

323. *Adducts of Protonic Acids with Co-ordination Compounds.*

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Infrared absorption due to the hydroxonium ion has been observed in "chloroplatinic acid dihydrate," best formulated as $(\text{H}_3\text{O})_2(\text{PtCl}_6)$, and in "chloromolybdic acid," best formulated as $(\text{H}_3\text{O})_2[\text{Mo}_6\text{Cl}_{14}]$. Infrared spectral studies of *trans*-dichlorobisethylenediaminecobalt(III) chloride hydrogen chloride dihydrate and some analogous compounds show that hydroxonium ions are not present. The best formulation is *trans*- $[\text{Co en}_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$, in agreement with X-ray studies. New adducts of this type are reported with formulæ: *trans*- $[\text{Rh en}_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$, *trans*- $[\text{Rh en}_2\text{Br}_2](\text{H}_5\text{O}_2)\text{Br}_2$, and *trans*- $[\text{Rh bipy}_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$. The *trans*-stereochemistry of the dichlorobisbipyridylrhodium(III) cation is demonstrated. The infrared spectrum of the bisquo-hydrogen ion is reported in nine compounds of chromium, cobalt, and rhodium. Some alleged adducts of organic acids with *trans*-dichlorobisethylenediaminecobalt(III) salts have been re-investigated.

A NUMBER of solid compounds exist in which one or more molecules of a protonic acid are combined with a complex ion. The manner in which the proton is combined with the remainder of the molecule is not always clear but existence as a bare proton is, of course, quite unlikely. We have previously shown¹ that the compound "hydrogen dichlorobisdimethylglyoximatorhodate(III)" is, in fact, *trans*-dichlorodimethylglyoximatodimethylglyoximerhodium(III), and a good deal of evidence has accumulated for the formulation of compounds $\text{HX}, \text{H}_2\text{O}$ as $[\text{H}_3\text{O}]^+\text{X}^-$, from broad-line proton magnetic resonance² and infrared spectra.³ For any "adduct" containing both a protonic acid and water, it is at least possible that hydroxonium ions are present.

Hydroxonium Complex Salts.—The compound commonly formulated $\text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$ or $\text{PtCl}_4, 2\text{HCl}, 2\text{H}_2\text{O}$ has been shown^{2b} by studies of its broad-line proton magnetic resonance spectrum to contain protons arranged in groups of three, strongly suggesting the presence

¹ Gillard and Wilkinson, *J.*, 1963, 6041.

² (a) Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261; (b) Smith and Richards, *Trans. Faraday Soc.*, 1952, **48**, 307; (c) Kakiuchi, Shono, Komatsu, and Kigoshi, *J. Chem. Phys.*, 1951, **19**, 1069.

³ (a) Ferriso and Hornig, *J. Amer. Chem. Soc.*, 1953, **75**, 4113; (b) Ferriso and Hornig, *J. Chem. Phys.*, 1955, **23**, 1464.

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of hydroxonium ions. Several examples of the hydroxonium ion have been established by infrared spectroscopy, and we now find that the infrared spectrum of the extremely deliquescent "chloroplatinic acid dihydrate" shows conclusively that hydroxonium ions are present. Results are presented in Table 1, with ranges of frequencies observed in the

TABLE I.
Infrared spectra of hydroxonium salts (in cm^{-1}).

Compound	ν_1^a	ν_3	ν_4	ν_2
$(\text{H}_3\text{O})_2(\text{PtCl}_6)$	3226 ^b	2825	1695	1070 ^c
$(\text{H}_3\text{O})^+$	3380—3150	2650—2468	1705—1670	1150—1130 1060—1048
$(\text{H}_3\text{O})_2[\text{Mo}_6\text{Cl}_8]\text{Cl}_6$	3203 ^b	2500	1680	1147

^a Notation follows that of ref. 3. ^b Observed as very broad absorption, partly masked by stretching modes of residue crystal water. ^c Broad band, on which a sharper peak at 1020 cm^{-1} is superimposed.

