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References

BILTZ, W. & HANSEN, W. (1923). *Z. anorg. Chem.* **127**, 1.
BILTZ, W. (1923). *Z. anorg. Chem.* **130**, 93.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* Oxford: Pergamon Press.
DISTANOV, G. K. (1938). *Zh. Obshch. Khim.* **8**, 783.
FRIEDRICHS, F. (1921). *Z. anorg. Chem.* **116**, 141.
GUYER, A., BIELER, A. & SCHMID, E. (1934). *Helv. Chim. Acta* **17**, 1530.
International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JOANNIS, M. (1891). *C. R. Acad. Sci., Paris*, **112**, 337.
LEONARD, G. W., LIPPINCOTT, E. R., NELSON, R. D. & SELLERS, D. E. (1955). *J. Amer. Chem. Soc.* **77**, 2029.
LIMINGA, R. & OLOVSSON, I. (1964). *Acta Polytech. Scand., Math. Computing Mach. Ser.* No. 10.
OLOVSSON, I. (1960a). *Acta Chem. Scand.* **14**, 1453.
OLOVSSON, I. (1960b). *Acta Chem. Scand.* **14**, 1466.
OLOVSSON, I. (1960c). *Ark. Kemi*, **16**, 437.
PATSCHEKE, G. (1933). *Z.phys. Chem.* A, **163**, 340.
PATSCHEKE, G. & TANNE, C. (1935). *Z. phys. Chem.* A, **174**, 135.
PICON, M. (1919). *C. R. Acad. Sci., Paris*, **168**, 825.

Packing Principles in the Structures of Metal Ammine Salts

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From simple considerations of the different ways in which ammonia may be introduced into the structures of metal ammine salts it is evident that while the ammonia molecules tend to be coordinated to the metal ions they otherwise behave as rather inactive groups towards their remaining environment. Accordingly a factor of major importance for the formation of these structures is the form of the most favourable packing of the large groups, namely the ammonia molecules and negative ions. This will be particularly true for the halides since the interaction between ammonia and halide ions appears to be quite small in general. Some metal ammine salt structures studied earlier, mainly halides, are briefly reviewed with the object of investigating to what extent such simple packing is realized in practice. It is shown that in the majority of such compounds the arrangement of the ammonia molecules and negative ions may be described approximately as cubic or hexagonal close-packed or as body-centred cubic, with the metal ions in tetrahedral or octahedral interstices.

Introduction

In the preceding paper the structure common to $NaCl . 5\frac{1}{3}NH_3$ and $NaBr . 5\frac{1}{7}NH_3$ is presented (Olovsson, 1965). It is found that this structure can be described as a nearly cubic close-packed arrangement of ammonia molecules and halide ions with sodium ions occupying some of the octahedral interstices. Subsequent interest has become focused on the structures of metal ammine halides in general since it appears very probable that simple building principles such as the close-packing of ammonia molecules and halide ions would be an important factor in the structures of many other ammines. A survey of some of the earlier published structures with this concept in mind therefore seems valuable.

General considerations

Let us first consider the different ways of inserting an ammonia molecule into the structure of a metal ammine salt. It is found by experience that ammonia is

almost always coordinated to the metal ion, to which the bond is formed by means of the lone pair as follows:

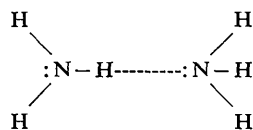$$\text{Me---:NH}_3\text{---} \qquad\qquad (a)$$

The strength of this bond varies considerably, from quite strong, as in many transition metal compounds, to very weak, as in alkali metal compounds.

'Extra' ammonia molecules not bonded to the metal are very seldom found. This situation appears quite natural when other possibilities for inserting ammonia molecules into the structure are considered. Thus, an ammonia molecule bonded to other ammonia molecules,

$$\text{NH}_3\text{---NH}_3\text{---NH}_3 \qquad\qquad (b)$$
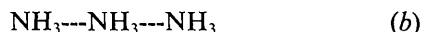
will be only very weakly bonded for two reasons: (1) Hydrogen bonds of the type:

$$
\begin{array}{ccc}
\text{H} & & \text{H} \\
\diagdown & & \diagup \\
& :\text{N}-\text{H}\text{---------}:\text{N}-\text{H} & \\
\diagup & & \diagdown \\
\text{H} & & \text{H}
\end{array}
$$

