

THE MOLECULAR VOLUME AS A CRITERION OF BOND TYPE IN COÖRDINATION COMPOUNDS

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Received December 12, 1949

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I. BOND CLASSIFICATION IN COÖRDINATION COMPOUNDS

The chemical and magnetic properties of the hexammines of trivalent cobalt suggest a much stronger bond between cobalt and nitrogen than is found in the hexammines of cobalt(II). One might logically expect the stronger bond to be accompanied by a decrease in the cobalt-nitrogen internuclear distance. Biltz (2) and his European contemporaries suggested that this decrease in bond distance might become apparent if the molecular volumes¹ of complexes such as $[\text{Co}(\text{NH}_3)_6]\text{X}_2$ and $[\text{Co}(\text{NH}_3)_6]\text{X}_3$ were compared. As a result, molecular volume data were introduced as a criterion of bond type (2, 7).

It is a curious fact that the molecular volume of hexamminecobalt(III) chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 = (156.4 \text{ cc.})$, is almost the same as that of hexamminecobalt(II) chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2 = (156.9 \text{ cc.})$. This unexpected observation has been generally attributed to a strong compression of the ammonias in formation of the complex containing trivalent cobalt (7a). Indeed, the name "Durchdringungskomplexe" or "penetration complex," introduced by Ray (16) for coördination compounds similar to hexamminecobalt(III) chloride, suggests the penetration of the ammonia into the metal cation. In view of the above interpretation it is rather disconcerting to note that the molecular volume measurements on hexamminecobalt(III) sulfate and hexamminecobalt(II) sulfate do *not* indicate significant compression of the ammonia in *either* case, even though chemical and magnetic data indicate a very strong bond between the cobalt(III) ion and the ammonia.

Because of these conflicting facts the real significance of molecular volume data as a tool in the study of coördination compounds is open to question. Ferneliu (9) emphasizes the uncertainty when he asks, "Can the difference in the molecular volume of the ammonia in the so-called normal and penetration complexes be related to bond type?" The present review seeks an answer to this question.

¹ Molecular volume of complex = $\frac{\text{molecular weight}}{\text{density}}$.

II. DETERMINING THE VOLUME OF THE COÖRDINATED GROUPS IN
 COMPLEX COMPOUNDS

The molecular volume of the coördinated ammonia in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and related compounds is referred to frequently in the literature (7, 9, etc.). Since no direct experimental measurement of this volume is possible, it seems useful to outline the method used in obtaining the values reported. Biltz and his coworkers (1, 3) applied Kopp's rule of additive volumes to simple and complex inorganic compounds. They found that if one determines the molecular volume of the halide salt of a transition element and then subtracts the atomic volume of the appro-

TABLE 1

Molecular volume of the halide ions in crystals as determined by Kopp's additivity relationship

A. Transition metal halides

METAL ION	VOLUME OF Cl^-	VOLUME OF Br^-	VOLUME OF I^-
	cc.	cc.	cc.
Mn^{+2}	17.4	20.8	26.8
Fe^{+2}	16.5	19.8	25.6
Co^{+2}	15.9	19.1	24.6
Ni^{+2}	15.1	18.3	23.5
Fe^{+3}	16.3		
Cr^{+3}	16.6	20.5	27.1

B. Alkali and alkaline earth metal halides

METAL ION	VOLUME OF Cl^-	VOLUME OF Br^-	VOLUME OF I^-
	cc.	cc.	cc.
Ca^{+2}	12.8	16.8	24.2
Sr^{+2}	9.5	12.9	21.0
Ba^{+2}	7.5	11.6	18.5
Li^+	7.5	12.1	20.0
Na^+	3.3	8.4	17.2
K^+	-7.9	-2.1	+7.8
Rb^+	-12.6	-6.4	+4.0
Cs^+	-28.7	-23.0	-13.4

priate metal, a value is obtained which can be interpreted as the volume of the halide ion in the original salt, i.e.

Molecular volume of FeCl_2 - atomic volume of Fe metal = volume 2Cl^- ions

Representative data for several metals of the first transition group are shown in table 1A. In these salts a reasonably constant value for the volume of each halide is obtained. And, as Biltz pointed out (1), the average value for each of the halides is fairly close to the volume usually ascribed to the halogen atom at absolute zero. Hertz (13) reported the following values which were calculated

from volume measurements at the boiling point, critical point, and melting point: Cl = 16.2 cc., Br = 19.2 cc., I = 24.3 cc. These data led to the conclusion that the volume of a transition metal halide is equal to the sum of the zero-point volumes of the components.

