

828. *Adducts of Co-ordination Compounds. Part I. Some Adducts of Hydrogen Halides*

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Several new adducts of the type *trans*-[MA<sub>4</sub>X<sub>2</sub>]X, HX, 2H<sub>2</sub>O, where M is Co or Rh, A is a nitrogenous ligand and X is Cl or Br, are reported. The formulation [MA<sub>4</sub>X<sub>2</sub>](H<sub>5</sub>O<sub>2</sub>)X<sub>2</sub> is supported by thermogravimetric results. The dichlorobis-*o*-phenanthroline-rhodium(III) cation is shown to have *trans*-stereochemistry. Both so-called isomers of *cis*-dibromotetrapyrindinerhodium(III) bromide hexahydrate in fact contain the *trans*-[Rhp<sub>4</sub>Br<sub>2</sub>]<sup>+</sup> cation; the yellow "isomer" is the bromide hexahydrate of this cation, and the orange "isomer" is the hydrogen bromide adduct, *trans*-[Rhp<sub>4</sub>Br<sub>2</sub>](H<sub>5</sub>O<sub>2</sub>)Br<sub>2</sub>.

THE nature of the bonding in adducts of hydrogen halides with co-ordination compounds has recently received some attention. In the hydrochlorides of bridged polynuclear complexes, the hydrogen chloride is thought<sup>1</sup> to be associated with the bridge. The addition of hydrogen halides to tris-(8-hydroxyquinolino)chromium(III) has been shown<sup>2</sup> to involve opening of the chelate rings. Infrared evidence suggested<sup>3</sup> that hydrohalides of the type [MA<sub>4</sub>X<sub>2</sub>]X, HX, 2H<sub>2</sub>O, where M = Co, Rh, or Cr, A = py, \* $\frac{1}{2}$ en,  $\frac{1}{2}$ pn, and X = Cl or Br, should be formulated MA<sub>4</sub>X<sub>2</sub>(H<sub>5</sub>O<sub>2</sub>)X<sub>2</sub>.

The most common adducts of hydrogen halides are those formed by parent salts of the type *trans*-[MA<sub>4</sub>X<sub>2</sub>]X; these have the formula [MA<sub>4</sub>X<sub>2</sub>]X, HX, 2H<sub>2</sub>O. No such adduct is known for the corresponding *cis*-isomers. A very few exceptional adducts of a totally different type are formed by parent salts other than *trans*-[MA<sub>4</sub>X<sub>2</sub>]X, such as [Rh(*o*-phen)<sub>3</sub>]Cl<sub>3</sub>, HCl, 15H<sub>2</sub>O. These exceptional adducts are not relevant to the present arguments and will be discussed elsewhere. For the common adducts, all studies except one have agreed on the stoichiometry [MA<sub>4</sub>X<sub>2</sub>]X, HX, 2H<sub>2</sub>O. In the one exceptional report,<sup>4</sup> the vapour pressure of aqueous hydrogen chloride over *trans*-dichlorobisethylenediamine-cobalt(III) chloride was studied, and results interpreted on the basis of the adduct's being a hexahydrate. Our thermogravimetric results on this adduct and others are completely consistent with the formulation as dihydrates. The weight loss up to 150° in the thermogravimetric analysis (*ca.* 20%) corresponds to the reaction



for which the theoretical weight loss is 20.5%. The differential thermal analysis shows two peaks at 109 and 143° in air, and at 103 and 134° in nitrogen. The peaks overlap, and although it is not possible to say which is due to loss of hydrogen chloride and which due to loss of water, it appears that the losses of these two constituents occur almost simultaneously, and their separation cannot be achieved. This could be construed as evidence in support of the structure [Co en<sub>2</sub>Cl<sub>2</sub>](H<sub>5</sub>O<sub>2</sub>)Cl<sub>2</sub>.

