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Note

The CCDC database of Crystal Structures of Tetraamminecopper (II) $[Cu(NH_3)_4]^{2+}$: Complicated Geometry of a Well-Known Complex Ion

Daisuke Noguchi
Graduate School of Engineering, Nagasaki University, Bunkyo-machi 1-14, Nagasaki 8528521, Japan.
E-mail: a.chemist.noguchi.d@gmail.com
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Tetraamminecopper (II), a complex ion with the formula $[Cu(NH_3)_4]^{2+}$, is a well-known metal complex ion in general chemistry and basic inorganic chemistry.[1,2] In addition, for over a century, $[Cu(NH_3)_4]^{2+}$ has played an important role in industrially producing the cuprammonium rayon (cupro) by regenerating cellulose in a cuprammonium solution, that is, Schweizer's reagent.[3,4] This process has been used as a challenging research project in high school,[5] and recently, $[Cu(NH_3)_4]^{2+}$ has been used as a catalyst in chemical reactions.[6,7]

Some textbooks on chemical education (including Japanese textbooks of high schools) describe the geometry of $[Cu(NH_3)_4]^{2+}$ as square planar[8] (*Fig*. 1). However, other textbooks describe it as a tetrahedral[9] or distorted octahedral[10] geometry with two water molecules ($[Cu(NH_3)_4(H_2O)_2]^{2+}$). Additionally, some researchers indicated that in an ammoniacal aqueous solution, $[Cu(NH_3)_4]^{2+}$ can exist as a distorted square planar with four-coordinated,[11,12] five-coordinated square pyramidal,[13,14] and six-coordinated distorted octahedral geometry with another H_2O or NH_3 molecule.[15,16] From these studies, at room temperature, $[Cu(NH_3)_4]^{2+}$ may dynamically exist as several inconstant structures in an aqueous ammoniacal solution of copper (II). If only one of the geometries of $[Cu(NH_3)_4]^{2+}$ is shown in the textbook, would that be appropriate for chemical education?

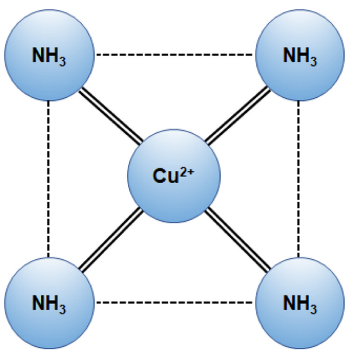

***Figure* 1.** $[Cu(NH_3)_4]^{2+}$ as square planar, one of representative geometry of metal complex ions learned in chemical education.

So far, the geometries of $[Cu(NH_3)_4]^{2+}$ in solution have been considered; however, in the crystalline state, X-ray analysis can help to determine the exact position of each atom in $[Cu(NH_3)_4]^{2+}$, which makes its structure clearer than in solution. In some textbooks of chemical education, as far as investigated by the author, only one crystal of $[Cu(NH_3)_4]SO_4{\cdot}H_2O$ is referred to establish its structure as a distorted octahedral.[10] In contrast, a variety of crystal structures of $[Cu(NH_3)_4]^{2+}$, with different counter anions and/or solvent molecules, have been reported, and no textbooks seem to refer to them.

Therefore, herein, the author reports the crystal structures of 34 compounds consisting $[Cu(NH_3)_4]^{2+}$, that were obtained from the data deposition of the Cambridge Crystallographic Data Centre (CCDC) to make these data available conveniently to the students and teachers of chemistry and to show the structures of $[Cu(NH_3)_4]^{2+}$ in detail regarding their coordination numbers, distribution of the distances between the copper (II) centers, and the nitrogen atoms of the ammine ligands in the square planar geometry. In the case of the five-coordinate geometry, the author discusses whether the square pyramid or trigonal bipyramid geometry is appropriate and also discusses the planarity of each $[Cu(NH_3)_4]^{2+}$ in every crystal.

