Adducts of Co-ordination Compounds. Part X.[1] Solvates and Adducts of Dihalogenotetrapyridinerhodium(III) Salts

By **A. W. Addison** and **R. D. Gillard**,* University of Kent at Canterbury, Kent

The cations *trans*-$[M(py)_4X_2]^+$, where M = Rh or Ir and X = Cl or Br, readily form stable salts with uncommon anions, such as polyhalides. This stabilisation in solids is illustrated by the new salts $[M(py)_4Cl_2](Cl_3)$ [M = Rh or Ir] and $[Rh(py)_4Cl_2](Br_2Cl)$ and some solvates, *e.g.*, $[Rh(py)_4Cl_2](ClO_4)MeNO_2$.

COMPLEX cations of the type *trans*-$[Rh(py)_4X_2]^+$ have been known for some time to form numerous 'adducts,' for example (i) $[Rh(py)_4X_2](NO_3)HNO_3$ (X = Cl or Br), which are[2] actually salts of the 'hydrogen dinitrate' ion, $[H(NO_3)_2]^-$; (ii) $[Rh(py)_4X_2]Y,AgY$ (Y = Cl or NO_3);[3] (iii) *trans*-$[Rh(py)_4Br_2]Br,HBr,2H_2O$, actually[4] *trans*-$[Rh(py)_4Br_2](H_5O_2)Br_2$, and many others, some discussed here.

We assemble here some of our results on the stabilisation of unusual anionic species such as $[Br_2Cl]^-$ and $\{(ClO_4)(solvent)_n\}$ by these complex cations, and offer some comments on relative stabilities of solid phases.

RESULTS

The tribromide and tri-iodide salts of $[Rh(py)_4Br_2]^+$ have previously been characterised.[5] We now find that when an aqueous solution of $Rh(py)_4Cl_3$ is shaken or allowed to stand under an atmosphere of chlorine, there are deposited cream silky crystals. The compound is anhydrous and has the composition $Rh(py)_4Cl_5$ (Table 1). A very similar compound is formed in the same way with *trans*-$Ir(py)_4Cl_3$, analogous in composition. The i.r. and Raman spectra (300—4000 cm^{-1}) show only bands associated with the *trans*-$[M(py)_4Cl_2]^+$; there is no C–Cl bond stretching absorption. However, both have very strong i.r. absorption centred at *ca.* 220 cm^{-1} and a remarkably strong Raman band at *ca.* 270 cm^{-1}. Evans and Lo[6] characterised (spectroscopically) tetrakis(n-propyl)ammonium trichloride and showed it contained the $[Cl_3]^-$ ion, which had the spectroscopic properties of the above compounds, which we therefore formulate *trans*-$[M(py)_4Cl_2](Cl_3)$. Similarly, $[Rh(py)_4Cl_2]I_3$ and $[Rh(py)_4Cl_2]Br_3$ have now been prepared, the latter by addition of bromine to the bromide salt in chloroform. The addition of Br_2 to a chloroform solution of $Rh(py)_4Cl_3$ gave a bright orange compound with very strong vibrational bands at 183 cm^{-1} (i.r.) and 170 cm^{-1} (Raman). We formulate it as $[Rh(py)_4Cl_2][Br_2Cl]$, although the analysis was 1% low in carbon.

TABLE 1

Analytical resullts forthe adducts

Compound	C(%)		H(%)		N(%)	
	Found	Calc.	Found	Calc.	Found	Calc.
$[Rh(py)_4Cl_2]I_3$	27·6	27·6	2·0	2·3	6·1	6·4
$[Rh(py)_4Cl_2]Cl_3$ [b]	40·4	40·3	3·4	3·4	9·7	9·4
$[Rh(py)_4Cl_2[[Br_2Cl]$	34·0	35·0	3·0	3·0	8·0	8·2
$[Rh(py)_4Cl_2]Br_3$	33·1	32·9	3·0	2·8	8·0	7·7
$[Ir(py)_4Cl_2]Cl_3$	35·0	35·0	3·6	3·0	8·5	8·2
$[Rh(py)_4Cl_2]ClO_4,MeNO_2$	39·4	38·8	3·9	3·6	11·4	10·8
$[Rh(py]_4Cl_2]ClO_4,Pr^nNO_2$	38·9	40·7	4·0	4·0	11·4	10·3
$[Rh(py)_4Cl_2]ClO_4,NC(CH_2)_4CN$	44·7	44·8	4·4	4·0	11·7	12·0

[a] All cations have *trans*-stereochemistry. [b] Cl, Found 28·9, calc. 29·7%.