For the formation of these hydrohalides with the general formula [MA<sub>4</sub>X<sub>2</sub>]X, HX, 2H<sub>2</sub>O, it is a necessary but not sufficient condition that the complex halide must have the general formula *trans*-[MA<sub>4</sub>X<sub>2</sub>]X. For example, in agreement with an earlier report,<sup>5</sup> we have been unable to obtain such an adduct from *trans*-dichlorotetrapyrindinecobalt(III) chloride, although the analogous salt of rhodium(III) readily forms<sup>3</sup> an adduct. Also, the *trans*-dichloro-complex of cobalt(III) containing unsubstituted six-membered chelate rings formed by trimethylenediamine is known<sup>6</sup> to form such an adduct, and we have now prepared a

\* Abbreviations used are: en, ethylenediamine; pn, 1,2-propylenediamine; py, pyridine; bipy,  $\alpha\alpha'$ -bipyridyl; and *o*-phen, *ortho*-phenanthroline.

<sup>1</sup> J. A. Connor and E. A. V. Ebsworth, *J. Inorg. Nuclear Chem.*, 1964, **26**, 549.

<sup>2</sup> M. M. Jones, K. V. Dandh, and G. T. Fisher, *J. Inorg. Nuclear Chem.*, 1964, **26**, 773.

<sup>3</sup> R. D. Gillard and G. Wilkinson, *J.*, 1964, 1640.

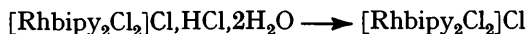
<sup>4</sup> N. Fogel and S. D. Christian, *J. Amer. Chem. Soc.*, 1958, **80**, 5356.

<sup>5</sup> T. S. Price, *J.*, 1920, 860.

<sup>6</sup> A. Werner, *Annalen*, 1912, **386**, 270.

typical adduct which readily loses hydrogen chloride, from the *trans*-dichloro-complex of cobalt(III) containing the quadridentate ligand bis-(*NN'*)- $\beta$ -aminoethyltrimethylenediamine,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHCH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ . However, neither the complex derived from the ( $\pm$ )-diamine 2,4-diaminopentane, nor its *meso*-isomer, could be induced to form such an adduct.<sup>7</sup>

There are now a sufficient number of adducts of the general formula *trans*- $[\text{MA}_4\text{X}_2]\text{-X, HX, 2H}_2\text{O}$  for the existence of an adduct with this formula to be taken as strong evidence for the *trans*-stereochemistry of the complex ion. The problems of the stereochemistry of the compounds  $[\text{Rhpy}_4\text{Br}_2]\text{Br}$  and  $[\text{Rh}(\text{AA})_2\text{Cl}_2]\text{Cl}$ , where AA is bipy or *o*-phen, have been resolved by this means. The catalytic formation of the complexes in the presence of reducing agents is extremely similar to that<sup>8</sup> of the known *trans*-dichlorotetrapyridinerhodium(III) chloride or of the *trans*-dichlorobisdimethylglyoximatorhodate(III) anion, so that the *trans*-structure appeared more likely. However, *cis*-stereochemistry had been assigned<sup>9</sup> to the complex of bipyridyl on the basis of the splitting of the in-plane out-of-phase CH vibrations. This is now seen to be an unreliable criterion, since the hydrochloride dihydrate adduct can be prepared simply by crystallising the parent chloride from concentrated hydrochloric acid. The analogous compound containing *ortho*-phenanthroline can be prepared in a similar fashion. The parent chlorides can be obtained either by crystallising the hydrochlorides from water, or by heating them. In view of this, and of the fact that the electronic spectra of the complexes in water and in hydrochloric acid are identical, it is clear that no isomerisation has occurred on passing from the adduct to the parent, so that the parent compounds may be assigned *trans*-stereochemistry. A thermogravimetric analysis of the adduct of the bipyridyl complex showed a single-stage weight loss from *ca.* 100° to *ca.* 180°, corresponding to the reaction



No further weight loss then occurred till 400°.

When rhodium tribromide is refluxed with aqueous pyridine for many hours, the product is dibromotetrapyridinerhodium(III) bromide hexahydrate. This was assigned<sup>10</sup> *cis*-stereochemistry on the basis of its reactions, and the further statement was made<sup>10</sup> that two *cis*-isomers could be isolated, which were distinguishable by their crystal forms, X-ray powder patterns, and solubilities in water. These were a yellow form, the first product, which occurred as prisms, and an orange form, which separated from the mother-liquor (which contained a large amount of hydrobromic acid). Poulenc pointed out<sup>10</sup> that the yellow form changed into the orange form under the mother-liquor, or in fairly concentrated hydrobromic acid, but not in aqueous solution. These facts, which were confirmed in this work, reproduce exactly the transformation<sup>3</sup> of *trans*-dichlorotetrapyridinerhodium(III) chloride into its hydrogen chloride dihydrate adduct.