$[Cu(NH_3)_4]^{2+}$ Categorized by Their Coordination Numbers

The data for the crystalline compounds containing $[Cu(NH_3)_4]^{2+}$ are listed in *Table* 1 (based on the cif files). These were categorized by their coordination numbers (Coord. No.); 4 indicates that four NH_3 ligands are bound

***Table* 1.** Crystal structures data of compounds containing $[Cu(NH_3)_4]^{2+}$ categorized by their coordination numbers

No.	Coord No.	Chemical Formulae	Distance / Å					Ref.	CCDC No.
			Cu-NH$_3$ (1)	Cu-NH$_3$ (2)	Cu-NH$_3$ (3)	Cu-NH$_3$ (4)	Cu-NH$_3$ (mean)		
1.	4	$[Cu(NH_3)_4](NO_2)_2$	1.98496(0)	1.98496(0)	1.98496(0)	1.98496(0)	1.98496	17	1604706
2.	4	$Na_{4n}[Cu(NH_3)_4]_n[Cu_n(S_2O_3)_{2n}]_2$	1.99439(0)	1.99439(0)	1.99439(0)	1.99439(0)	1.99439	18	1595758
3.	4	$[Cu(NH_3)_4][PtCl_4]$	1.99714(0)	1.99714(0)	1.99714(0)	1.99714(0)	1.99714	19	1591920
4.	4	$[Cu(NH_3)_4](CuBr_2)_2$	1.99743(0)	1.99743(0)	1.99743(0)	1.99743(0)	1.99743	20	1595621
5.	4	$Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2\cdot NH_3$	2.01002(0)	2.01002(0)	2.01002(0)	2.01002(0)	2.01002	21	1607060
6.	4	$[Cu(NH_3)_4][N(NO_2)_2)]_2$	2.00835(0)	2.00835(0)	2.01720(0)	2.01720(0)	2.01278	22	1727862
7.	4	$[Cu(NH_3)_4]I_4$	2.01284(0)	2.01284(0)	2.01284(0)	2.01284(0)	2.01284	23	1592782
8.	4	$[Cu(NH_3)_4Ag(SCN)_3]_n$	2.014(3)	2.014(3)	2.016(3)	2.016(3)	2.015	24	636781
9.	4	$[Cu(NH_3)_4](NO_3)_2$	2.01212(0)	2.01212(0)	2.01985(0)	2.01985(0)	2.01599	25	1590901
10.	4	$\{[Cu(NH_3)_4][Cu(CN)_3]_2\}_n$	2.008(5)	2.008(5)	2.029(4)	2.029(4)	2.019	26	867006
11.	4	$[Cu(NH_3)_4](C_3H_2N_7O)_2$	2.013(3)	2.013(3)	2.024(3)	2.024(3)	2.019	27	1843781
12.	4	$[Cu(NH_3)_4](CuI_2)_2$	2.00960(0)	2.00960(0)	2.02884(0)	2.02884(0)	2.01922	28	1606693
13.	4	$[Cu(NH_3)_4](CuCl_2)_2\cdot H_2O$	2.02472(0)	2.02472(0)	2.02472(0)	2.02472(0)	2.02472	19	1595622
14.	4	$[Cu(NH_3)_4]I_2\cdot I_2$	2.02483(0)	2.02483(0)	2.02483(0)	2.02483(0)	2.02483	29	1606167
15.	4	$[Cu(NH_3)_4][Cu_4(CN)_6]$	2.01771(0)	2.01771(0)	2.04646(0)	2.04646(0)	2.03209	30	1643737
16.	4	$[Cu(NH_3)_4](SCN)_2$	2.03765(0)	2.03765(0)	2.03765(0)	2.03765(0)	2.03765	31	1603503
17.	4	$[Cu(NH_3)_4](I_3)_2$	2.04066(0)	2.04066(0)	2.04066(0)	2.04066(0)	2.04066	29	1606168
18.	4	$[Cu(NH_3)_4]S_2O_6$	2.04115(0)	2.04115(0)	2.05065(0)	2.05065(0)	2.04590	32	1594950