are in general weak. (2) It is difficult for ammonia to form an ideal three-dimensional network of normal hydrogen bonds since there are too many hydrogen atoms in comparison with the number of free electron pairs. This difficulty is clearly demonstrated in the structure of solid ammonia, where each lone pair is involved in three hydrogen bonds, each of which is therefore weaker than a normal hydrogen bond. For a further discussion of N–H---N distances and their dependence on the molecules involved in bonding the reader is referred to an article by Olovsson (1960a).
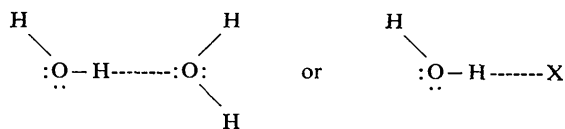
Similar arguments apply to 'extra' ammonia molecules which are linked both to the negative ion (X) and some other ammonia molecule, as in the following:

$$\text{Me}:\text{NH}_3\text{---NH}_3\text{---X} \qquad\qquad (c)$$
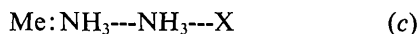
The weakness of the interaction between an ammonia molecule and a chloride ion is evident from the characteristic distances NH₃---Cl found in different compounds, e.g. NH₄Cl . 3NH₃: 3·59 Å (Olovsson, 1960b) and in NaCl . 5⅓NH₃: 3.63 Å (Olovsson, 1965). (However, in ClO_4^-, SO_4^{2-} and similar cases the interaction with the negative ion X may be appreciable since the hydrogen bonds are here generally stronger).

From this discussion it follows that in metal ammine salts, particularly in halides, the ammonia molecules will nearly always be bonded to the metal ions. The well-known fact that the number of ammonia molecules in metal ammine salts seldom exceeds the charateristic coordination number of the metal is a direct consequence of these general tendencies.

The situation in the hydrates is somewhat different. Firstly, an extra water molecule, not coordinated to the metal, is more strongly bonded since hydrogen bonds of the type

$$
\begin{array}{ccccc}
\text{H} & & \text{H} & & \text{H} \\
\diagdown & & \diagup & & \diagdown \\
:\text{O}-\text{H}\text{--------}:\text{O}: & & or & & :\text{O}-\text{H}\text{-------}\text{X} \\
& & \diagdown & & \\
& & \text{H} & &
\end{array}
$$

are generally stronger than those in cases (b) and (c) above. (The interaction between a water molecule and a halide ion is rather weak, however, and extra water molecules are seldom inserted here. In consequence, metal halide hydrates are seldom formed in which the number of water molecules exceeds the characteristic coordination number of the metal.) Secondly, the water molecule has two lone pairs and two hydrogen atoms available for bonding and this leads to an easier formation of hydrogen-bonded networks. This is very much the situation in ice in contrast to that found in solid ammonia.

In this connexion can be mentioned another general feature of metal ammine structures. In hydrate structures it is not uncommon to find metal ions enclosed by water octahedra which share corners or even edges with other octahedra. This situation does not seem too difficult to achieve as each water molecule has two lone pairs available and a given water molecule may therefore be able to coordinate more than one metal ion with ease. Such corner sharing would seem quite impossible whenever ammonia occupies the corners of the coordination polyhedra. In the structures of NaX . 5⅓NH₃, however, some of the ammonia octahedra enclosing sodium ions do, as a matter of fact, share two of the corners with adjacent octahedra. This rather improbable situation is made possible by distorting the octahedron in such a way that only five of the ammonia ligands are directly bonded to one sodium, the sixth ammonia lying at a greater distance. The above example then does not contradict the general rule that ammonia octahedra are unable to share corners with other octahedra (with ammonia simultaneously bonded to more than one metal atom).

To return to the general discussion of ammine structures: If each ammonia molecule present in the structure is coordinated to the metal ion the lone pairs will point in that direction and no lone pairs will remain for hydrogen bonding between different ammonia molecules. Consequently there can be no strong forces which demand a certain relative arrangement of the ammonia molecules. Analogously, the relative arrangement of ammonia and negative ions cannot be very critical if there is only a weak interaction between these groups. (This is particularly the case in the halides, as discussed above.)

From these considerations it is evident that while the ammonia molecules tend to be coordinated to the metal ions they will otherwise, at least in the halides, behave as rather inactive groups towards their remaining environment and the main factors determining the arrangement will be:

(1) The most favorable way of packing the ammonia molecules and negative ions.

