squares plane being 0.009 Å and 0.017 Å. Carbon–carbon distances (see Table II) show the short-long-short pattern characteristic of naphthalenes, although bond lengths and angles in the C(8)—N(2) region show the effects of complexation. For example, the 4.4° difference in the exocyclic bond angles at C(8) moves N(2) closer to Zn. Additionally, the 1.437 Å C(8)—N(2) distance indicates the absence of any substantial amount of C═N character, and is in line with the expected change in hybridization of N(2) from sp^2 in the free molecule to sp^3 in the complex. This value is identical to the 1.437 Å found in an 8-amino-2-methyl-quinoline-nickel(II) complex,[4] and close to the 1.452 Å value reported[12] to be typical of an N(sp^3)—

TABLE II
Bond distance (Å), angles (°) and estimated standard deviations in parentheses.

Zn(1)—N(1)	2.11(1)	C(5)—C(6)	1.37(1)
Zn(1)—N(2)	2.102(8)	C(6)—C(7)	1.43(1)
Zn(1)—O	2.011(7)	C(7)—C(8)	1.37(1)
Zn(2)—Cl(1)	2.271(5)	C(8)—C(8a)	1.386(9)
Zn(2)—Cl(2)	2.275(2)	O—H	0.82(9)
N(1)—C(2)	1.335(9)	N(2)—H(2a)	1.00
N(1)—C(8a)	1.371(8)	N(2)—H(2b)	0.68(5)
N(2)—C(8)	1.437(9)	C(2)—H(2)	0.95(6)
C(2)—C(3)	1.40(1)	C(3)—H(3)	0.95(5)
C(3)—C(4)	1.35(1)	C(4)—H(4)	0.89(6)
C(4)—C(4a)	1.42(1)	C(5)—H(5)	1.25(4)
C(4a)—C(5)	1.39(9)	C(6)—H(6)	1.19(8)
C(4a)—C(8a)	1.426(9)	C(7)—H(7)	1.11(4)
N(1)—Zn(1)—N(2)	79.8(2)	C(4)—C(4a)—C(5)	123.5(5)
N(1)—Zn(1)—N(1′)	169.4(2)	C(4)—C(4a)—C(8a)	116.8(5)
N(2)—Zn(1)—N(2′)	96.1(2)	C(5)—C(4a)—C(8a)	119.7(5)
N(1)—Zn(1)—O	95.3(1)	C(4a)—C(5)—C(6)	118.8(5)
N(2)—Zn(1)—O	112.7(2)	C(5)—C(6)—C(7)	122.4(7)
Cl(1)—Zn(2)—Cl(2)	109.67(6)	C(6)—C(7)—C(8)	118.3(6)
Cl(1)—Zn(2)—Cl(1′)	110.75(6)	C(7)—C(8)—N(2)	121.9(5)
Cl(1)—Zn(2)—Cl(2′)	109.31(5)	C(7)—C(8)—C(8a)	120.6(5)
Cl(2)—Zn(2)—Cl(2′)	108.07(6)	C(8a)—C(8)—N(2)	117.5(5)
C(2)—N(1)—Zn(1)	127.6(4)	C(8)—C(8a)—N(1)	118.4(4)
C(2)—N(1)—C(8a)	119.5(4)	C(8)—C(8a)—C(4a)	120.2(5)
C(8a)—N(1)—Zn(1)	112.6(3)	C(4a)—C(8a)—N(1)	121.4(5)
C(8)—N(2)—Zn(1)	111.0(4)	H—O—H′	131(7)
N(1)—C(2)—C(3)	121.9(6)	C(8)—N(2)—H(2a)	109
C(2)—C(3)—C(4)	119.9(6)	C(8)—N(2)—H(2b)	114(5)
C(3)—C(4)—C(4a)	120.6(5)	H(2a)—N(2)—H(2b)	98

The primes refer to atoms related by the C_2 axis.

$C(sp^2)$ bond. That the C—N distances in the aminoquinoline complexes are a bit shorter than the 1.452 Å value may simply be an effect of electron withdrawal by the zinc(II) atom and may not indicate a significant amount of π-bonding.