19.	4	$\{[Cu(NH_3)_4][Ag_2S_3(SCN)_3]\}_2$	2.06148(0)	2.06148(0)	2.06715(0)	2.06715(0)	2.06432	33	1608097
20.	5	$[Cu(NH_3)_4]SeO_4$	1.99145(0)	1.99996(0)	2.01167(0)	2.01658(0)	2.00492	34	1599333
21.	5	$[Cu(NH_3)_4](ReO_4)_2$ (monoclinic)	2.003(6)	2.011(7)	2.018(6)	2.024(8)	2.014	35	1789130
22.	5	$[Cu(NH_3)_4](MnO_4)_2$	2.01290(0)	2.01290(0)	2.01603(0)	2.01603(0)	2.01447	36	1624776
23.	5	$[Cu(NH_3)_4(CN)_3Pt(\mu\text{-}CN)]$	2.016(5)	2.016(5)	2.018(6)	2.018(6)	2.017	37	1423609
24.	5	$[Cu(NH_3)_4][Ni(CN)_4]$	2.0148(12)	2.0148(12)	2.0238(12)	2.0238(12)	2.0193	38	1056583
25.	5	$[Cu(NH_3)_4\text{-}(\mu_2\text{-}NC)\text{—}Pd(CN)_3]$	2.016(3)	2.016(3)	2.025(3)	2.025(3)	2.021	39	1431685
26.	5	$[Cu(NH_3)_4]_2[Cu(NH_3)_2]_2\text{-}(\mu_2\text{-}CN)_8\text{-}[Pd_2(CN)_4]_2$	2.013(5)	2.013(5)	2.037(5)	2.037(5)	2.025	40	1526147
27.	5	$[Cu(NH_3)_4]_2[Cu(NH_3)_2]_2\text{-}(\mu_2\text{-}CN)_8\text{-}[Ni_2(CN)_4]_2$	2.023(4)	2.023(4)	2.034(4)	2.034(4)	2.029	41	1434064
28.	5	$[Cu(NH_3)_4]SO_4\cdot H_2O$	2.03079(0)	2.03079(0)	2.03157(0)	2.03157(0)	2.03118	34	1599332
29.	5	$\{[Cu(NH_3)_4\text{-}\mu\text{-}(NC)Ni(CN)_2\text{-}\mu\text{-}(CN)\}_2\text{—}$ $\{[Cu(NH_3)_2]\text{-}\mu\text{-}[Ni(CN)_4]\}_2$	2.01979(0)	2.01979(0)	2.05607(0)	2.05607(0)	2.03793	42	1643734
30.	5	$[Cu(NH_3)_4]BeF_4\cdot H_2O$	1.95300(0) 2.03366(0) 2.03506(0) 2.02765(0)	1.95300(0) 2.03366(0) 2.03506(0) 2.02765(0)	2.04429(0) 2.11450(0) 2.07480(0) 2.05086(0)	2.04429(0) 2.11450(0) 2.07480(0) 2.05086(0)	2.04173	43	1592756
31.	6	$[Cu(NH_3)_4]\cdot H[CoMo_6O_{18}(OH)_6]\cdot 10H_2O$	1.95581(0)	1.95581(0)	1.96610(0)	1.96610(0)	1.96095	44	1716363
32.	6	$\{\mu\text{-}[Cu(NH_3)_4]\}\{VO(O_2)_2(NH_3)\}_2$	2.02556(0)	2.02556(0)	2.02642(0)	2.02642(0)	2.02599	45	1731114
33.	6	$[Cu(NH_3)_4](ReO_4)_2$ (triclinic)	2.02465(0)	2.02465(0)	2.02835(0)	2.02835(0)	2.02650	46	1685300
34.	6	$[Cu(NH_3)_4]_3[ScF_6]_2$	2.022(9) 2.027(8) 2.017(9)	2.022(9) 2.027(8) 2.017(9)	2.026(8) 2.031(7) 2.098(9)	2.026(8) 2.031(7) 2.098(9)	2.037	47	1774152

to the copper (II) center, and there are no atoms at a distance less than 2.5 Å in axial direction. Although 2.5 Å is greater than the sum of the ionic radii of each Cu^{2+} and donor atom, the interatomic interactions were considered to be non-negligible.[48,49]