The above relationship is not general. Table 1B indicates that serious deviations are encountered if one considers the alkali or alkaline earth halides; for instance, the atomic volume of cesium metal (71.0 cc.) is actually greater than the molecular volume of cesium chloride (42.3 cc.). This then gives a *negative* volume for the chloride ion. Biltz was fully aware of such limitations and restricted his discussion to certain transition halides, particularly those which form stable amines.

An extension of the concept of additivity to hexamines of the transition chlorides led to the consideration of molecular volume data in determining bond type. The zero-point volume of the ammonia molecule has been given as 18–21.5 cc. (3). For simplicity a value of about 20 cc. is frequently selected. Using this value for ammonia and the zero-point volumes of the transition metal and the

TABLE 2
Molecular volumes of metal ammine salts

AMMINE	CALCULATED BY ADDING ZERO-POINT VOLUMES*	OBSERVED MOLECULAR VOLUME (3)	AMMINE	CALCULATED BY ADDING ZERO-POINT VOLUMES	OBSERVED MOLECULAR VOLUME (3)
[Co(NH ₃) ₆]Cl ₂	159.2	156.9	[Cr(NH ₃) ₆]Cl ₂	160.2	161.8
[Co(NH ₃) ₆]Br ₂	167.1	171.6	[Cr(NH ₃) ₆]Br ₂	168.0	182.8
[Co(NH ₃) ₆]I ₂	177.7	198.0	[Fe(NH ₃) ₆]Cl ₂	160.0	160.3

* Zero-point volumes: NH₃ = 20 cc., Cl⁻ = 16.3 cc., Br⁻ = 19.7 cc., I⁻ = 25.5 cc., Co = 6.6 cc., Cr = 7.6 cc., Fe = 7.4 cc.

halide, the volume of the hexamines may be estimated. Data in table 2 indicate good agreement between observed and calculated values for the hexamines of cobaltous chloride, chromous chloride, and ferrous chloride but poorer agreement when bromide or iodide is the anion. Deviations with the larger halides may be attributed, in part, to changes in the polarization and thus in the volumes of the bromide and iodide ions as one goes from the small positive cations of the simple salt to the large positive cations of the complex compound. The influence of polarization on lattice distances of simple compounds has been discussed by Fajans (8).

An alternative assignment of volume differences is also possible. It may be assumed arbitrarily that the *metal ion* and the *anion exhibit* their *zero-point volumes* in all hexamine complexes; then the volume of the ammonia molecules may be adjusted until the calculated volume for the entire complex agrees with the experimental value. Ammonia volumes below 20 cc. are assumed to indicate compression of ammonia, while values above 20 cc. supposedly indicate expansion of the ammonia.

III. THE MOLECULAR VOLUME OF AMMONIA AS A CRITERION OF BOND TYPE

If the additivity relationship were applicable to amines of trivalent cobalt, one would expect the volume of the hexamminecobalt(III) complexes to exceed the volume of the hexamminecobalt(II) complexes by an amount equal to the volume of the extra anion (i.e., about 16 cc. for chloride). Data for the molecular volumes of several amines in table 3 indicate that this is not usually the case

TABLE 3

A. A comparison of molecular volumes for selected "normal" and "penetration" complexes, showing the near identity of volume in comparable amines of di- and tri-valent cations

NORMAL COMPLEXES			PENETRATION COMPLEXES		
Amine	Appar-ent molecular volume of NH ₃	Molecu-lar volume of ammine	Amine	Appar-ent molecular volume of NH ₃	Molecu-lar volume of ammine
	cc.	cc.		cc.	cc.
[Co(NH ₃) ₆]Cl ₂	20	156.9	[Co(NH ₃) ₆]Cl ₃	17	156.4
[Co(NH ₃) ₆](NO ₃) ₂	22	193.2	[Co(NH ₃) ₆](NO ₃) ₃	17	192.5
[Co(NH ₃) ₆](ClO ₄) ₂		225.4	[Co(NH ₃) ₆](ClO ₄) ₃		224.4
[Co(NH ₃) ₆](CNS) ₂	21	217.3	[Co(NH ₃) ₆](CNS) ₃	14.5	218.2
[Co(NH ₃) ₆]Br ₂	21	171.6	[Co(NH ₃) ₆]Br ₃	18	171.3
[Co(NH ₃) ₆]I ₂	24	198.0	[Co(NH ₃) ₆]I ₃	19	197.3
[Cr(NH ₃) ₆]Br ₂	22	182.8	[Cr(NH ₃) ₆]Br ₃	19	183.2
[Cr(NH ₃) ₆]I ₂	27	220.3	[Cr(NH ₃) ₆]I ₃	22	220.6