hydroxonium halides,³ and hydroxonium perchlorate⁴ and nitrate.⁵ The specimen used to obtain the infrared spectrum was not completely dehydrated, despite intensive drying. Bands due to the very small amount of residual crystal water appeared at 3509 and 3472 cm^{-1} (stretching modes) and at 1613 cm^{-1} (deformation). The absorption due to the ν_2 mode of the hydroxonium ion appeared with incipient structure; this feature has been noted previously for ν_2 of $[\text{H}_3\text{O}]^+$. It may be due either to the non-equivalence of several molecules in each unit cell, or to combinations with lattice modes. In most previous studies, an overtone ($2\nu_2$) at around 2100 cm^{-1} has been reported; despite a careful search, we were unable to find any evidence for absorption in this region. However, this overtone was not observed in hydroxonium fluoride.^{3b}

When "molybdenum dichloride," best represented as octa- μ_3 -chlorohexamolybdenum(II) tetrachloride,⁶ is crystallized from hydrochloric acid, yellow needles of "chloromolybdic acid," $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4 \cdot 2\text{HCl} \cdot 8\text{H}_2\text{O}$, are obtained.⁷ By pumping at 55° , the "dihydrate" can be obtained, in agreement with the earlier finding⁷ that two of the water molecules are much more firmly retained than the other six. The compound has been formulated,⁶ without evidence, as $(\text{H}_3\text{O})_2[\text{Mo}_6\text{Cl}_{14}]$, and we now confirm that the infrared spectrum indicates very clearly the presence of hydroxonium ions. Results are given in Table I. The bands due to hydroxonium ion are readily observed at all stages from the octahydrate to the dihydrate. Bands due to the unprotonated water are observed at 3430 and 1605 cm^{-1} until the pure dihydroxonium salt is obtained.

X-Ray crystallographic studies⁸ have indicated that the dihydrate of tetraphosphimic acid, $\text{P}_4\text{N}_4(\text{OH})_8 \cdot 2\text{H}_2\text{O}$, probably contains two hydroxonium ions. However, the infrared spectrum is indicative of very strong hydrogen bonding (as pointed out by Corbridge^{8a}), and the characteristic vibrations of the hydroxonium ion are obscured. The presence of hydroxonium ions in the acid dihydrate is supported by its isomorphism^{8a} with the diammonium salt, but our infrared study has not, so far, given conclusive support.

trans-Dichlorobisethylenediaminecobalt(III) chloride forms⁹ mica-like crystals of the formula *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$, which are discussed later. It has been reported¹⁰ that the cation forms certain other "adducts" which were alleged to contain protonic acids and water of crystallization in some cases. The infrared spectrum of *trans*-dichlorobisethylenediaminecobalt(III) hydrogen oxalate dihydrate shows no absorption characteristic of the hydroxonium ion; the best formulation is *trans*- $[\text{Co en}_2\text{Cl}_2](\text{HC}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$.

⁴ (a) Mullhaupt and Hornig, *J. Chem. Phys.*, 1956, **24**, 169; (b) Taylor and Vidale, *J. Amer. Chem. Soc.*, 1956, **78**, 294, 5999.

⁵ Bethell and Sheppard, *J. Chem. Phys.*, 1953, **21**, 1421.

⁶ Sheldon, *J.*, 1961, 750.

⁷ Lindner, Haller, and Heling, *Z. anorg. Chem.*, 1923, **130**, 209.

⁸ (a) Corbridge, *Acta Cryst.*, 1953, **6**, 104; (b) Michelsen and Vos, Abs. 4.62 of Sixth Internat. Congr. Int. Union Crystallography, Rome, 1963, A40.

⁹ Jørgensen, *J. prakt. Chem.*, 1890, **41**, 440.

¹⁰ Price and Brazier, *J.*, 1915, 1713.

It is relevant that oxalic acid dihydrate itself, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, was shown by solid-state nuclear magnetic resonance^{2b} not to contain hydroxonium ions. Price and Brazier¹⁰ reported that, when aqueous solutions of malonic acid and *trans*-dichlorobisethylenediaminecobalt(III) chloride are mixed, after a short time dark green crystals of the composition $[\text{Co en}_2\text{Cl}_2][\text{CH}_2(\text{COO})(\text{CO}_2\text{H})][\text{CH}_2(\text{CO}_2\text{H})_2] \cdot 2\text{H}_2\text{O}$ were formed. We have confirmed this observation; the infrared spectrum of the compound is quite individual, and it indicates the presence of non-hydrogen-bonded OH (3500 cm^{-1}), non-hydrogen-bonded $-\text{NH}_2$ ($3328 + 3250 \text{ cm}^{-1}$, as in *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$), unusually strong unsymmetrical hydrogen bonds (broad bands at 2480 and 1940 cm^{-1}), and symmetrical hydrogen bonding. The evidence for this last is that a very broad strong absorption is obvious from 1400 cm^{-1} downwards, centred about 750 cm^{-1} , with marked "absorption windows" at 1100 cm^{-1} (due to a strong absorption of the complex cation) and at 940 cm^{-1} (due to a strong absorption of the malonic acid). Carboxylate absorption occurs at 1700 cm^{-1} , suggesting that the carboxylate groups are all involved in hydrogen bonding. The possibilities of hydrogen bonding are such that we feel speculation to be worthless. We have not been able to obtain analogous compounds from any other *trans*-dichlorotetraamminecobalt(III) cation with malonic acid.