(2) The possibility of introducing the metal ions into interstices of this ammonia–negative ion arrangement in such a way that the metal ion will attain a distribution of its ligands close to the normal.

The most common types of packing are those of the familiar cubic and hexagonal close-packed arrangements; however, cubic body-centring also results in a fairly favorable packing. Thus many metals crystallize with both a close-packed and cubic body-centred configuration and this dimorphism may be taken as an indication that the energy difference between these arrangements is not very large. It turns out that in the majority of metal ammine halide structures the arrangement may be described in terms of a cubic or hexagonal close-packing, or of a cubic body-centring of ammonia molecules and halide ions with the smaller metal ions in some of the tetrahedral or octahedral interstices. This does not mean that the crystal symmetry is actually cubic or hexagonal, but only that the arrangement approaches one of these three types. In many cases there is an appreciable deviation from the ideal configuration.

The discussion in this paper is concerned mainly with halides, but applies in many cases to other metal ammine salts. Such salts are included in the treatment only when they are directly related to the halide structures. In the same way, hydrate structures are included only in certain simple cases. It is in no way intended that the list of structures presented below should be complete. A number of the structure determinations were made many years ago and, since they are based on powder data, more accurate studies may change the parameters somewhat. Nevertheless the main features of the structures should be correct. In order to avoid a very extended list of references here the reader is referred to Wyckoff (1948) or to other similar works for references to the original publications.

The packing in some metal ammine salts

Cubic close-packing of NH_3 *and* X

(1) K_2PtCl_6 type: Most of the simple ammonia compounds so far investigated crystallize with this structure; about sixty are listed in Table 1. The structure is illustrated in Fig. 1. In the ammines with the formula $MX_2 . 6NH_3$, the six chlorine positions in K_2PtCl_6 are occupied by the ammonia molecules and the potassium positions by the negative ions X. From the figure it is evident that the ammonia molecules and negative ions together form a face-centred cubic arrangement with the metal ions located in certain of the octahedral interstices (in the positions occupied by platinum in K_2PtCl_6.)

In certain of the compounds comprising this group, some of the ammonia molecules are replaced by halide ions, as in $PtCl_2[2Cl . 4NH_3]$, or water molecules, as in $Co(SO_4)I[5NH_3 . H_2O]$. As is evident from Table 1, many other combinations are also possible,

and it seems probable that many more compounds of this type should exist. Compounds for which a distortion of the cubic K_2PtCl_6 configuration has been reported are indicated in the table by an asterisk.