B. The approximate additivity relationship in certain hexamminecobalt(II) and (III) salts

NORMAL COMPLEXES			PENETRATION COMPLEXES		
Amine	Appar-ent molecular volume of NH ₃	Molecu-lar volume of ammine	Amine	Appar-ent molecular volume of NH ₃	Molecu-lar volume of ammine
	cc.	cc.		cc.	
[Co(NH ₃) ₆]SO ₄	19.1	155.5	[Co(NH ₃) ₆] ₂ (SO ₄) ₃	18.7	339.8 (169.9)
[Co(NH ₃) ₆]C ₂ O ₄	19.5	165.6	[Co(NH ₃) ₆] ₂ (C ₂ O ₄) ₃	19.1	368.1 (184.0)
[Co(NH ₃) ₆](C ₁₀ H ₇ SO ₃) ₂	18.3	408.7	[Co(NH ₃) ₆](C ₁₀ H ₇ SO ₃) ₃	18.0	553.4

for complexes containing monovalent anions (table 3A), but is the case for cobalt(III) complexes containing divalent anions (i.e., SO₄⁻², C₂O₄⁻²) or extra large monovalent anions [(C₁₀H₇SO₃)⁻, table 3B]. The molecular volumes of ammonia in table 3 are calculated as described above, using the assumption that the metal and the anion show their zero-point volumes in each compound.

For the normal (ionic type) complexes such as those containing divalent cobalt

the molecular volume of ammonia runs from 20 to 27 cc., while for penetration (covalent) compounds such as those containing cobalt(III) the values range from 14.5 to 22 cc. Obviously, classification of an ammine as a normal or penetration compound on the basis of these ammonia volumes is not possible unless consideration is given to the anion. It is also rather curious that the assumed contraction in the volume of the coördinated ammonia is always just great enough to compensate for the increase in volume due to the added anion. This is true whether a small chloride or large perchlorate ion is introduced into the crystal of the cobalt(II) complex. One is then led to the improbable conclusion that a greater compression of ammonia occurs when perchlorate is the anion than occurs when chloride is the negative component. Data in table 4, which are taken from Biltz (2), emphasize the importance of the anion in determining the apparent compression of the ammonia.

IV. MOLECULAR VOLUME AND LATTICE TYPE

An explanation of the above facts becomes apparent if one realizes that molecular volume depends as much upon the packing of ions and molecules as upon

TABLE 4
Ammonia volume in hexammines of various di- and tri-valent cobalt salts
(From Biltz (2))

Anion	F ⁻	Cl ⁻	Br ⁻	I ⁻	NO ₂ ⁻	SCN ⁻	R ^{-*}	SO ₄ ⁻	C ₂ O ₄ ⁻
Approximate volume of anion	7.5	16	19	25	28	41	146	34	42
Volume of NH ₃ in Co ⁺² salt		20	21	24	22	21	18.3	19.1	19.5
Volume of NH ₃ in Co ⁺³ salt	16.5	17	18	19	17	14.5	18.0	18.7	19.1

* R⁻ = β-naphthalenesulfonate.

the actual volume of the ions and molecules themselves. In this connection, crystal structure data are pertinent. The lattice of [Co(NH₃)₆]I₂ is typical of that found for many compounds of the formula [MR₆]X₂ (4, 5, 19). The structure is a cube of the calcium fluoride type, in which the iodide ions take the place of the fluorides and the complex [Co(NH₃)₆]⁺² groups take the place of the calcium ions. The structure is shown in figure 1. It will be noticed that the cubic crystallographic unit cell may be subdivided into eight smaller cubes, each of which has an iodide ion at every corner. Four of these smaller sub-cells contain [Co(NH₃)₆]⁺² cations at their centers, while the remaining four sub-cells are empty. The unit cell contains four formula weights of the compound [Co(NH₃)₆]I₂.