We have been unable to confirm several other observations by Price and Brazier;¹⁰ for example, they reported another compound from the malonic acid system, said to be possibly *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{CH}_2(\text{CO}_2\text{H})_2 \cdot \text{H}_2\text{O}$. However, its infrared spectrum is a superposition of those of malonic acid and the complex chloride; it appears that no water is present, and we feel that the alleged adduct is merely a mixture; the variations in composition which we have observed support this suggestion. Chloroacetic acid was also said¹⁰ to form a compound, *trans*- $[\text{Co en}_2\text{Cl}_2](\text{CH}_2\text{Cl} \cdot \text{COO})(\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H})$; however, although we have obtained an exactly similar material by the same method it proved to be simply the chloroacetate salt, *trans*- $[\text{Co en}_2\text{Cl}_2][\text{CH}_2\text{Cl} \cdot \text{COO}]$.

Bisquoohydrogen Ion Complexes.—Salts of the type *trans*-dihalogenotetramminemetal(III) halide, where the metal is chromium, cobalt, or rhodium and the halogen is chlorine or bromine, are well known to form adducts with hydrogen halides and water of formula $[\text{MA}_4\text{X}_2]\text{X} \cdot \text{HX} \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Cr, Co, Rh}$; $\text{A} = \frac{1}{2} \text{en, } \frac{1}{2} \text{pn, py}$; $\text{X} = \text{Cl or Br}$). There has been only one disagreement with this formula where, on the basis of a thermogravimetric study, the adduct of *trans*-dichlorobisethylenediaminecobalt(III) chloride with hydrogen chloride was formulated¹¹ as a hexahydrate. However, on the basis of extensive analyses by ourselves and previous workers^{9,12,13} and the X-ray molecular weight,¹⁵ there can be no doubt that the original formulation is correct.

There is a serious discrepancy between the infrared results¹⁴ for *trans*-dichlorobisethylenediaminecobalt(III) chloride hydrogen chloride dihydrate, $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ and the earlier X-ray data¹⁵ for the same compound. The infrared spectrum was said¹⁴ to show the presence of hydroxonium ions, while the X-ray results showed¹⁵ the presence of isolated pairs of oxygen atoms, with an O—O distance of 2.66 \AA . Infrared¹⁴ and X-ray studies¹⁶ of the analogous bromo-compound (where O—O is 2.60 \AA) also led to different conclusions. While the protons were not, of course, located in the X-ray work, it was tentatively suggested that $[\text{H}_5\text{O}_2]^+$ ions were present. We shall call this cation the bisquoohydrogen ion.

We have measured the infrared spectra of nine compounds of the type $[\text{MA}_4\text{X}_2]\text{X} \cdot \text{HX} \cdot 2\text{H}_2\text{O}$, of which three adducts of rhodium(III) are new. All the spectra are very similar in the regions due to the added " $\text{HX} \cdot 2\text{H}_2\text{O}$;" in no case is there absorption characteristic of molecular hydrogen chloride or bromide, or the HCl_2^- ion, or the $[\text{H}_3\text{O}]^+$

¹¹ Fogel and Christian, *J. Amer. Chem. Soc.*, 1958, **80**, 5356.

¹² Werner, *Ber.*, 1901, **54**, 1733.

¹³ Uspensky and Tschibisov, *Z. anorg. Chem.*, 1927, **164**, 329.

¹⁴ Curtis, *Proc. Chem. Soc.*, 1960, 410.

¹⁵ Nakahara, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1952, **25**, 311.

¹⁶ Ooi, Komiyama, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1959, **32**, 263.