The value of 2.5 Å was chosen on the basis that in the case of tetraamminecopper (II), donor atoms at distances larger than approximately 2.5 Å are not generally considered to interact with the copper (II) center.[48,49] Coord. No. 5 in the *Table* 1 means that there is one atom within a distance of 2.5 Å from the copper (II) center, and Coord. No. 6 means that two atoms exist within a distance of 2.5 Å in

***Table* 2.** Distances between copper(II) center and fifth or sixth ligands of complexes of $[Cu(NH_3)_4X]^{2+}$ and $[Cu(NH_3)_4XY]^{2+}$

	Coord No.	Chemical Formulae	Distance / Å		Angle /°	Axial Atoms	Ref.	CCDC No.
			Cu-X	Cu-Y				
20.	5	$[Cu(NH_3)_4]SeO_4$	2.45105(0)			O of SeO_4^{2-}	34	1599333
21.	5	$[Cu(NH_3)_4](ReO_4)_2$ (monoclinic)	2.458(5)			O of ReO_4^-	35	1789130
22.	5	$[Cu(NH_3)_4](MnO_4)_2$	2.45624(0)			O of MnO_4^-	36	1624776
23.	5	$[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$	2.394(8)			N of CN^-	37	1423609
24.	5	$[Cu(NH_3)_4][Ni(CN)_4]$	2.3777(15)			N of CN^-	38	1056583
25.	5	$[Cu(NH_3)_4\text{-}(\mu_2\text{-}NC)\text{—}Pd(CN)_3]$	2.384(5)			N of CN^-	39	1431685
26.	5	$[Cu(NH_3)_4]_2[Cu(NH_3)_2]_2\text{-}(\mu_2\text{-}CN)_8\text{-}[Pd_2(CN)_4]_2$	2.322(6)			N of CN^-	40	1526147
27.	5	$[Cu(NH_3)_4]_2[Cu(NH_3)_2]_2\text{-}(\mu_2\text{-}CN)_8\text{-}[Ni_2(CN)_4]_2$	2.309(4)			N of CN^-	41	1434064
28.	5	$[Cu(NH_3)_4]SO_4\cdot H_2O$	2.33979(0)			O of H_2O	34	1599332
29.	5	$\{[Cu(NH_3)_4\text{-}\mu\text{-}(NC)Ni(CN)_2\text{-}\mu\text{-}(CN)\}_2$— $\{[Cu(NH_3)_2]\text{-}\mu\text{-}[Ni(CN)_4]\}_2$	2.30984(0)			N of CN^-	42	1643734
30.	5	$[Cu(NH_3)_4]BeF_4\cdot H_2O$	2.39890(0)			O of H_2O	43	1592756
31.	6	$[Cu(NH_3)_4]\cdot H[CoMo_6O_{18}(OH)_6]\cdot 10H_2O$	2.34920(0)	2.34920(0)	180.0000(0)	O of $[CoMo_6O_{18}(OH)_6]^-$	44	1716363
32.	6	$\{\mu\text{-}[Cu(NH_3)_4]\}\{VO(O_2)_2(NH_3)\}_2$	2.48395(0)	2.48395(0)	180.0000(0)	O of $VO(O_2)_2NH_3$	45	1731114
33.	6	$[Cu(NH_3)_4](ReO_4)_2$ (triclinic)	2.48465(0)	2.48465(0)	180.0000(0)	O of ReO_4^-	46	1685300
34.	6	$[Cu(NH_3)_4]_3[ScF_6]_2$	2.0428(5) 2.0432(5) 2.0448(5)	2.0428(5) 2.0432(5) 2.0448(5)	180.0000(0) 180.0000(0) 180.0000(0)	F of ScF_6^{3-}	47	1774152

the axial direction with four-coordinate of NH_3.