The hexamminecobalt(III) iodide differs from the corresponding cobalt(II) complex in that four extra iodide ions must be packed into the unit cell to give one extra anion for each formula weight. Space relationships appear to be such that the extra anions can fit, with only minor volume changes, into the four empty sub-cubes of the unit cell. As a matter of fact, the length of the unit cube decreases *very* slightly in the cobaltic complex because of the somewhat smaller size and greater field strength of the trivalent cation. For the cobalt(II) complex

the length of the unit cell is 10.91 Å. (4, 5), while for the cobalt(III) compound the values reported range from 10.88 to 10.91 Å. (12, 14, 15, 21), with the lower value favored. The crystal lattice of $[\text{Co}(\text{NH}_3)_6]_2\text{I}_2$ is indicated in figure 2.

The above pictures of the crystal structures for the two ammine iodides immediately explain Biltz's observation (table 3A) that the hexammine iodides of divalent and trivalent cobalt have almost the same molecular volume despite the fact that the cobalt(III) iodide contains one extra anion per formula weight. *The equal volume is not due primarily to a large decrease in the volume of the coordinated ammonias, as was suggested by early workers, but is due to the fact that a lattice of*

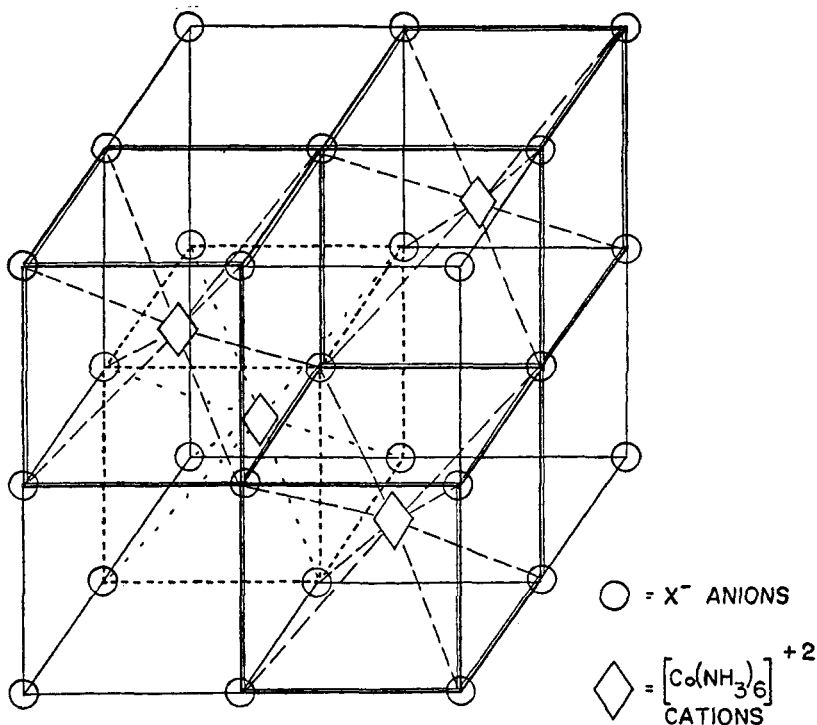


FIG. 1. Schematic diagram of $[\text{Co}(\text{NH}_3)_6]_2\text{I}_2$ crystal lattice. Note four sub-cells which are empty.

the calcium fluoride type contains four holes in the unit cell wherein four extra iodide ions may be placed without seriously distorting the crystal.

It has been established that the hexamminecobalt(II) chloride, bromide, iodide, nitrate, perchlorate, fluoborate, and fluophosphate all have a lattice of the calcium fluoride type (19). Similarly, the hexamminecobalt(III) perchlorate, fluoborate, and fluophosphate have lattices similar to that of the hexamminecobalt(III) iodide (6, 10). It seems logical to assume, by analogy with the cobalt(II) complexes, that the hexammnes of cobalt(III) chloride, bromide, nitrate, and thiocyanate will probably have lattices similar to that of the hexamminecobalt(III) iodide.

It now becomes obvious why the apparent contraction in ammonia volume is dependent upon the anion of the complex. The third anion, which produces the salt of trivalent cobalt, fills the four void spaces in the unit cell. In the cobalt(II) salt the volume of these void spaces was, by the method of calculation, included as part of the volume of the ammonia; thus in lattices such as the iodides, which contain large holes, the ammonia appears to have a somewhat larger volume than in lattices with smaller holes such as the chlorides.

