

The Crystal Structure of Tetraamminezinc(II) Diiodide, $\text{Zn}(\text{NH}_3)_4\text{I}_2$

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The crystal structure of $\text{Zn}(\text{NH}_3)_4\text{I}_2$ has been determined from four-circle diffractometer X-ray data. The compound crystallizes in space group $Pm\bar{3}n$ with the cell dimensions $a=7.538(1)$ Å, $b=10.396(2)$ Å, $c=13.098(3)$ Å, $Z=4$. The structure was refined to $R=0.034$ for 1415 independent reflections. The structure contains tetrahedral tetraamminezinc(II) ions with Zn–N bond distances of 1.997(7), 2.010(5) and 2.030(6) Å. The iodine ions are surrounded by nine nitrogen atoms with average interatomic distances I(1)–N and I(2)–N of 3.927(4) and 3.790(5) Å, respectively.

Tetraamminezinc(II) complexes have been studied mainly by vibrational spectroscopic methods, both in the solid state and in solution.¹ At the commencement of this work, no three-dimensional structural analysis of this complex was available, probably because of difficulties involved in preparing stable single crystals. During the course of this study, a structural investigation of the related compound $\text{Zn}(\text{NH}_3)_4(\text{I}_3)_2$ appeared.² The structures of $\text{Zn}(\text{NH}_3)_4^{2+}$ and $\text{ZnCl}(\text{NH}_3)_3^+$ ions have also been determined in an X-ray diffraction study of ammoniacal aqueous solution of ZnCl_2 .³ In the solution diffraction study,³ it was shown that hexaamminezinc(II) ions were not formed, even in a solution of high ammonia content (NH_3/Zn molar ratio ≈ 10), although $\text{Zn}(\text{NH}_3)_6^{2+}$ occurs in the solid state.⁴

The tetraamminezinc(II) ion forms very few stable compounds with simple anions. The iodide is, however, comparatively stable, and it proved possible to prepare single crystals of $\text{Zn}(\text{NH}_3)_4\text{I}_2$ suitable for an X-ray investigation.

EXPERIMENTAL

The crystals were prepared by slow evaporation of an ammoniacal aqueous solution saturated with ZnI_2 over KOH pellets in a desiccator.

A crystal suitable for X-ray diffraction measurements was enclosed in a 0.1 mm glass capillary since the compound decomposes in air, with loss of ammonia, within a few hours.

Cell constants were determined by a least-squares fit to the setting angles of 10 reflections measured on a Syntex $P2_1$ four-circle diffractometer. The systematic absences indicated the space group to be either $Pm\bar{3}n$ or $P2_1/nb$. The intensity data were collected at room temperature using graphite monochromatized $\text{MoK}\alpha$ -radiation ($\lambda=0.7107$ Å) and a scintillation counter. The $\theta/2\theta$ scan mode was used and the 2θ scan speed was varied in the range $2-12^\circ \text{ min}^{-1}$, depending on the peak intensities. A 96-step profile was recorded for each reflection and the Lehmann-Larsen profile analysis⁵ method was used to evaluate the intensities (program LELA⁶). A standard reflection was measured after every 50 reflections to check the stability of the crystal. No significant fluctuation was observed. Among a total of 2597 reflections collected up to $2\theta=70^\circ$, 1415 independent reflections with $I>3\sigma(I)$ were used in subsequent calculations. Intensities were corrected for Lorentz and polarization effects in the usual way, while corrections for absorption and extinction were made after an approximate structure had been deduced.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by the heavy atom method. A three-dimensional Patterson synthesis was calculated (program DRF⁷), which showed the

Table 1. Crystal Data.

Tetraamminezinc(II) diiodide, $\text{Zn}(\text{NH}_3)_4\text{I}_2$	
FW = 387.30	orthorhombic
Crystal size	0.10 × 0.12 × 0.15 mm
Space group	<i>Pmnb</i>
Cell dimensions	
<i>a</i>	7.538(1) Å
<i>b</i>	10.396(2) Å
<i>c</i>	13.098(3) Å
<i>Z</i>	4
<i>V</i>	1024.5 Å ³
<i>D_x</i>	2.51 Mg/m ⁻³
$\mu(\text{MoK}\alpha)$	8.49 mm ⁻¹
Crystal habit	colourless, transparent rods.

iodine atoms to occupy two positions 4(*e*) and the zinc atom one position 4(*e*) in space group *Pmnb*. The nitrogen atoms were located in a subsequent difference Fourier summation.

A preliminary block-diagonal least-squares refinement (program BLOCK⁸) gave a conventional *R*-value of 0.051. At this stage, an absorption correction was applied (program DATAPH⁹).