Table 1. *Selected compounds with the* K_2PtCl_6 *type structure*

$MgCl_2 . 6NH_3$	$CoCl_2 . 6NH_3$
$MgBr_2 . 6NH_3$	$CoBr_2 . 6NH_3$
$MgI_2 . 6NH_3$	$CoI_2 . 6NH_3$
$Mg(BF_4)_2 . 6NH_3$	$Co(BF_4)_2 . 6NH_3$
$Mg(ClO_4)_2 . 6NH_3$	$Co(ClO_4)_2 . 6NH_3$
$CaBr_2 . 6NH_3$	$Co(SO_3F)_2 . 6NH_3$
$CaI_2 . 6NH_3$	$Co(PF_6)_2 . 6NH_3$
	$Co(ClO_3)(SO_4) . 6NH_3$
$Cr(SO_4)Br . 5NH_3 . H_2O$	$Co(ClO_3)(SO_4) . 5NH_3 . H_2O$
$CrCl_2[Cl . 5NH_3]^*$	$Co(ClO_4)(SO_4) . 6NH_3$
	$Co(ClO_4)(SO_4) . 5NH_3 . H_2O$
$MnCl_2 . 6NH_3$	$Co(SO_4)Br . 6NH_3$
$MnBr_2 . 6NH_3$	$Co(SO_4)Br . 5NH_3 . H_2O$
$MnI_2 . 6NH_3$	$Co(SO_4)I . 6NH_3$
$Mn(BF_4)_2 . 6NH_3$	$Co(SO_4)I . 5NH_3 . H_2O$
$Mn(ClO_4)_2 . 6NH_3$	$Co(SeO_4)Br . 5NH_3 . H_2O$
$Mn(SO_3F)_2 . 6NH_3$	$Co(SeO_4)I . 6NH_3$
	$CoCl_2[Cl . 5NH_3]^*$
$FeCl_2 . 6NH_3$	$CoI_2[Cl . 5NH_3]^*$
$FeBr_2 . 6NH_3$	
$FeI_2 . 6NH_3$	$RhCl_2[Cl . 5NH_3]^*$
$Fe(BF_4)_2 . 6NH_3$	$RhI_2[Cl . 5NH_3]^*$
$Fe(ClO_4)_2 . 6NH_3$	$PtCl_2[2Cl . 4NH_3]$
$Fe(SO_3F)_2 . 6NH_3$	
$Fe(NH_4)_2[5Cl . H_2O]^*$	
$FeK_2[5Cl . H_2O]^*$	$CuBr_2 . 6NH_3$
$NiCl_2 . 6NH_3$	$CuI_2 . 6NH_3$
$NiBr_2 . 6NH_3$	
$NiI_2 . 6NH_3$	$ZnBr_2 . 6NH_3$
$Ni(BF_4)_2 . 6NH_3$	$ZnI_2 . 6NH_3$
$Ni(ClO_4)_2 . 6NH_3$	
$Ni(NO_3)_2 . 6NH_3$	$CdBr_2 . 6NH_3$
$Ni(SO_3F)_2 . 6NH_3$	$CdI_2 . 6NH_3$
$Ni(PF_6)_2 . 6NH_3$	$Cd(BF_4)_2 . 6NH_3$
	$Cd(ClO_4)_2 . 6NH_3$
	$Cd(SO_3F)_2 . 6NH_3$
	$In(NH_4)_2[5Cl . H_2O]^*$

* Distortion of the K_2PtCl_6 structure.
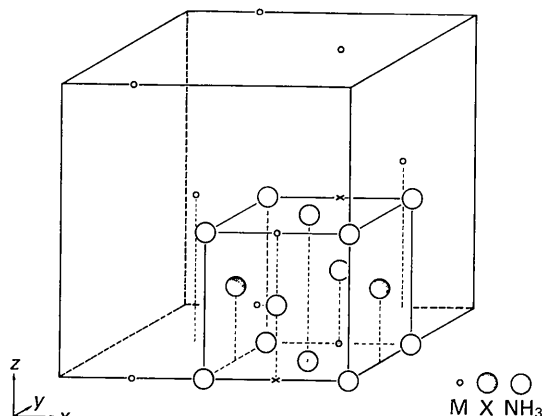

Fig. 1. The structure of $MX_2 . 6NH_3$ of the K_2PtCl_6 type. The true cubic unit cell is outlined. The positions of NH_3 and X are indicated in one octant (small cube) and are the same for the remaining octants. However, the M ions are as seen located at different edges in the different octants. In the related structure of $[CoI_2 . 6NH_3]I$ the additional iodide ions are inserted at the points marked by crosses (*cf.* text).

It appears probable that on more detailed analysis several other compounds claimed to be cubic will reveal some deviation from this ideal arrangement.

(2) $(NH_4)_3FeF_6$ type: In fact not all of the large molecules and ions in this structure type are arranged in a close-packed configuration. It is so closely related to the K_2PtCl_6 type, however, that its inclusion here seems worth while. The ammines belonging to this type of structure exhibit the following characteristics:

Cubic close-packing of ammonia and two-thirds of the negative ions; one-third of the negative ions in octahedral holes. $CoI_3 . 6NH_3$ and a number of similar compounds have a cubic $(NH_4)_3FeF_6$ structure; some are listed in Table 2. This structure is sometimes referred to as the cryolite structure although the mineral cryolite itself does not crystallize with the ideal cubic structure. If $CoI_3 . 6NH_3$ is written as $[CoI_2 . 6NH_3]I$, the atoms within the brackets are arranged in the same way as those in the compounds formulated as $MeX_2 . 6NH_3$ and discussed above (K_2PtCl_6 structure). The extra iodide ion is inserted at the mid-points of certain of the cell edges, as shown in Fig. 1 (at the points marked by crosses). This iodide ion then occupies octahedral holes similar to those of the cobalt ion (all six neighbours are ammonia molecules). In view of the large size of an iodide ion it is surprising to find compounds of this type crystallizing with the ideal cubic structure. Many other A_3BX_6 compounds do, in fact, show departures from cubic symmetry.