In each category (Coord. No. 4, 5 and 6), they are arranged in the ascending order of the distances of the mean Cu-NH_3. Interestingly, there were two modifications to $[Cu(NH_3)_4](ReO_4)_2$: No. 21 (monoclinic), and No. 33 (triclinic). It was demonstrated in *Table* 2 that in the present cases of Coord. No. 6, the distance between the Cu^{2+} and the bounded sixth atom (= Y) in the axial direction are same as the values of Cu-X (X = fifth atom of the ligands out of the equatorial plane).

Distribution of Mean Cu-NH_3 Distances

A histogram of the range of the mean Cu-NH_3 distances is shown in *Fig.* 2. The mean distance of Cu-NH_3 for all 34 crystalline $[Cu(NH_3)_4]^{2+}$-containing compounds was found to be 2.020 Å. In addition, the minimum value was 1.96095 Å for $[Cu(NH_3)_4]\cdot H[CoMo_6O_{18}(OH)_6]\cdot 10H_2O$ (No. 31), and the maximum value was 2.06432 Å for $\{[Cu(NH_3)_4][Ag_2S_3(SCN)_3]\}_2$ (No. 19).

For comparison, in the crystal of $NH_4[Cu(NH_3)_5](ClO_4)_3$, the mean Cu-$NH_3$ distance in the equatorial plane of pentaamminecopper (II) $[Cu(NH_3)_5]^{2+}$ was reported to be 2.06681(0) Å,[50] and in the crystal of $[Cu(NH_3)_6][F(H_2O)F]$ containing hexaamminecopper (II) $[Cu(NH_3)_6]^{2+}$, the mean Cu-NH_3 distance in the equatorial plane was reported to be 2.09229(0) Å[51] (except for the each axial Cu-NH_3). Both these distances were larger than the maximum value of

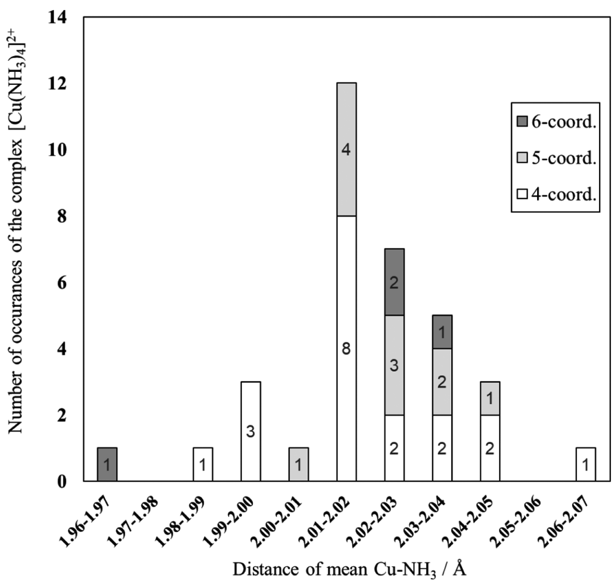

***Figure* 2.** Distribution of the range of the distance of Cu-NH_3.

2.06432 Å for Cu-NH_3 in $[Cu(NH_3)_4]^{2+}$ for the 34 tetraamminecopper (II) compounds.

τ_5 Parameters in 5-Coordinated $[Cu(NH_3)_4X]^{2+}$

The geometry of the five-coordinate copper(II) complexes can be a square pyramid and a trigonal bipyramid. The value of τ_5 is known as the index of the degree of trigonality of five-coordinate transition metal complexes, with

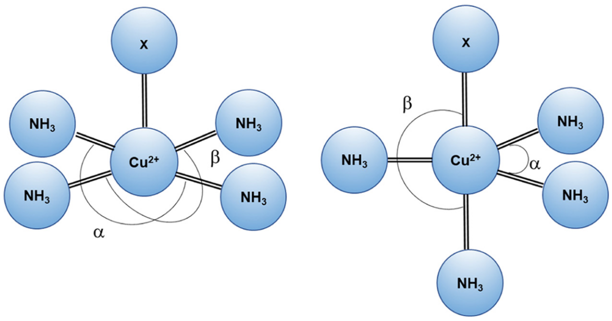

***Figure* 3.** The idealized geometry of 5-coordinated tetraaminecopper (II) complexes with another ligand (X); square pyramidal (left, $\alpha = \beta = 180°$) and trigonal bipyramidal (right, $\alpha = 120°$, $\beta = 180°$).