When recrystallised from certain organic solvents, the

---

[1] Part IX, A. W. Addison and R. D. Gillard, preceding paper.

[2] R. D. Gillard and R. Ugo, *J. Chem. Soc. (A)*, 1966, 549.

[3] (*a*) P. Poulenc, *Ann. Chim. (France)*, 1935, **4**, 634; (*b*) J. A. Creighton, (Miss) R. A. Davies, and R. D. Gillard, unpublished work.

[4] D. Dollimore, R. D. Gillard, and E. D. McKenzie, *J. Chem. Soc.*, 1965, 4479.

[5] B. N. Figgis, R. D. Gillard, R. S. Nyholm, and G. Wilkinson, *J. Chem. Soc.*, 1964, 5189.

[6] J. C. Evans and G. Y-S Lo, *J. Chem. Phys.*, 1966, **44**, 3638.

perchlorate salts of $[RhL_4X_2]^+$ may retain solvent of crystallisation, even though they form as anhydrates from water. The methyl cyanide solvate of $[Rh(py)_4Cl_2]ClO_4$ forms as yellow, translucent rhombs, but rapidly loses solvent to the atmosphere and becomes opaque. Higher-boiling solvents lead to more stable solvates. These have been analysed spectrophotometrically by measuring their absorbances in MeCN solution. The results are in Table 2

TABLE 2

Compositions of solvates $[RhL_4X_2]ClO_4,(S)_n$

$[RhL_4X_2](ClO_4)$	Solvent (S)	n
L = py, X = Cl	Acetonitrile	2·2
L = py, X = Cl	Propionitrile	0·56 [a]
L = py, X = Cl	Isobutyronitrile	0
L = py, X = Cl	Adiponitrile	0·98 [b,c]
L = py, X = Cl	Benzonitrile	0
L = py, X = Cl	Nitromethane	1 [b,d]
L = py, X = Cl	Nitroethane	0·65, 0·57
L = py, X = Cl	1-Nitropropane	1·02 [b]
L = py, X = Cl	2-Nitropropane	0·94
L = py, X = Br	Nitromethane	0·87
L = pic, X = Cl	Nitromethane	1·0 [b]

[a] $\nu(C\equiv N) = 2250$w cm^{-1}. [b] See Table 1. [c] $\nu(C\equiv N) = 2245$s cm^{-1}. [d] $\nu(N-O) = 1560$s, 1377m cm^{-1}.

while analytical results for some very stable ones are in Table 1. The spectrophotometric method relies on the insensitivity of the molar extinction coefficient, ε, of the band at 410 nm to the environment, although the anion and solvent used have been held constant. An outline of the method is appended, whereby one obtains n in the formula $[RhL_4X_2]ClO_4(solvent)_n$.

Thus $[Rh(py)_4Cl_2]ClO_4$ forms hemisolvates with propionitrile * and nitroethane, monosolvates with nitromethane, 1- and 2-nitropropane, and adiponitrile (1,4-dicyanobutane) and a much less stable disolvate with methyl cyanide. Isobutyronitrile appears to be too bulky or too paraffinic for inclusion, while benzonitrile is almost certainly too bulky.

DISCUSSION

The species *trans*-$[M(py)_4X_2]^+$ (M = Rh or Ir) seem to be the cations *par excellence* for the stabilisation of large uninegative anions. Thus *inter alia* the perchlorate, tetrafluoroborate, hexafluorophosphate, thiocyanate, tribromide, tri-iodide, trichloride, tetrachlorodipyridinerhodate(III), and bromochlorobromate(I) salts are all insoluble in water. The stabilisation is clear since Chattaway and Hoyle stated [7] that Cl_3^- was stable only below 25 °C even in the presence of a large cation, while $[Rh(py)_4Cl_2]Cl_3$, $[Rh(py)_4Cl_2](Br_2Cl)$, and $[Rh(py)_4Cl_2]Br_3$ show no change in enthalpy on differential thermal analysis until 260 °C. $[Rh(py)_4Cl_2]Cl_3$ and $[Ir(py)_4Cl_2]Cl_3$ can indeed be kept at 120 °C without loss of weight, although, while wet, they lost chlorine as the equilibrium $Cl_3^- \rightleftharpoons Cl^- + Cl_2$ becomes effective, presumably through preferential solvation of chloride.