Introducing anisotropic temperature factors and an isotropic extinction parameter, a full-matrix least-squares calculation (program LINUS¹⁰) gave a final *R* of 0.034 (*R_w* = 0.047) for 41 parameters.

The *F_o* values were weighted according to $w = (\sigma^2(F_o) + 0.0004 F_o^2)^{-1}$ which gave a satisfactory

weight analysis. Scattering factors for neutral atoms were taken from International Tables, Vol. IV,¹¹ The I and Zn scattering values were corrected for the real part of the anomalous dispersion, obtained from the same source.¹¹

A final difference Fourier map showed a maximum electron density of 1.5 e/Å³, close to the I atoms. It was not possible to locate the hydrogen atoms. The final atomic coordinates and thermal parameters are listed in Table 2. A list of structure factors and the weight analysis are available from the authors on request. All calculations were carried out on an IBM 360/370 computer.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

A stereoscopic view of the structure along the *a*-direction is shown in Fig. 1. The structure contains tetraamminezinc(II) cations and iodide anions. The Zn, N(1), N(2), I(1) and I(2) atoms are located on mirror planes.

Interatomic distances and bond angles within the tetraamminezinc(II) complex are given in Table 3. The N–Zn–N bond angles deviate only slightly from the regular tetrahedral value. The mean value of the Zn–N bond lengths is 2.012 Å, which is in good agreement with the value 2.03(2) Å obtained in solution.³

Table 2. Fractional coordinates and thermal parameters ($\times 10^5$). Estimated standard deviations are given in parentheses. The temperature coefficient is $\exp(-h^2\beta_{11} + \dots + 2kl\beta_{23})$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	1/4	0.35096(6)	0.39555(4)	1766(11)	1192(6)	709(4)	0	0	118(4)
I(2)	1/4	0.02569(5)	0.67580(4)	1702(9)	918(5)	568(3)	0	0	-2(3)
Zn	1/4	0.75026(8)	0.41424(6)	1353(14)	812(7)	496(5)	0	0	-7(5)
N(1)	1/4	0.70004(75)	0.56134(51)	2433(153)	1225(77)	587(41)	0	0	278(47)
N(2)	1/4	0.94406(58)	0.39604(48)	2356(148)	833(60)	629(43)	0	0	1(41)
N(3)	0.02680(62)	0.68172(45)	0.35034(41)	2017(96)	1077(48)	969(35)	188(60)	-458(54)	170(38)

Table 3. Bond distances (Å) and angles (°) within the $\text{Zn}(\text{NH}_3)_4^{2+}$ ion. Standard deviations are given in parentheses.

Distances	Angles		
Zn–N(1)	1.997(7)	N(1)–Zn–N(2)	111.9(3)
Zn–N(2)	2.030(6)	2 × N(1)–Zn–N(3)	108.0(2)
Zn–2N(3)	2.010(5)	2 × N(2)–Zn–N(3)	107.7(2)
		N(3)–Zn–N(3)	113.7(3)

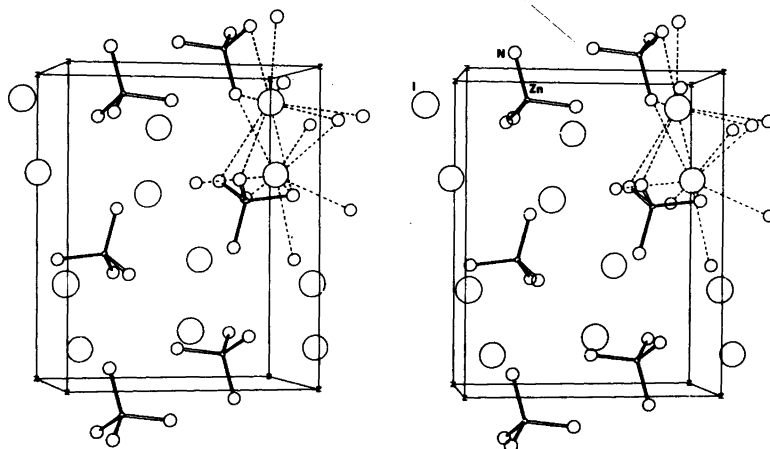


Fig. 1. Stereoscopic view of the $\text{Zn}(\text{NH}_3)_4\text{I}_2$ structure (program ORTEP²⁰).

Steffen and Palenik¹² reported that in tetrahedral ZnCl_2L_2 complexes (L = nitrogen donor ligands) the Zn–N bond lengths correlate roughly with the ligand $\text{p}K_b$ values with small perturbations due to steric effects. Table 4 gives the Zn–N bond distances

within some tetrahedral and octahedral zinc(II) complexes with N donor ligands of similar $\text{p}K_b$ values. None of previously reported values for the Zn–N coordination distance within the $\text{Zn}(\text{NH}_3)_4^{2+}$ complex may be significantly different from the mean

Table 4. Comparison of Zn–N bond distances for some tetrahedral and octahedral complexes of the zinc(II) ion in solids and in aqueous solution.