$\tau_5 = 0$ indicating a perfect square pyramidal geometry and $\tau_5 = 1$ indicating a perfect trigonal bipyramidal geometry,[52,53] and it is described as:

$$\tau_5 = (\beta - \alpha)/60$$

where β is the larger of the two angles (*Fig*. 3). Thus, to identify the geometry of the $[Cu(NH_3)_4X]^{2+}$ with Coord. No. 5, τ_5 was calculated (*Table* 3). Consequently, it was revealed that nine compounds had square pyramidal geometries and two had distorted square pyramidal geometries. None of these were observed to have a trigonal bipyramidal geometry.

Out-of-plane Distortion of $[Cu(NH_3)_4]^{2+}$

The perpendicular distance from the metal ion to the calculated mean plane of the equatorial donor atoms is known. *Table* 4 lists the *d* value, which is the perpendicular distance from the Cu^{2+} ion to the calculated mean plane of $[Cu(NH_3)_4]^{2+}$. However, in the case of $[Cu(NH_3)_4]_3[ScF_6]_2$ (No. 34), the calculation could not be conducted because of disordering. From these data, the complex ion of $[Cu(NH_3)_4]^{2+}$ with the most out-of-planarity in $[Cu(NH_3)_4]^{2+}$ seemed to be $[Cu(NH_3)_4]SO_4{\cdot}H_2O$ (No. 28), whose *d* value was 0.114. Therefore, the case where the textbook describes the geometry of $[Cu(NH_3)_4]^{2+}$ is based only on the relatively unusual geometry of $[Cu(NH_3)_4]^{2+}$.

For Application in Chemical Education Using Computer

In recent years, the geometry of the coordination compounds of $[Cu(NH_3)_4]^{2+}$ have been taught using computational chemistry.[54] In the article,[54] the fifth and sixth bounded atoms were not considered. The data shown in the present study is fundamental to not only preparing learning materials to inform students and teachers about metal complex ions but also for calculations using computational chemistry to teach geometries of coordination compounds exhibiting phenomenon such as the Jahn-Teller effect in Cu(II) complex ions with fifth and sixth coordinated atoms.

Presumed Reasons for the Differences Between Four-, Five-, and Six-coordination

Further discussion on the differences between the four-, five-, and six-coordinate complexes of each $[Cu(NH_3)_4]^{2+}$ are of great significance. Focusing on the halogen atoms in counter anions, if F (fluorine) atoms (the smallest among halogens) were present, such as in $[Cu(NH_3)_4]BeF_4{\cdot}H_2O$ (No. 30) and in $[Cu(NH_3)_4]_3[ScF_6]_2$ (No. 34), the complexes of $[Cu(NH_3)_4]^{2+}$ were five- and six-coordinate geometries. In contrast, if the counter anions included I (iodine) atoms (larger than other halogens), such as in $[Cu(NH_3)_4]I_4$ (No. 7), $[Cu(NH_3)_4](CuI_2)_2$ (No. 12), $[Cu(NH_3)_4]I_2{\cdot}I_2$ (No. 14), and $[Cu(NH_3)_4](I_3)_2$ (No. 17), all of them exhibited four-coordinate geometries. Therefore, to form a higher coordinate geometry than four, small atoms in the counter anion may