The factors which affect the position of equilibria involving solid phases, such as $C^+(AX_n)^- \rightleftharpoons C^+X^- + (AX_{n-1})$ are generally recognised: Basolo has given a general discussion [8] of the stabilisation of charged species by appropriate counter ions, and Evans [9] comments on hydration of cations in the context of improving packing.

It is helpful to assess the factors in terms of Scheme 1.

$$\begin{tikzcd}
C_1(AX_n^-) & & C_1(X^-) \\
(AX_n)^- \arrow[u, "(C_1)^+", "U_{C_1A}"'] \arrow[d, "(C_2)^+"', "U_{C_2A}"] \arrow[rr, phantom, "\rightleftharpoons"] & & X^- + (AX_{n-1}) \quad (1) \arrow[u, "U_{C_1X}"'] \arrow[d, "U_{C_2X}"] \\
(C_2)^+(AX_n)^- & & C_2(X^-)
\end{tikzcd}$$

SCHEME 1

The equilibrium (1), in the vapour phase, is perturbed by interaction with cations C_1^+ or C_2^+, the interaction energies being defined as U_{C_1A}, U_{C_1X}, U_{C_2A}, and U_{C_2X} in an obvious symbolism.

Now, the distinction between the effects of C_1^+ and C_2^+ on the equilibrium (1) arise from the relative sizes of $U_{C_1A} - U_{C_2A}$ and of $U_{C_1X} - U_{C_2X}$.

The two major contributors to variations of U are: (*a*) the size effect [the smaller is C^+, the greater will be the vapour-phase ion-pairing interaction to give (C^+X^-) or $(C^+AX_n^-)$ monomers] and (*b*) the energy differences arising from differing packing geometries of C^+ with X^- or with $(AX_n)^-$. This (for simple ionic lattices) is reflected in different Madelung constants for different co-ordination numbers. Factor (*a*) will often be outweighed by (*b*).

As an illustration of the familiar (although implicit) notions inherent in the discussion so far, Table 3 collects a few examples of equilibria (1). The last entry of Table 3 is an acknowledgement of the fact [10] that it is

TABLE 3

Stabilisation of solid phases from equilibria [a]

$$(AX_n)^- \rightleftharpoons (X)^- + (AX_{n-1})$$

$(C_2)^+$ [b,d]	$(AX_1)^-$ [b] $\rightleftharpoons$	(AX_{n-1}) +	$(X)^-$ [c,d]	$(C_1)^+$ [c]
trans-$[Rh(py)_4X_2]^+$	$[H(NO_3)_2]^-$	HNO_3 +	NO_3^-	$(pyH)^+$
$[Ph_4As]^+$	$[H(NO_3)_2]^-$	HNO_3 +	NO_3^-	$(NH_4)^+$
trans-$[Rh(py)_4X_2]^+$	$(Cl_3)^-$	Cl_2	Cl^-	$(NMe_4)^+$
$\{H^+(H_2O)_4\}$ [e]	$[ICl_4]^-$	ICl_3	Cl^-	$(H_3O)^+$
trans-$[Rh(py)_4X_2]^+$	$[Cl(H_2O)_4]^-$	$4H_2O$	Cl^-	$(pyH)^+$

[b] The few examples given here have been restricted to uninegative anions: there are many equilibria involving more highly charged species that could be treated similarly, *e.g.*,[8b] $[Rh(NH_3)_6]\{H(NO_3)_4\}$. [b] These columns $(C_2)^+$ and $(AX_n)^-$ represent the larger ions. [c] These columns represent the smaller ions: $r(C_2)^+ > r(C_1)^+$ and $r(AX_n)^- > r(X^-)$. [d] In each case, larger $(C_2)^+$ crystallises with larger $(AX_n)^-$, whereas smaller $(C_1)^+$ crystallises with smaller X^-. [e] The structure of this aggregate of proton and waters in '$HICl_4,4H_2O$' is not known: it might be $(H_9O_4)^+$, but the analogous $H[AuCl_4],4H_2O$ is properly formulated $(H_5O_2)^+[AuCl_4]^-,2H_2O$.

---

* Nitrile solvates are known for some co-ordination compounds; *e.g.*, Grinberg mentions $[Cr(py)_3Cl_3],2C_2H_5CN$.

[7] F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, 1923, **654**.

[8] (*a*) F. Basolo, *Co-ord. Chem. Rev.*, 1968, **3**, 213 and *cf.* (*b*) R. Ugo and R. D. Gillard, *Inorg. Chim. Acta*, 1967, **1**, 313 and refs. therein.