It also becomes apparent why the equal volume relationship is limited to the monovalent anions. Complexes of divalent cations combined with divalent

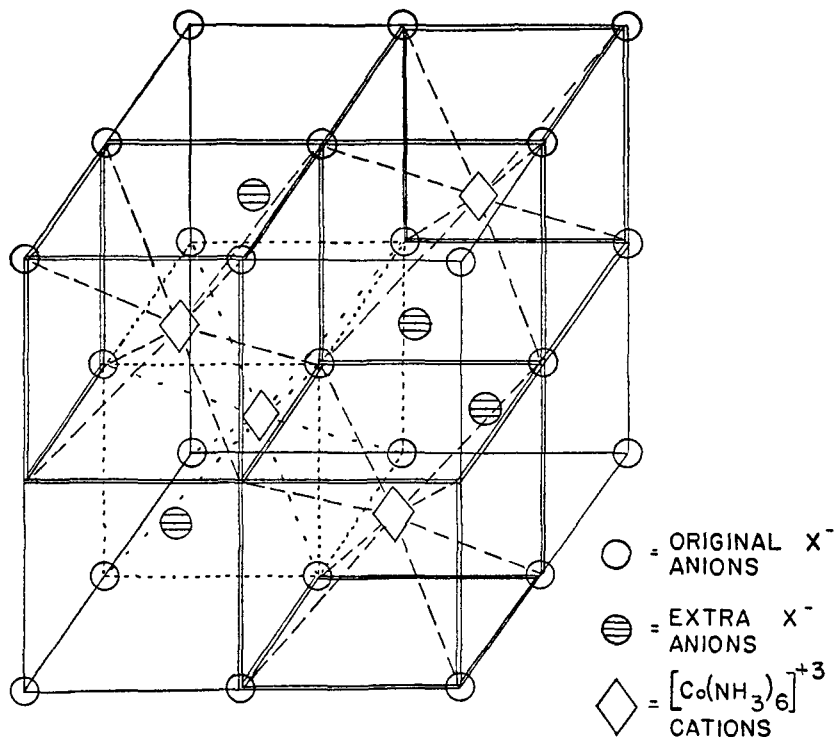


FIG. 2. $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ lattice. Note extra iodide ions in center of four sub-cells which were empty.

anions (i.e., $[\text{Co}(\text{NH}_3)_6]\text{SO}_4$ or $[\text{Co}(\text{NH}_3)_6]\text{C}_2\text{O}_4$) fall into a different structural class, $[\text{MR}_6]\text{X}$, instead of $[\text{MR}_6]\text{X}_2$ and thus cannot have a lattice of the calcium fluoride type. Crystal data on $[\text{Co}(\text{NH}_3)_6]\text{SO}_4$ are not available, but molecular volume measurements indicate that the lattice does *not* contain holes which will permit the inclusion of extra anions without a volume increase or structural rearrangement. Similarly, complexes containing the very large univalent anion such as β -naphthalenesulfonate, $\text{C}_{10}\text{H}_7\text{SO}_3^-$, would not be expected to crystallize in the calcium fluoride structure, as do ions with a smaller anion/cation radius ratio. From these data it would appear that the equal volume relationship found

in the hexamminecobalt halides may actually be a criterion of lattice type rather than an indication of a large compression of the coördinated ammonia. X-ray diffraction data on $[\text{Fe}(\text{NH}_3)_6]\text{I}_3$ would be particularly interesting as a test of the above generalization, since $[\text{Fe}(\text{NH}_3)_6]\text{I}_2$ shows the fluorite structure yet the di- and tri-valent iron amines do *not* have the same molar volume: $[\text{Fe}(\text{NH}_3)_6]\text{I}_2 = 160.3$ cc.; $[\text{Fe}(\text{NH}_3)_6]\text{I}_3 = 171.7$ cc. (3). Apparently certain electronic characteristics of the cation are necessary in order to stabilize a lattice of the $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ type. It is interesting to note that cobalt(III) complexes of the form $[\text{MR}_6]\text{X Y}$, such as $[\text{Co}(\text{NH}_3)_6]\text{SO}_4 \text{I}$, $[\text{Co}(\text{NH}_3)_6]\text{SO}_4\text{ClO}_3$, etc., have a lattice of the calcium fluoride type even though they contain the trivalent cobalt cation (10, 11).