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ion; in particular, for the last case the ν_2 vibration at 1050—1100 cm^{-1} is not observed. If the formulation ¹⁴ $[\text{Co en}_2\text{Cl}_2](\text{H}_3\text{O})\text{Cl}_2 \cdot \text{H}_2\text{O}$ were correct, in addition to the spectrum of the hydroxonium ion, bands due to the crystal water ¹⁷ should appear. No bands due to free water were observed. For the complexes of the diamines, in the region characteristic of O-H and N-H stretching modes, no absorption occurs in the adducts higher than the highest N-H stretching frequency in the parent compounds; the region of the H_2O deformation frequency in these complexes containing diamines is less clear, since, as Curtis ¹⁴ assumed to be true, the NH_2 deformation frequency would possibly overlap the OH_2 deformation. However, in the case ¹⁸ of the dichlorotetrapyridinerhodium(III) cation, the highest absorption, which is very sharp, is at 1608 cm^{-1} . The absorption due to deformation of the crystal water in dichlorotetrapyridinerhodium(III) chloride hexahydrate is completely separate from this pyridine mode, so that one might expect to see clearly the deformation frequency of the "spare" crystal water in any molecule $[\text{Rhpy}_4\text{Cl}_2](\text{H}_3\text{O})\text{Cl}_2 \cdot \text{H}_2\text{O}$. In fact, the spectrum from 1600—1650 cm^{-1} shows only one absorption, at 1606 cm^{-1} , due to the pyridine vibration.¹⁹ The spectrum above 3000 cm^{-1} also provides cogent evidence for the absence of crystal water, since no absorption at all can be seen above the band at 2910 cm^{-1} . Crystal water is not present. It therefore seems certain that the structural unit containing the proton is, in fact, the bisaquohydrogen ion, $(\text{H}_5\text{O}_2)^+$, first postulated by Huggins ²⁰ as a component of acid solutions. Additional support is provided by the thermogravimetric study ¹¹ where it was found that all the molecules of water and of hydrogen chloride were released in a single step and it was concluded that "the presence of both water and hydrogen chloride is necessary in order to stabilize the bonding of either." However, in view of the wrong formula found in that work, this evidence must at present be considered unreliable.

The infrared spectrum of the $(\text{H}_5\text{O}_2)^+$ ion, deduced from differences between spectra of adducts and parents, shows four broad absorptions, at much lower frequencies than those observed for hydroxonium ions, except the ν_4 mode of $(\text{H}_3\text{O})^+$, which is comparable with what we call band III of $(\text{H}_5\text{O}_2)^+$. Results are presented in Table 2, from which also it is

TABLE 2.
Infrared spectra of $(\text{H}_5\text{O}_2)\text{X}$ (in cm^{-1}).

Compound ^a	Band I	Band II	Band III	Band IV ^b
1 <i>trans</i> - $[\text{Co en}_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$	2850	2240	1670	950
2 <i>trans</i> - $[\text{Co en}_2\text{Br}_2](\text{H}_5\text{O}_2)\text{Br}_2$	2880	2240	1670	960
3 <i>trans</i> - $[\text{Co}(\pm\text{pn})_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$	2920	2230	1680	1000
4 <i>trans</i> - $[\text{Co}(-\text{pn})_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$...	2915	2230	1682	1002
5 <i>trans</i> - $[\text{Rh en}_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$	2810	2205	1684	950
6 <i>trans</i> - $[\text{Rh en}_2\text{Br}_2](\text{H}_5\text{O}_2)\text{Br}_2$	2830	2215	1680	960
7 <i>trans</i> - $[\text{Rh py}_4\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$	2910	2210	1660	970
8 <i>trans</i> - $[\text{Rh dipy}_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$	2990	2215	1700	970
9 <i>trans</i> - $[\text{Cr en}_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$	2860	2255	1668	972
10 $(\text{H}_3\text{O})^+ \text{ }^c$	3380—3150	2650—2468	1705—1670	1150—1130, 1060—1048

^a This column gives the formula of the adduct; the bands given are for *trans*- $[\text{MA}_4\text{X}_2](\text{H}_5\text{O}_2)\text{X}_2$ — *trans*- $[\text{MA}_4\text{X}_2]\text{X} = (\text{H}_5\text{O}_2)\text{X}$. ^b Band IV is extremely broad in all cases; e.g., for compound 1 it extends from 775 to 1400 cm^{-1} ; however, the maximum intensity could be located to ± 10 cm^{-1} . ^c See Table 1.

obvious that the adducts do not contain hydroxonium ions, and must be formulated *trans*- $[\text{MA}_4\text{X}_2](\text{H}_5\text{O}_2)\text{X}_2$. A typical spectrum of $(\text{H}_5\text{O}_2)^+$ is shown in the Figure, with that of $(\text{H}_3\text{O})^+$ for comparison.