Although coordination numbers for metals of the first transition series are usually four or six,[13] five-coordinate species are becoming increasingly well known for these metals[14] including zinc.[15] However, the factors stabilizing five-coordinate configurations are rather poorly understood. On the basis of repulsions alone, five coordination should always be less stable than four or six coordination. The preference of a coordination number greater than four in our cation is clearly related to the small bite angle of the 8-aminoquinoline. The bite angle, N(1)—Zn—N(2) = 79.8°, is largely dictated by the 8-aminoquinoline framework, since only the NH_2 of the two nitrogen atoms is free to rehybridize. We suggest that this small bite angle precludes tetrahedral coordination which would be favored by a value close to 109.5°. This factor is also shown in the closely related bisaquabis(8-hydroxyquinoline)zinc(II) complex which is approximately octahedral with bond angles and lengths similar to our values.[16]

The two idealized geometries of coordination number five are the trigonal bipyramid (TBP) and the square pyramid (SP). In the absence of ligand field stabilization ($Zn^{++} = d^{10}$), the trigonal bipyramidal (TBP) configuration is favored over the square pyramidal (SP) configuration, though recently more subtle electronic effects have been investigated with respect to stabilization of these configurations.[17] In addition, Muetterties and Guggenberger[18] have shown that a complete spectrum of five-coordinate geometries exists between these two extremes. The ORTEP view (Figure 1) seemingly emphasizes the SP aspects of the structure, with four AQ nitrogen atoms at the base and the water at the apex. However, on the basis of the dihedral angles used to classify these geometries,[18] together with a quantitative analysis suggested by Sheldrick,[19] the "TBP : SP ratio" (the extent of deformation from TBP towards SP) in the $[Zn(AQ)_2H_2O]^{++}$ complex is 60 : 40. The Zn—N(1) and Zn—N(2) distances are identical and agree with values observed in other five-coordinate Zn complexes.[13] These values are slightly larger than those found in tetrahedral complexes, showing the expected relationship between distance and coordination number.

Of the two limiting five-coordinate geometries, SP appears to be favored over TBP by the small bite angle and the presence of water as one of the ligands. For example, of the two possible TBP structures, the $(N_{ax}—N_{eq})_2(H_2O)_{eq}$ geometry with both bite angles of 90° is favored over the $(N_{ax}—N_{eq})$-$(N_{eq}—N_{eq})(H_2O)_{ax}$ configuration which requires one large bite angle of 120°. However, the H_2O_{eq}-TBP structure forces the water molecule, the poorest sigma-donor with the most electronegative ligating atom, to accept an equatorial position in contrast to the well-known[20] apicophilicity of electronegative substituents in d^0 and d^{10} systems.

In contrast, the small bite angle clearly favors a square pyramidal configuration since a 90° angle occurs in the idealized geometry if the metal is in the plane of the pyramidal base. If the metal lies above this plane (as it does in the present case), the angle becomes less than 90°. Furthermore, to the extent that the quinoline system favors synergistic back-bonding, its presence as a basal ligand would be energetically more favorable[17] than as an apical ligand because of the possibility of some π-acceptor character to be expressed by quinoline. However, the identity of the Zn—N(1) and Zn—N(2) distances indicates that there is little or no back-bonding to the quinoline π-system.

Why then is there so much distortion, from square pyramidal towards trigonal bipyramidal? The N(1)—Zn—N(1′) angle of 169.4° is not far from 180° nor is the N(2)—Zn—N(2′) angle of 134.6° far from 120°. Viewed as a trigonal bipyramid with N(1) and N(1′) axial, the molecule provides insight into the electronic factors operating in five coordination. The more electronegative, sp^2-hybridized quinoline nitrogen atoms occupy the pseudoaxial ("apical") position and the less electronegative, sp^3-hybridized amino nitrogen atoms are found at the pseudoequatorial positions. Thus the distribution is such that the energies associated with Bent's rule[21] can provide some stabilization, though not enough to push the complex completely to the TBP configuration.

Intermolecular contacts are primarily those involving Cl···H—O and Cl···H—N. The interactions more-or-less parallel to the central 2-fold axis are Cl(2)$[-x, y, 1\frac{1}{2} - z]$···H (on O) at 2.59 Å and Cl(1)-$[x, -1 + y, z]$···H(2b) at 2.68 Å. (Cl(1) is further involved via a Cl(1)$[\frac{1}{2} - x, \frac{1}{2} + y, 1\frac{1}{2} - z]$···H(2a) contact at 2.29 Å.

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