The most direct estimate of the amount of ammonia compression in hexamminecobalt(III) halides can be obtained from the metal-nitrogen bond distances; unfortunately, such data are of very limited accuracy. Available values for the metal-nitrogen distances in several di- and tri-valent cobalt amines are contained in table 5. The best of these data indicate that the cobalt-nitrogen distance in the covalent or penetration complex, $[\text{Co}(\text{NH}_3)_6]\text{X}_3$, is about 10–20 per cent shorter than the distance in the ionic or normal complex, $[\text{Co}(\text{NH}_3)_6]\text{X}_2$. This

TABLE 5
Metal-nitrogen distances in di- and tri-valent cobalt amines

NORMAL COMPOUND	METAL-AMMONIA DISTANCE	REFERENCE	PENETRATION COMPOUND	METAL-AMMONIA DISTANCE	REFERENCE
	<i>A.</i>			<i>A.</i>	
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$	About 2.5	(4, 5, 17)	$[\text{Co}(\text{NH}_3)_6]\text{I}_3$	1.65–1.8	(12)
$[\text{Co}(\text{NH}_3)_6]\text{I}_2$	About 2.5	(4, 5, 17)		2.2	(21)
				1.9	(14)
			$[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$	2.2	(20)

contraction in distance suggests a stronger metal-ammonia bond in the penetration complex, but it certainly is not sufficient to explain the equal volume relationship unless consideration is given to lattice type. The situation is illustrated by the case of $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$.

V. MOLECULAR VOLUME AND THE STABILITY OF A SERIES OF COMPLEXES

In view of the above facts it appears that attempts (7b) to correlate the stability of a series of amines with the apparent molecular volume of ammonia or other coördinated group in the complex are of little significance. For a series of compounds such as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$, and $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$, substitution of one water molecule for an ammonia brings about a slight contraction in the length of the unit cell without changing the type of lattice; however, substitution of two or more water molecules for amonias brings about a change from cubic to hexagonal symmetry (11, 15). The change in type of lattice has not been considered in determining changes in the molecular volume of the ammonia or water.

The increase in the molecular volume of the ammonia as one goes from $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ to $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ has also been related to the stability of the complex (7b). Again crystallographic data are pertinent. Werner had suggested that when one ammonia is driven out of a $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ molecule, the empty position is taken by a chloride ion, i.e., $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. X-ray data obtained by West (18) confirm Werner's postulate completely. $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was studied because large crystals are easily obtained and the complex is isomorphous with $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{I}_2$, and $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

The $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ structure is produced from the $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ lattice (figure 2) by removing one of the ammonia molecules and then moving the added anion (cross-lined circle in figure 2) into the vacancy. Because the chloride ion is larger than the ammonia molecule, one of the six faces of each sub-cube of chloride ions is expanded and the original cubic symmetry is destroyed. The best estimates on cobalt-nitrogen internuclear distances suggest a small increase in bond length, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 =$ about 1.9–2.0 Å. and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 =$ about 2.0 Å., but values are too uncertain to be significant. In a case such as this it is meaningless to assign individual molecular volumes to the components of these complexes, since any assignment involves a strictly arbitrary division of the total volume between the component parts of the compound and makes no provision for structural changes. Furthermore, correlations with stability are difficult because no unequivocal experimental criterion for the stability of these compounds is available. Accurate metal-ammonia distances in a series of ammines of this type would provide interesting information on bond strength and bond type, but arbitrary molecular volume data can have very little fundamental significance if crystal structure data are neglected in the calculation of the molecular volume of the components.

VI. SUMMARY

1. The equal volume relationships observed by Biltz for di- and tri-valent cobaltamine halides is explained on the basis of the fact that $[\text{Co}(\text{NH}_3)_6]\text{X}_2$ crystallizes in a lattice of the calcium fluoride type. This lattice contains holes into which four extra anions per unit cell may be packed without destroying the basic crystal pattern.

2. The equal volume relationship can *not* be attributed in any appreciable degree to a compression of the ammonias in the ammines of trivalent cobalt.

3. Metal-ammonia distances, when available, might be used as a criterion of bond strength, but attempts to relate stability of a complex to arbitrary values of the molecular volume are subject to numerous fundamental errors.

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