The new adducts, which we have been able to prepare by allowing the parent salt to crystallize slowly from the relevant acid, are, firstly, *trans*-dichlorobisethylenediamine-

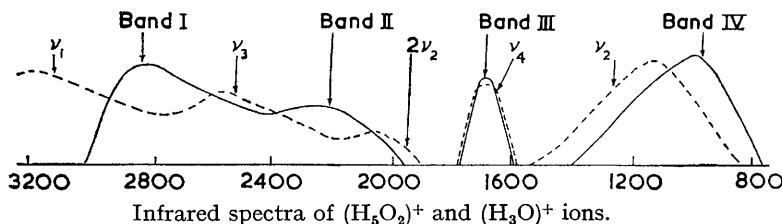
¹⁷ Lucchesi and Glasson, *J. Amer. Chem. Soc.*, 1956, **78**, 1347.

¹⁸ Gillard and Wilkinson, *J.*, 1964, 1224.

¹⁹ Gill, Nuttall, Scaife, and Nyholm, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

²⁰ Huggins, *J. Phys. Chem.*, 1936, **40**, 723.

rhodium(III) bisaquohydrogen chloride, $\text{trans}[\text{Rh en}_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$, and the bromo-analogue, $\text{trans}[\text{Rh en}_2\text{Br}_2](\text{H}_5\text{O}_2)\text{Br}_2$; this affords a novel confirmation of the *trans*-stereochemistry of these cations. We have also prepared *trans*-dichlorobisbipyridylrhodium(III) bisaquohydrogen chloride, which is very similar to the known⁹ *trans*-dichloro-



Full curve, $(\text{H}_5\text{O}_2)^+$ in $\text{trans}[\text{Co en}_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$. Dotted curve, $(\text{H}_3\text{O})^+$

tetrapyridinerhodium(III) bisaquohydrogen chloride. This provides the most direct evidence for the configuration of the bispyridyl complex which had previously²¹ been assigned *cis*-stereochemistry on the rather unreliable basis of the splitting of the in-phase out-of-plane C-H vibrations in the infrared spectrum. No cation with *cis*-stereochemistry is recorded as forming adducts with hydrogen halides, nor have we succeeded in preparing such adducts from any of the *cis*-species corresponding to the *trans*-dihalogeno compounds used in this work. This difference between *cis*- and *trans*-isomers is presumably due to packing in the crystal lattice.

The presence of water appears to be essential in the formation of such adducts of hydrogen halides; there are two reports of anhydrous adducts of hydrogen halides with *trans*-dichlorotetramminecobalt(III) species. Thus Drew and Pratt²² claimed to have made *trans*-dichlorobisethylenediaminecobalt(III) chloride hydrogen chloride; however, the compound we obtained (as short blocky crystals, in agreement with their description) under the conditions alleged to yield the anhydrous compound was, in fact, the dihydrate. In the preparation²³ of *trans*-dibromotriethylenetetramminecobalt(III) bromide, the isolation of an adduct with hydrogen chloride was reported, apparently anhydrous. We have repeated this work, but the very dark green product contained water, as shown by a direct oxygen analysis, and absorption in the infrared spectrum at 3550 cm^{-1} , due to an O-H stretching mode; the product was a mixture of colourless needles and almost black plates.

The first case described where the product of crystallization from hydrochloric acid was different from that in water was with the prototype, *trans*-dichlorotetramminecobalt(III) chloride. Rose²⁴ reported that "in strong hydrochloric acid, shiny grass-green crystals were obtained, which on washing with water become matted and leek-green." Since this parallels exactly the behaviour of *trans*-dichloroethylenediaminecobalt(III) bisaquohydrogen chloride, we feel that the dichlorotetramminecobalt(III) must be similar. However, no other report of this adduct or indeed of others containing ammonia as the nitrogenous ligand has ever appeared. We have not yet been able to obtain Rose's shiny grass-green crystals. The only other so-called "chlorhydrate" known to us, which we have not examined, is that of *trans*-dichlorobis(trimethylenediamine)cobalt(III) chloride,²⁵ which we formulate as $\text{trans}[\text{Co}(\text{trime}_2)_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$. Some other adducts of substituted diamine complexes, $\text{trans}[\text{Co}(\text{diamine})_2\text{Cl}_2]\text{Cl}_n\text{HCl}$, have been described;²⁶ before the alcohol-ether washing which was employed, the crystals presumably contained the bisaquohydrogen ion.