Table 2. *Compounds with the* $(NH_4)_3FeF_6$ *type structure*

$CoI_3 . 6NH_3$
$CoI_3 . 5NH_3 . H_2O$
$Co(ClO_4)_3 . 6NH_3$
$Co(ClO_4)_3 . 5NH_3 . H_2O$
$Co(BF_4)_3 . 6NH_3$
$Co(PF_6)_3 . 6NH_3$
$Cr(ClO_4)_3 . 6NH_3$
$Cr(ClO_4)_3 . 5NH_3 . H_2O$

(3) Miscellaneous: Cubic close-packing of NH_3 and X is also encountered in $NaCl . 5\frac{1}{7}NH_3$ and $NaBr . 5\frac{1}{7}NH_3$ as described in the preceding paper. Some notable features of this structure are further discussed at the end of the present article.

Hexagonal close-packing of NH_3 *and* X

Only one example of this type has been found: The structure proposed for *trans*-$Pt(NH_3)_2Cl_4$ has been described as a body-centred arrangement of $Pt(NH_3)_2Cl_4$ octahedra. It turns out that the ammonia molecules and chloride ions together form a hexagonal close-packed arrangement in which the platinum ions occupy some of the octahedral interstices.

Cubic body-centred arrangement of NH_3 *and* X

In two cases ($ZnCl_2 . 2NH_3$ and $ZnBr_2 . 2NH_3$) the metal ions occupy tetrahedral interstices, but in the

majority of structures belonging to this group the metal ions have an octahedral environment, as is the case in all previously discussed compounds. The tetrahedral and octahedral interstices in the body-centered arrangement are illustrated in Fig. 2.

(1) $ZnX_2 . 2NH_3$. The zinc diammine chloride and bromide are isomorphous and the structure can be described as a slightly distorted cubic body-centred arrangement of ammonia groups and halide ions, the zinc ions lying at the centres of tetrahedra formed by two ammonia molecules and two halide ions.

(2) $CdX_2 . 2NH_3$. The isomorphous cadmium diammine chloride and bromide structures have arrangements of ammonia and halogen like those in the corresponding zinc compounds. In this instance, however, the cadmium ion is surrounded by two ammonia molecules and four halide ions in an octahedral arrangement, distorted so that the two diametrically opposite ammonia molecules are closest to the cadmium ion. These octahedra share edges in such a way that each chloride ion is common to two octahedra and a chain structure results.

(3) $HgX_2 . 2NH_3$. In the structures discussed so far the metal ions occupy certain of the available octahedral interstices. In the structure proposed for mercury diammine chloride and bromide, however, the mercury ions are statistically distributed among *all* of the octahedral interstices available in the body-centred arrangement of the ammonia molecules and halide ions. This fact deserves further study. As in the instance of the cadmium compounds, the octahedron around the mercury ion is distorted in such a way that two diametrically opposite ligands (ammonia) are close relative to the other four (chlorine).

(4) $CuCl_2 . 2H_2O$. Here, too, an approximate body-centred arrangement is formed by water and halogen with copper occupying certain of the octahedral interstices. The distortion of the octahedron around
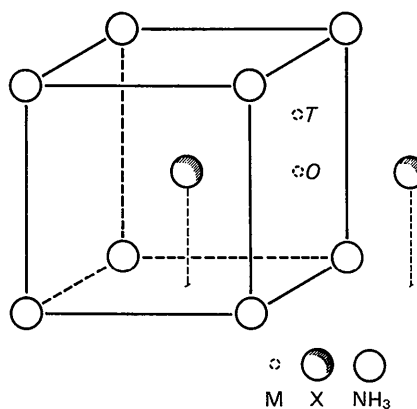

Fig. 2. Tetrahedral (T) and octahedral (O) interstices in a cubic body-centred arrangement formed by NH_3 and X.

M   X NH_3

copper, however, is opposite to that found in the cadmium and mercury compounds and the usual arrangement around copper is formed with four close neighbours in a square configuration (two water molecules and two chloride ions) and two more distant neighbours (chloride ions).