The "yellow isomer" is *trans*-dibromotetrapyridinerhodium(III) bromide hexahydrate, identical with the product of the hydride-catalysed reaction of aqueous pyridine with rhodium bromide. The infrared spectrum is extremely similar to that of the analogous chloro-compound *trans*- $[\text{Rhpy}_4\text{Cl}_2]\text{Cl, 6H}_2\text{O}$ , notably in the quite characteristic region from 1600 to 1650  $\text{cm}^{-1}$ . Further, the X-ray powder photographs of the "yellow isomer" and of *trans*- $[\text{Rhpy}_4\text{Cl}_2]\text{Cl, 6H}_2\text{O}$  are virtually identical. The "orange isomer" is, in fact, the hydrogen bromide adduct, *trans*- $[\text{Rhpy}_4\text{Br}_2](\text{H}_5\text{O}_2)\text{Br}_2$ ; its infrared spectrum superimposes on that of the corresponding hydrogen chloride adduct, *trans*- $[\text{Rhpy}_4\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$ . The orange adduct, on recrystallising from water, gives the yellow parent compound, which can be reconverted into the hydrogen bromide adduct by crystallising from fairly concentrated hydrobromic acid. Both dibromo-compounds show identical electronic spectra

<sup>7</sup> C. J. Dippel and F. M. Jaeger, *Rec. Trav. chim.*, 1931, **50**, 547.

<sup>8</sup> R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J.*, 1965, 1951.

<sup>9</sup> B. Martin and G. M. Waind, *J.*, 1958, 4284.

<sup>10</sup> P. Poulenc, *Ann. chim. (France)*, 1935, **4**, 621.

in aqueous solution, the positions of the absorption maxima further supporting the *trans*-stereochemistry. The only previous observations<sup>11</sup> on these alleged *cis*-isomers unfortunately relied on rhodium and nitrogen analyses only, which, of course, are extremely similar for the parent hexahydrate and the hydrogen bromide dihydrate. It was then shown<sup>11</sup> that both compounds gave the same iodides, nitrates, and hydrogen sulphates. These observations are explained by the present work.

From the present work, it is clear that all the recorded preparations of the salts  $[\text{RhA}_4\text{X}_2]\text{Y}$ , where A is py,  $\frac{1}{2}$  bipy, or  $\frac{1}{2}$  *o*-phen, X is Cl or Br, and Y is an anion, in fact refer to the *trans*-isomers. *cis*-Isomers of complexes containing chelate ligands can sometimes be obtained by heating the tris-chelate salts; the possibility of preparing *cis*-isomers of rhodium(III) complexes by this means is being studied.

Infrared spectra obtained in this work are collected in the Table, with those<sup>3</sup> of two prototypic compounds. The formulation *trans*- $[\text{MA}_4\text{X}_2](\text{H}_5\text{O}_2)\text{X}_2$  is further supported. It is noteworthy that the previously unknown compound, *trans*-dichlorobispropylenediaminerhodium(III)chloride, was isolated<sup>12</sup> from a mixture of products as its hydrochloride dihydrate. The infrared spectrum of this adduct superimposes on that of the analogous compound of cobalt(III); in particular, no band occurs at frequencies higher than 3300  $\text{cm}^{-1}$ , supporting the suggestion that neither of the water molecules is present as crystal water.

