The Crystal Structure of Diamminedichlorozinc(II), $ZnCl_2(NH_3)_2$. A New Refinement

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Complexes of Zn(II) with ammonia and chloride ion, $Zn(NH_3)_4^{2+}$ and $ZnCl(NH_3)_3^+$, have been investigated in solution by the X-ray diffraction method.[1] To further clarify the tetrahedral coordination of Zn(II) and compare the structures both in solution and in the solid state, a single crystal structure determination was performed for $Zn(NH_3)_4I_2$.[2] The structure of mixed ligand complex, $ZnCl_2(NH_3)_2$, was not determined in aqueous solution since a sample solution containing the species predominantly could not be prepared. However, MacGillavry and Bijvoet[3] reported the crystal structures of $ZnCl_2(NH_3)_2$ and its isomorphous $ZnBr_2(NH_3)_2$ in 1936 but the structures were not refined. In the present investigation, the structure of $ZnCl_2(NH_3)_2$ has been refined and compared with the $ZnCl(NH_3)_3^+$ and $Zn(NH_3)_4^{2+}$ ions as determined from the solution diffraction measurement.

The crystals were prepared by slow evaporation of ammoniacal aqueous solution of $ZnCl_2$ at pH of around 5 adjusted by the addition of NH_4Cl. A single crystal 0.06 × 0.07 × 0.09 mm was mounted on a glass fiber. The intensity data were measured by a Syntex $P2_1$ four-circle diffractometer using graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) to $2\theta = 80°$. The experimental details were described previously.[2] Cell dimensions were refined by a least-squares fit to the setting angles of 11 reflections measured on the diffractometer.

The compound crystallizes in space group *Imam* (No. 74) with parameters: M.W. = 170.4, $a = 7.809(2)$ Å, $b = 8.512(2)$ Å, $c = 8.114(2)$ Å, $D_x = 2.10$ g cm^{-3}, $\mu = 5.49$ mm^{-1}, $Z = 4$.

A total of 3285 symmetry related *hkl* and *hkl̄* reflections were collected, those 1435 reflections with $I > 3\sigma(I)$ were considered significant and used in the subsequent calculations. The intensities were corrected for Lorentz-polarization and absorption effects. The transmission factor varied from 0.494 to 0.582. The refinement was started from the positions previously reported except that the origin was shifted to $(0, -1/4, 0)$.[3] The full-matrix least-squares refinement of an overall scale factor, positional and anisotropic thermal parameters for all non-hydrogen atoms gave a final $R = 0.029$ ($R_w = 0.047$ when unobserved reflections were included). The data were also corrected for the secondary extinction effect according to Coppens and Hamilton[9] giving $g = 0.15(3) \times 10^4$. The weighting function was $w = (\sigma^2(F_o) + 0.0004F_o^2)^{-1}$. The scattering factors for neutral Zn, Cl and N atoms were taken from the International Tables.[4] A final difference Fourier map did not locate positions of hydrogen atoms. Final atomic coordinates and thermal parameters are given in Table 1 with their standard deviations. A list of structure factors and the weight analysis are available from the authors on request.

A stereoscopic view of the structure is shown in Fig. 1 and some interatomic distances and angles are

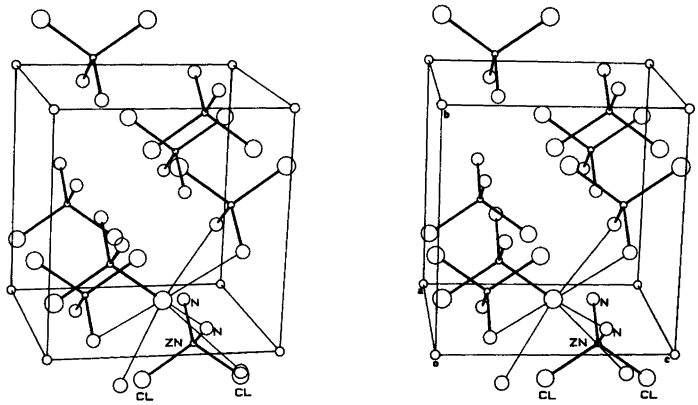

Fig. 1. Stereoscopic view of the structure $ZnCl_2(NH_3)_2$. Possible Cl···N hydrogen bonds are shown for one Cl atom for clarity.

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Table 1. Fractional coordinates and thermal parameters. Standard deviations are given in parentheses. The temperature factor is $\exp\{-(h^2\beta_{11}+\cdots+2hk\beta_{12}+\cdots)\times 10^{-5}\}$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0	0.38583(3)	1/4	961(5)	777(4)	1007(4)	0	0	0
Cl	0	0.23111(5)	0.02170(6)	1218(6)	1009(5)	1022(6)	0	0	−182(4)
N	0.21467(2)	0.51902(18)	1/4	1121(22)	940(18)	1410(22)	−164(16)	0	0

given in Table 2. The Zn atom is coordinated by two ammonia molecules and two chloride ions in a distorted tetrahedron (C_{2v} symmetry). The Zn−N bond distance within $ZnCl_2(NH_3)_2$ (2.024 Å) is not significantly different from the corresponding values within the $Zn(NH_3)_4^{2+}$ ion (2.03 Å[1] and 2.012 Å[2]) and within the $ZnCl(NH_3)_3^+$ ion (2.00 Å[1]). This fact indicates strong covalent character in the bonds between the zinc and the ammonia N atoms.

Steffen and Palenik [5] compared the Zn−Cl bond lengths in a series of $ZnCl_2L_2$ (L = N donor ligands) and stated that the Zn−Cl distances in $ZnCl_2(NH_3)_2$ and $ZnCl_2(C_3H_4N_2)_2$ are significantly longer than those in the other compounds. In the $ZnCl_2(C_3H_4N_2)_2$ compound, the chloride ion is hydrogen-bonded to the imidazol nitrogen atoms.[6] As seen in Fig. 1 and Table 2B, the Cl atoms in $ZnCl_2(NH_3)_2$ may also be hydrogen-bonded to the ammonia nitrogen atoms, though hydrogen atoms could not be located in the present study. Thus, lengthened Zn−Cl bonds in the two structures may in both cases be due to the hydrogen bonds. In aqueous solution, the Cl atom in $ZnCl(NH_3)_3^+$ is probably hydrogen-bonded with nearest neighbor water molecules, which results in similar values as found in the $ZnCl_2(NH_3)_2$ crystal. These Zn−Cl distances are comparable with those in $ZnCl_4^{2-}$ ions (2.267 Å[7] and 2.270 Å[8]).

Table 2. Interatomic distances (Å) and angles (°). Estimated standard deviations are given in parentheses.

(A) Within $ZnCl_2(NH_3)_2$ complex	
Zn−2N	2.024(2)
Zn−2Cl	2.273(1)
4×N−Zn−Cl	108.94(3)
N−Zn−N	111.86(12)
Cl−Zn−Cl	109.19(4)
(B) Possible Cl−N hydrogen bonds	
Cl−2N	3.492(2)
Cl−2N	3.596(2)
Cl−2N	3.617(2)

Table 2A shows that the bond angles in the $ZnCl_2(NH_3)_2$ complex do not deviate appreciably from the tetrahedral angle found in $Zn(NH_3)_4^{2+}$ and $ZnCl_4^{2-}$. Hence it seems reasonable to assume that the bond angles within other mixed complexes, $ZnCl(NH_3)_3^+$ and $ZnCl_3(NH_3)^-$, are tetrahedral with Zn−Cl and Zn−N bond lengths similar to those found in $ZnCl_2(NH_3)_2$.

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