²¹ Martin and Waind, *J.*, 1958, 4284.

²² Drew and Pratt, *J.*, 1937, 508.

²³ Selbin and Bailar, *J. Amer. Chem. Soc.*, 1960, **82**, 1524.

²⁴ Rose, "Untersuch. über ammoniakal Kobaltverbind.," Heidelberg, 1871, 43 (quoted also as footnote in ref. 9).

²⁵ Werner, *Annalen*, 1912, **386**, 270.

²⁶ Basolo, *J. Amer. Chem. Soc.*, 1953, **75**, 227.

EXPERIMENTAL

Microanalyses were by the Microchemical Laboratory, Imperial College. Infrared spectra were taken on a Perkin-Elmer model 21 instrument with calcium fluoride or sodium chloride optics, and on a Grubb-Parsons grating Spectromaster instrument.

"Chloromolybdic Acid."—This was prepared according to Sheldon.⁶

Tetraphosphonic Acid Dihydrate.—This crystallized according to Corbridge.^{8a}

Hydroxonium Hexachloroplatinate(IV).—The sample used was prepared essentially by the method of Smith and Richards;² in our modification, all the operations were carried out on a vacuum line. Gravimetric analysis of the sample was by reduction to platinum [Found: Pt, 43.6. Calc. for (H₃O)₂PtCl₆: Pt, 43.8%]. While this analysis is not very sensitive to water content, it was clear from the spectra that only a very small percentage of crystal water had not been removed. The mulls (in Nujol and Fluorolube, previously dried with molecular sieves) were prepared in a dry-box, swept with nitrogen, previously passed through a column of dry molecular sieves.

trans-Dichlorobisethylenediaminecobalt(III) Hydrogen Malonate Malonic Acid Dihydrate.—This was prepared according to Price and Brazier¹⁰ (Found: C, 24.8; H, 5.7; Cl, 14.7. Calc. for C₁₀H₂₆Cl₂CoN₄O₁₀: C, 24.4; H, 5.5; Cl, 14.4%).

Other preparations and analyses are summarized in Table 3.

TABLE 3.
Preparations and analyses of adducts.

Compound	Prepn.	Found			Calc.		
		X ^{-a}	HX, 2H ₂ O	O	X ^{-a}	HX, 2H ₂ O	O
1 <i>trans</i> -[Co en ₂ Cl ₂]Cl.HCl.2H ₂ O	9	—	30.2	8.8	—	30.3	9.0
2 <i>trans</i> -[Co en ₂ Br ₂]Br.HBr.2H ₂ O	9	—	36.7	5.8	—	36.7	6.0
3 <i>trans</i> -[Co(±pn) ₂ Cl ₂]Cl.HCl.2H ₂ O ...	27	—	27.8	—	—	28.0	—
4 <i>trans</i> -[Co(-pn) ₂ Cl ₂]Cl.HCl.2H ₂ O ...	<i>b</i>	—	28.1	—	—	28.0	—
5 <i>trans</i> -[Rh en ₂ Cl ₂]Cl.HCl.2H ₂ O	<i>c</i>	18.3	26.6	—	17.7	26.9	—
6 <i>trans</i> -[Rh en ₂ Br ₂]Br.HBr.2H ₂ O	<i>c</i>	27.5	—	—	27.6	—	—
7 <i>trans</i> -[Rh py ₄ Cl ₂]Cl.HCl.2H ₂ O	9	11.6	18.1	—	11.9	18.1	—
8 <i>trans</i> -[Rh(dipy) ₂ Cl ₂]Cl.HCl.2H ₂ O ...	<i>c</i>	11.9	18.3	—	11.9	18.2	—
9 <i>trans</i> -[Cr en ₂ Cl ₂]Cl.HCl.2H ₂ O	<i>c</i>	40.2 ^d	30.5	8.9	40.4 ^d	30.8	9.1

^a X⁻ = ionic halide; HX, 2H₂O was measured by the weight loss at 110°; O is a direct oxygen analysis. ^b Compound 4 was made by a method similar to that for 3; (±)-1,2-diaminopropane was resolved by the method of Dwyer, Garvan, and Shulman.²⁸ ^c See text. ^d Total chlorine.