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

Compound <sup>a</sup>	Band I <sup>b</sup>	Band II	Band III	Band IV
<i>trans</i> - $[\text{Co en}_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$ <sup>c</sup> .....	2850	2240	1670	950
<i>trans</i> - $[\text{Rhpy}_4\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$ <sup>c</sup> .....	2910	2210	1660	970
<i>trans</i> - $[\text{Rhpy}_4\text{Br}_2](\text{H}_5\text{O}_2)\text{Br}_2$ .....	2920	2200	1660	950
<i>trans</i> - $[\text{Rh}(\text{bipy})_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$ .....	2870	2210	1690	965
<i>trans</i> - $[\text{Rh}(\text{phen})_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$ .....	2900	2200	1680	975
<i>trans</i> - $[\text{Rh}(\pm\text{pn})_2\text{Cl}_2](\text{H}_5\text{O}_2)\text{Cl}_2$ .....	2920	2230	1680	1000

<sup>a</sup> This column gives the formula of the adduct; the bands listed are for *trans*- $[\text{MA}_4\text{X}_2](\text{H}_5\text{O}_2)\text{X}_2$  — *trans*- $[\text{MA}_4\text{X}_2]\text{X}$  =  $(\text{H}_5\text{O}_2)\text{X}$ . <sup>b</sup> Nomenclature as in ref. 3; all bands are broad, especially Band IV. <sup>c</sup> Data from ref. 3.

## EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Sheffield University. Thermogravimetric analyses were performed in a much modified Stanton thermal balance. Differential thermal analysis was studied using apparatus incorporating part of the Netzsch D.T.A. equipment. Infrared spectra were measured using a Perkin-Elmer model 21 spectrophotometer, and electronic spectra using either a Perkin-Elmer model 350 spectrophotometer, or a Unicam S.P. 700 spectrophotometer. Preparations of parent compounds were as earlier described.<sup>3,8</sup>

*Preparations of Adducts.*—*trans*-Dichlorobisbipyridylrhodium(III) chloride hydrogen chloride dihydrate. *trans*-Dichlorobisbipyridylrhodium(III) chloride (0.4 g.) prepared by a catalytic method,<sup>8</sup> was dissolved in concentrated hydrochloric acid (5 ml.) at 90°. The solution was allowed to cool slowly, and yellow micaceous plates of the desired adduct were obtained, which were collected and dried over sodium hydroxide (Found: Cl, 23.7; Rh, 17.0.  $\text{C}_{20}\text{H}_{21}\text{Cl}_4\text{N}_4\text{O}_2\text{Rh}$  requires Cl, 23.9; Rh, 17.3%). The thermogravimetric analysis, in air, showed no weight loss up to 100°, an apparently single-stage loss (12%) of  $\text{HCl}\cdot 2\text{H}_2\text{O}$  from 100 to 180°, a stable plateau representing the parent salt,  $[\text{Rh}(\text{bipy})_2\text{Cl}_2]\text{Cl}$ , from 180 to 400°, then further weight loss (79%) to 600°, where the product,  $\text{Rh}_2\text{O}_3$  lost no further weight up to 1000°. An inflection in this curve between 430 and 480° possibly represented intermediate formation of another chloro-bipyridylrhodium(III) complex.

*trans*-Dichlorobis(*o*-phenanthroline)rhodium(III) chloride hydrogen chloride dihydrate. This was prepared as yellow needles in a manner exactly similar to that for the analogous compound of bipyridyl (Found: Cl, 22.2; Rh, 16.4.  $\text{C}_{24}\text{H}_{21}\text{Cl}_4\text{N}_4\text{O}_2\text{Rh}$  requires Cl, 22.1; Rh, 16.1%). No detailed thermogravimetric analysis was performed on this compound; it was found, however, that when the adduct was kept at 180°, the parent salt was formed by loss of hydrogen chloride and water.

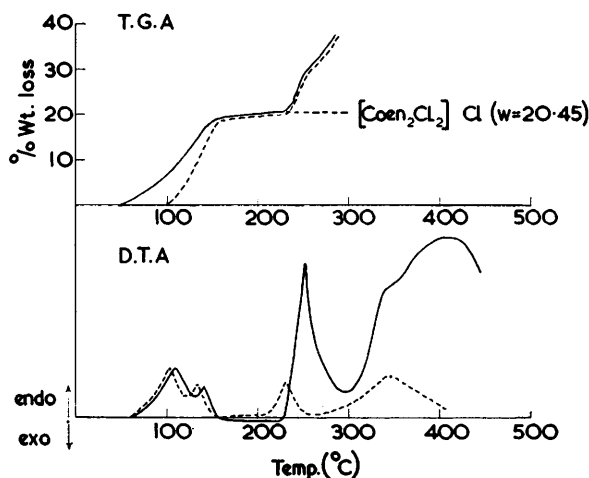
<sup>11</sup> J. Meyer and H. Kienitz, *Z. anorg. Chem.*, 1939, **242**, 281.