[9] R. C. Evans, 'Crystal Chemistry,' 2nd edn., 1964, Cambridge Univ. Press, pp. 283 *et seq.*, especially 285.

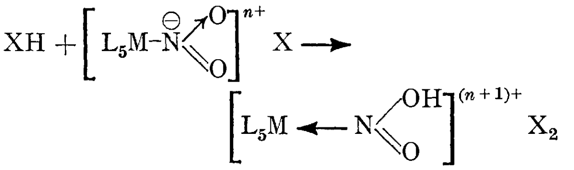
[10] R. D. Gillard and B. T. Heaton, unpublished work.

not possible by heating to remove water * from hydrated *trans*-$[Rh(py)_4Cl_2]Cl,xH_2O$ without decomposition of the cation. That is, the lattice energy (U_{C_2X}) of the chloride $[M(py)_4Cl_2]Cl$ is extraordinarily low relative to that (U_{C_2A}) of $[M(py)_4Cl_2](AX_n)$ where $(AX_n)^-$ [*e.g.*, $[Cl(OH_2)_4]^-$, $(Cl_3)^-$ *etc.*] is much bigger than Cl^-.

This importance of solvent (often water) attaching to the *anion* to make it sufficiently bulky to give good AB packing is at the root of many other observations relating in particular to hydration of salts of complex cations of heterocyclic nitrogen ligands (where hydrogen bonding is presumably unimportant). (i) *cis*$[Rh(phen)_2Cl_2]NO_3,nH_2O$ is isomorphous [11a] with α-*cis*-$[Rh(phen)_2Cl_2]Cl,xH_2O$: the analogues containing cobalt(III) and chromium(III) are also isomorphous.[11b]

(ii) We find the solubility product at 17 °C of *trans*-$[Rh(py)_4Cl_2]Cl,xH_2O$ is a mere 7×10^{-4} mol^2 l^{-2}. However, on warming (thereby disrupting water and reducing the concentration of $[Cl(H_2O)_4]^-$) solubility increases dramatically. In a similar way, the stoicheiometric compositions of solid solvates as a function of temperature can be seen as a comment on the way that the nature of solvated species varies with temperature.

(iii) The cations *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[M(py)_4X_2]^+$ ($M = Rh$ or Ir, $X = Cl^-$ or Br^-) form ' double salts ' with silver salts of formula $[ML_4X_2]Y,AgY$ ($Y = Cl^-$ or NO_3^-). These we would now [3b] formulate $[ML_4X_2]^+[AgY_2]^-$. In the context of adducts of protons or silver ions, there are of course situations in which the ligands are involved in extra equilibria such as (2) [12] or (3),[13] and where the nature of solid products may depend



$$XH + \left[L_5M{-}\overset{\ominus}{N}(\rightarrow O)(=O)\right]^{n+} X \longrightarrow \left[L_5M \longleftarrow N(OH)(=O)\right]^{(n+1)+} X_2 \quad (2)$$

(*e.g.*,[12] $M = Co^{III}$, $L = NH_3$, $X = (NO_3^-)$

$$[L_5M{-}NCS]^{n+} + Ag^+ \rightleftharpoons [L_5M{-}NCSAg]^{(n+1)+} \quad (3)$$

both on factors discussed here and others. It is also not uncommon for extra equilibria involving covalent attachment of a polar solvent to become important, *e.g.*,[14] *trans*-$[Rh(py4CHO)_4Cl_2]ClO_4,4H_2O$ is actually *trans*-$[Rh\{py4CH(OH)_2\}_4Cl_2]ClO_4$: the ' water ' in this case *can* be removed by heating {contrast $[Rh(py)_4Cl_2]$-$[Cl{\cdot}(H_2O)_4]$}.

(iv) The existence of ' acid adducts ' of certain complex cations, *e.g.*,[4] $[Rh(py)_4Cl_2](H_5O_2)Cl_2$: clearly this is another mechanism whereby the cation can improve on the very poor lattice energy of $[Rh(py)_4Cl_2]Cl$. By incorporating the smaller cation, the packing improves.

(v) Among the complex halides which will form ' hydrohalic acid adducts ' are *cis*-$[Rh(aa)_2Cl_2]^+$ (aa = 2,2′-bipyridyl or 1,10-phenanthroline). This was initially believed [15] to be a specific shape effect associated with the stereochemistry of the cation, but is more sensibly attributed to a more general size effect arising from the small size of the anion: it has no stereochemical significance other than the fact that complex cation and anion are incompatible.