***Table* 3.** τ_5 parameters of 5-coordinated tetraaminecopper (II)

	α/°	β/°	τ_5	Geometry
20.	177.2009(0)	179.9517(0)	0.0125133	distorted sp
21.	168.8(3)	173.2(3)	0.07333	distorted sp
22.	179.0844(0)	179.0844(0)	0	sp
23.	173.2(3)	173.2(3)	0	sp
24.	172.06(5)	172.06(5)	0	sp
25.	172.07(13)	172.07(13)	0	sp
26.	174.10(15)	174.10(15)	0	sp
27.	173.45(14)	173.45(14)	0	sp
28.	171.9262(0)	171.9262(0)	0	sp
29.	173.9523(0)	173.9523(0)	0	sp
30.	173.7740(0)	173.7740(0)	0	sp

sp = square pyramid

***Table* 4.** Cu-to-meanplane distances (*d*) for $[Cu(NH_3)_4]^{2+}$ (The cases of both *d* and RMSD equal to 0.000 are omitted)

	d / Å	RMSD / Å		*d* / Å	RMSD / Å
8.	0.000	0.011	24.	-0.111	0.056
9.	-0.003	0.002	25.	0.098	0.049
11.	-0.026	0.013	26.	-0.079	0.039
19.	0.000	0.063	27.	0.089	0.044
20.	0.009	0.012	28.	-0.114	0.057
21.	-0.031	0.141	29.	-0.079	0.040
22.	-0.009	0.005	30.	0.094	0.047
23.	0.096	0.048	31.	0.000	0.039

RMSD = root mean square distances

be helpful to allow the construction of five- and six-coordinate geometries by weakening the repulsions between the $[Cu(NH_3)_4]^{2+}$ cations and the counter anions in the crystals. Although F-containing anions such as BF_4^- and PF_6^- are known to exist, there are no reports on the crystal structures of $[Cu(NH_3)_4]BF_4$ and $[Cu(NH_3)_4]PF_6$. Hence, it would be needed that making the synthesis and X-ray crystal analyses of $[Cu(NH_3)_4]BF_4$ and $[Cu(NH_3)_4]PF_6$ crystals a challenging task to ensure the reason mentioned above hereafter.

Furthermore, the type of halogen atom is not the only factor determining the coordination number of $[Cu(NH_3)_4]^{2+}$. Crystal packing is believed to play an important role in coordination. The previously reported crystals of $[Cu(NH_3)_4]^{2+}$, with an organic anion, were only $[Cu(NH_3)_4](C_3H_2N_7O)_2$ (No. 11), where $C_3H_2N_7O^-$ is an anion formed by the deprotonation of 4-amino-3-(5-tetrazolate)-furazan. The synthesis and analysis of crystals with typical organic anions such as CH_3COO^- and $CF_3SO_3^-$, linear organic anions, and $C_6H_5COO^-$ and picrate $C_6H_2(NO_2)_3O^-$, which have high planarity, may also contribute to a deeper understanding of the reason behind the formation and differences of the four-, five-, and six-coordinates because they may change the crystalline packing.

The effects of the solvent molecules are not sufficiently clear. Only water molecules were included as a solvent in the crystals of $[Cu(NH_3)_4]^{2+}$, as reported previously (*Table* 1). Polar solvents, such as methanol, dimethylsulfoxide, and dimethylformamide can also be used to synthesize solvent-containing crystals in addition to water molecules.

It was demonstrated that the Cu-N distances in $[Cu(NH_3)_4]^{2+}$ are approximately 2.0–2.1 Å in the crystalline state. Therefore, it is concluded that a slight difference existed owing to the difference in counter ions or crystalline solvents. In other words, the basic geometry of $[Cu(NH_3)_4]^{2+}$ is a four-coordinate square planar crystal. However, the existence of $[Cu(NH_3)_4]^{2+}$ with five- and six-coordinate geometries is also non-negligible in the crystalline state. This tendency of $[Cu(NH_3)_4]^{2+}$ to exist as a four-coordinate square planar geometry, and additionally, as a five-coordinate square pyramid and six-coordinate distorted octahedral geometry is similar to that in solution.

The deeper understanding of the structure of $[Cu(NH_3)_4]^{2+}$ in the crystalline state reported herein may motivate further studies to use another advanced research material and contribute to the improvement and development of chemical education in the future.

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