<sup>12</sup> R. D. Gillard, unpublished work.

*trans-Dichlorobisethylenediaminecobalt(III) chloride hydrogen chloride dihydrate.* This adduct, prepared by the standard method<sup>13</sup> as micaceous green plates, was analysed thermogravimetrically. Results are shown in the Figure. In the differential thermal analysis, in both air and nitrogen, the compound was studied as a 10% mixture with alumina, the heating rate being 5° per minute.

(I) *trans-Dibromotetrapyridinerhodium(III) bromide hexahydrate.* This was prepared by two methods: (a) the hydride-catalysed reaction<sup>8</sup> of rhodium tribromide with aqueous pyridine; (b) the method described<sup>10</sup> by Poulenc as giving rise to the yellow *cis*-isomer of  $[\text{Rhpy}_4\text{Br}_2]\text{Br}\cdot 6\text{H}_2\text{O}$ . The mother-liquor was reserved. The products from (a) and (b) were identical in crystal form (glistening yellow plates) and both showed the very characteristic sudden change of solubility in water with temperature. Chemical behaviours towards a variety of reagents were identical, as were the X-ray powder photographs, and infrared and electronic spectra [ $\lambda$  443 m $\mu$ ,  $\epsilon$  132, in ethanol; cf. lit.,<sup>14</sup> for preparation (b);  $\lambda$  443 m $\mu$ ,  $\epsilon$  133]. The water of crystallisation is lost at 110° [Found (a) Br, 31.7; (b) Br, 31.5. Calc. for  $\text{C}_{20}\text{H}_{32}\text{Br}_3\text{N}_4\text{O}_6\text{Rh}$ : Br, 31.2%].

(II) *trans-Dibromotetrapyridinerhodium(III) bromide hydrogen bromide dihydrate.* This was prepared by several methods: (a) the product of the catalytic reaction I (a) above was allowed



Thermogravimetric data for *trans*- $[\text{Coen}_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ .

T.G.A. ——— weight loss in air;  
 - - - - weight loss in nitrogen.

D.T.A. ——— result in air; - - - -  
 result in nitrogen.

to crystallise from 1 : 1 hydrobromic acid-water; (b) the product of the reaction I (b) above was allowed to crystallise from 1 : 1 hydrobromic acid-water; (c) Poulenc's "orange isomer"<sup>10</sup> was isolated from the mother-liquor of I (b) above as he described.

The products IIa, IIb, and IIc were identical [Found: Br, (a) 41.0; (b) 41.3; (c) 42.4. Calc. for  $\text{C}_{20}\text{H}_{25}\text{Br}_4\text{N}_4\text{O}_2\text{Rh}$ : Br, 41.3%]. All dissolved in water to give fairly strongly acid solutions with identical electronic spectra, which on crystallisation gave yellow *trans*- $[\text{Rhpy}_4\text{Br}_2]\text{Br}\cdot 6\text{H}_2\text{O}$ . On heating the adducts to 120° aqueous hydrogen bromide was lost, and the parent yellow *trans*- $[\text{Rhpy}_4\text{Br}_2]\text{Br}$  remained, identical with the product of heating the hexahydrate. Finally, infrared spectra were identical, and superposable on that<sup>3</sup> of the hydrogen chloride adduct of *trans*-dichlorotetrapyridinerhodium(III) chloride.

*trans-Dichlorotetrapyridinerhodium(III) chloride hexahydrate.* This was prepared by the convenient catalytic method.<sup>8</sup> X-Ray powder photographs for this compound and the bromoanalogue (I above) were extremely similar.

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<sup>13</sup> S. M. Jorgensen, *J. prakt. Chem.*, 1890, **41**, 440.

<sup>14</sup> H. H. Schmidtke, *Z. phys. Chem.*, 1962, **34**, 295.