(5) $R_2CuX_4 \cdot 2H_2O$. To this group belong the following isomorphous compounds: $(NH_4)_2CuCl_4 \cdot 2H_2O$, $(NH_4)_2CuBr_4 \cdot 2H_2O$, $K_2CuCl_4 \cdot 2H_2O$ and $K_2CuBr_4 \cdot 2H_2O$. The R ions (ammonium or potassium), halide ions and water molecules together form a distorted body-centred arrangement, and copper occupies some of the octahedral interstices. The neighbours to copper are: four close neighbours (two water molecules and two chloride ions) in a square configuration and two chloride ions at a greater distance.

The corresponding ammine compounds, $(NH_4)_2CuCl_4 \cdot 2NH_3$ and $(NH_4)_2CuBr_4 \cdot 2NH_3$ have unit cells similar to those of the hydrates, but is is reported that the atomic arrangements are not identical. It has been suggested that some of the copper ions are irregularly distributed in the structure but further study of these compounds is needed.

Discussion

In the ammines which have been described above, the large groups — ammonia molecules and negative ions (or related groups) — are approximately arranged in accordance with simple packing. It is clear, however, that the weak directed forces which nevertheless exist, as for instance between the ammonia molecules and negative ions, may cause distortions of this simple packing. It is therefore not surprising that a number of compounds exist (although small) in which the relative arrangement of ammonia molecules and halide ions is not so simple. Nevertheless a high degree of close-packing is to be found even in these instances, although here and there it is disturbed to an extent which precludes description of the overall arrangement as cubic or hexagonal close-packed or body-centred.

The fact that there is a simple packing in most of the metal ammine halides indicates that this factor is of major importance in determining the solid state configuration. It may be argued that the tendency of the metal ions to attain a particular coordination is the primary factor. Thus in many instances a specific metal–ligand arrangement can be identified in solution and this arrangement is found to be maintained in the crystal. But this observation cannot be taken as a safe indication that this coordination tendency is determinative when the structure is formed in the solid state. Firstly, very little is known about conditions existing in solution and in many cases a fairly well packed arrangement of adjacent molecules may exist. Secondly, and this seems more relevant in the

present context, the compounds discussed in this paper demonstrate greatly differing strengths for the metal–ligand bonds, ranging from very strong, as in many transition metal compounds, to very weak, as in the alkali metal compounds. However, in all these cases the ammonia molecules and halide ions evidently try to pack themselves in the best possible way.

The situation in $NaX \cdot 5\frac{1}{7}NH_3$ appears particularly illuminating in this respect. Thus in these structures the indications are that a favorable packing of the large groups (ammonia and halogen) is first established. Sodium has then to accept that the ideal metal ion coordination of six ammonia molecules is unattainable and accordingly bonds with the five which are available. It is true that a further ammonia molecule occupies the sixth corner of the distorted octahedron around sodium, but this ammonia cannot be regarded as bonded to the metal ion since the lone pair on this ammonia is evidently directed in the opposite direction. This sixth ammonia molecule must essentially be regarded as filling up an otherwise empty space. If the tendency to an ideal sixfold configuration around sodium were the primary factor then clearly the arrangement would assume a very different character.

Considering the structures of the different kinds of ammonia compounds it seems best to interpret the structures of metal ammine halides mainly as a result of the factors previously discussed namely:

(1) The most favorable way of packing the ammonia molecules and negative ions.

(2) The possibility of introducing the metal ions into interstices of this ammonia–negative ion arrangement so that the metal ion will attain a close-to-normal distribution of its ligands.

A decision as to which of these factors plays the determining role in a specific case is a difficult task (and mostly of doubtful value) and amongst other things must take into account the strengths of the metal–ammonia bonds.

The metal ammine salt structures are mostly described in the literature in terms of the distribution of metal–ligand octahedra and negative ions. $Ni(NH_3)_6Cl_2$ with the K_2PtCl_6-type structure may e.g. be described as a fluorite structure, in which $Ni(NH_3)_6$ octahedra occupy the calcium positions and chloride ions occupy the fluorine positions. For purposes of systematization, however, the alternative description of these structures in terms of the packing arrangement of the large groups, ammonia molecules and negative ions, is one that should be emphazised.

References

OLOVSSON, I. (1960a). Ark. Kemi, 16, 437.
OLOVSSON, I. (1960b). Acta Chem. Scand. 14, 1453.
OLOVSSON, I. (1965). Acta Cryst. 18, 879.
WYCKOFF, R. W. G. (1948). Crystal Structures. Vol. III. New York, London: Interscience.