trans-Dichlorobisethylenediaminerhodium(III) Bisoquoxygen Chloride.—A saturated solution of *trans*-dichlorobisethylenediaminerhodium(III) chloride in concentrated hydrochloric acid at 90° was allowed to cool slowly to room temperature, during 3 hr., and then further cooled in ice. The shiny yellow plates of the separated compound were collected and dried (CaCl₂). The yield was 87%. The compound could also be obtained from a hot solution of *trans*-dichlorobisethylenediaminerhodium(III) nitrate in concentrated hydrochloric acid.

trans-Dibromobisethylenediaminerhodium(III) Bisoquoxygen Bromide.—By a method similar to that used for the chloro-compound, the bromo-compound was obtained as orange-yellow plates (52%).

trans-Dichlorobisbipyridylrhodium(III) Bisoquoxygen Chloride.—A mixture of dichlorobisbipyridylrhodium(III) chloride²¹ (0.5 g.) and concentrated hydrochloric acid was kept at 90° for 8 hr., allowed to cool, and the hydrochloric acid replaced with fresh acid. The mixture was again heated to 75° and maintained at this temperature for 6 hr., with occasional shaking. The desired compound (yellow plates) was collected by filtration, washed with concentrated hydrochloric acid, and dried (CaCl₂). The yield was 0.53 g.

trans-Dichlorobisethylenediaminechromium(III) Bisoquoxygen Chloride.—Because of the rather inconvenient method²⁹ previously used to prepare *trans*-dichlorobisethylenediaminechromium(III) cation, a much more rapid, small-scale preparation was developed, based on Pfeiffer's method.³⁰ *cis*-Dichlorobisethylenediaminechromium(III) chloride (1.2 g., 5 × 10⁻³

²⁷ Werner and Fröhlich, *Ber.*, 1907, **40**, 2228.

²⁸ Dwyer, Garvan, and Shulman, *J. Amer. Chem. Soc.*, 1959, **81**, 290.

²⁹ Slaten and Garner, *J. Phys. Chem.*, 1959, **63**, 1214.

³⁰ Pfeiffer, *Ber.*, 1904, **37**, 4255.

mole) in water (12 ml.) was treated with mercuric chloride (2.72 g., 10^{-2} mole), and the mixture allowed to evaporate to dryness on the steam-bath. Concentrated hydrochloric acid (5 ml.) was added, and the mixture kept for 15 min. on the steam-bath, with occasional stirring. The mixture was then filtered hot, and the green filtrate cooled rapidly to 20° , when mercuric chloride crystallized and was removed. The filtrate was kept in a closed container overnight, plate-like green crystals of *trans*-dichlorobisethylenediaminechromium(III) bisaquohydrogen chloride then forming. These were collected, and washed with 1:1 hydrochloric acid (yield 0.5 g., 32%).

Weight Loss at 110° .—The products of heating the adducts were the anhydrous compounds except in the cases of compounds 3, 4, and 6; 3 and 4 [the green adducts of hydrogen chloride with *trans*-dichlorobispropylenediaminecobalt(III) chlorides] both became purple when heated, due to conversion into the *cis*-isomer. Compound 6 [*trans*-dibromobisethylenediaminerhodium(III) bisaquohydrogen bromide] readily decomposed when heated, evolving bromine. Because the nature of the residual solid is unknown, no weight-loss data are recorded in Table 3 for this compound. The anhydrous *trans*-compounds 3, 4, and 6 could be obtained either by precipitating a solution of the adduct in 95% alcohol with ether or by washing the adduct with hot alcohol.

The System trans-Dibromotriethylenetetraminecobalt(III) Bromide-Hydrogen Chloride.—The product of the reaction²³ of *cis*-dichlorotriethylenetetraminecobalt(III) chloride with constant-boiling hydrobromic acid was collected. The properties of the dark green product agreed closely with those reported.²³ However, the formulation *trans*-[Co trienBr₂]Br.HCl given²³ by Bailar and Selbin is inaccurate; the infrared spectrum of the dried material showed a strong band at 3550 cm.^{-1} , due to water. Oxygen was also present (Found: O, 3.0%). Under the microscope, the non-homogeneous nature of the material was obvious. We have not yet been able to separate the components, one colourless, the other green-black.

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