Compounds	Zn–N distances (Å)	Configuration	Ref.
Solids			
$\text{Zn}(\text{NH}_3)_4\text{B}_5\text{H}_8$	2.05(1)	Tetrahedral	14
$[\text{Zn}(\text{NH}_3)_4]\text{Mo}(\text{O}_2)_4$	2.05(3)	Tetrahedral	15
$\text{Zn}(\text{NH}_3)_4\text{I}_2$	1.997(7)	Tetrahedral	This study
	2.030(6)		
	2.010(5)		
	2.02(4)		
$\text{Zn}(\text{NH}_3)_4(\text{I}_3)_2$	2.07(4)	Tetrahedral	3
	2.02(4)		
$\text{Zn}(\text{C}_3\text{H}_4\text{N}_2)_4(\text{ClO}_4)_2$	1.997(7)	Tetrahedral	18
$\text{ZnCl}_2(\text{NH}_3)_2$	2.001(7)	Distorted tetrahedral	13
	2.024(2)		
$\text{Zn}(\text{C}_3\text{H}_4\text{N}_2)_2\text{Cl}_2$	1.995(11)	Distorted tetrahedral	19
	2.020(11)		
$\text{Zn}(\text{C}_3\text{H}_4\text{N}_2)_6\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	2.15–2.26(3)	Octahedral	16
Solution			
$\text{Zn}(\text{NH}_3)_4^{2+}$	2.03(2)	Tetrahedral	3
$\text{ZnCl}(\text{NH}_3)_3^+$	2.00(3)	Distorted tetrahedral	3
$\text{Zn}(\text{en})_2^{2+}$	2.131(9)	Tetrahedral	17
$\text{Zn}(\text{en})_3^{2+}$	2.276(5)	Octahedral	17

Table 5. Interatomic distances (Å) I---N shorter than 4.1 Å.

I(1)–2N(1)	3.848(2)	I(2)–N(1)	3.704(8)
I(1)–2N(3)	3.875(5)	I(2)–2N(3)	3.705(5)
I(1)–N(2)	3.941(6)	I(2)–N(2)	3.762(6)
I(1)–2N(3)	3.943(5)	I(2)–2N(3)	3.773(5)
I(1)–2N(3)	4.038(5)	I(2)–2N(2)	3.897(2)

value of 2.012(4) Å obtained in the present study. The standard deviation in $\text{Zn}(\text{NH}_3)_4\text{B}_8\text{H}_8$ appears to be slightly underestimated, since 25 parameters were refined to $R=0.078$ using 265 reflections. Since ammonia has the lowest pK_b value (=4.74) in the ZnCl_2L_2 series, the minimum value of the Zn–N bond distance may be expected to occur in $\text{ZnCl}_2(\text{NH}_3)_2$. In a reinvestigation of this compound, the Zn–N(NH_3) bond length has been refined to 2.024(2) Å.¹³ This value is consistent with those within the $\text{Zn}(\text{NH}_3)_4^{2+}$ complex and that found in the $\text{ZnCl}(\text{NH}_3)_3^+$ complex, which shows no effect of Cl coordination to Zn(II) on the Zn–N(NH_3) distance.

For octahedrally coordinated zinc(II), an increased Zn–N bond length has been observed in the imidazole¹⁶ and in the ethylenediamine¹⁷ complexes (cf. Table 4). The hexaammine complex has been reported to exist in $\text{Zn}(\text{NH}_3)_6\text{X}_2$, X=Cl, Br, I, ClO_3 and ClO_4 .⁴ Although no single crystal study has been performed, it is reasonable to assume that the Zn–N bond distance in the hexaammine complex has a value close to that found in $\text{Zn}(\text{C}_3\text{H}_4\text{N}_2)_6\text{Cl}_2 \cdot 4\text{H}_2\text{O}$.¹⁶

The iodine atoms are surrounded by nine ammonia molecules, the average interatomic distances I(1)---N(NH_3) and I(2)---N(NH_3) being 3.927 and 3.790 Å, respectively (cf. Table 5). It was not possible to detect hydrogen atom positions from the diffraction study but these distances may well correspond to N–H...I hydrogen bonds. In aqueous solution, the ammonia ligands in the $\text{Zn}(\text{NH}_3)_4^{2+}$ complex are probably hydrogen-bonded to water molecules in a second coordination sphere, so that the Zn–N bond distances are of the same magnitude in aqueous solution and in the solid state.

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