(vi) Among large cations, those of $[M(phen)_3]^{2+}$ are well known. Many of their salts are highly hydrated, *e.g.*, $[M(phen)_3]X_2,6H_2O$ and it has been pointed out [16] that there are three pockets in the cation structure which would each hold two water molecules. However, in view of the data in Table 3, it would perhaps be more sensible to formulate these salts as $[M(phen)_3][X(H_2O)_n]_2$. Interestingly, among the few known structures of these salts, the water is not in the pockets.

This work has demonstrated the utility of the complexes *trans*-$[M(py)_4X_2]^+$ as suitable cations for the stabilisation in lattices of relatively high energy of a range of counter ions of an appropriate size. A good deal of scattered and diverse information is thereby collated.

EXPERIMENTAL

Preparations.—(i) $[Rh(py)_4Cl_2]Cl_3$. An aqueous solution (100 ml) of $[Rh(py)_4Cl_2]Cl,5H_2O$ (0·2 g) was shaken under an atmosphere of dichlorine, producing feathery cream crystals. These were collected, washed with cold water, then with ether (100 ml), and dried *in vacuo* over sulphuric acid (yield 0·16 g); molar conductivity (Λ hereafter, for 10^{-3}M solution in nitromethane) 64 Ω^{-1} cm^2 mol^{-1}.

(ii) $[Ir(py)_4Cl_2]Cl_3$ had Λ 61 Ω^{-1} cm^2 mol^{-1}.

(iii) $[Rh(py)_4Cl_2]I_3$. This known compound [5] resulted from an attempted Karl Fischer titration of *trans*-$[Rh(py)_4Cl_2)Cl,xH_2O$ (0·44 g) which gave 0·63 g of shiny brown platelets, Λ 54 Ω^{-1} cm^2 mol^{-1}.

(iv) The known [5] $[Rh(py)_4Cl_2]Br_3$ was made by adding bromine to the bromide of the dichloro-compound in chloroform (λ 410 nm), orange crystals, Λ 65 Ω^{-1} cm^2 mol^{-1}.

(v) *trans*-$[Rh(py)_4Cl_2]Br,HBr,3H_2O$. Ethanolic *trans*-$[Rh(py)_4Cl_2]Cl,5H_2O$ was treated with HBr–NaBr at *ca.* 70 °C (1 h); no halide exchange occurred. Instead, yellow laths of this new hydrobromic acid adduct were obtained: properties included (i) 10^{-2}M solution had pH 2; (ii) electronic absorption at 410 nm, characteristic of the dichloro-cation; (iii) an i.r. absorption at 365 cm^{-1}, due to ν_{as} $RhCl_2$; (iv) Found: C, 33·6; H, 3·2; N, 8·2. Calc. for $C_{20}H_{27}Br_2Cl_2N_4O_3Rh$: C, 34·1; H, 3·8; N, 8·0% (*cf.* Calc. for the dihydrate *trans*-$[Rh(py)_4Cl_2]Br,HBr,2H_2O$: C, 34·9; H, 3·6; N, 8·2%).

---

* Although it is noteworthy that J. P. Collman and H. F. Holtzclaw (*J. Amer. Chem. Soc.*, 1958, **80**, 2054) claim that vacuum desiccation gives the anhydrate and the original description of the compound by S. M. Jørgensen was of the anhydrous compound (*J. prakt. Chem.*, 1883, **27**, 478) made by keeping the hydrate at 100 °C.

[11] (*a*) E. D. McKenzie and R. A. Plowman, *J. Inorg. Nuclear Chem.*, 1970, **32**, 199; (*b*) J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.*, 1969, 2637.

[12] R. Ugo and R. D. Gillard, *J. Chem. Soc.* (*A*), 1967, 2078.

[13] W. C. Waggener, J. A. Mattern, and G. H. Cartledge, *J. Amer. Chem. Soc.*, 1959, **81**, 2958.

[14] R. D. Gillard and B. T. Heaton, *J. Chem. Soc.* (*A*), 1968, 1405.

[15] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1964, 1640.

[16] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 339.

Spectrophotometric Determination of Solvate Compositions.—This simply uses the Beer–Lambert law, $A = \varepsilon c l$. If $l = 1$, and ε is known, then A is measured and we obtain equation (4), where W = apparent gram-formula weight,

$$W = \frac{\varepsilon m}{AV} \qquad (4)$$

m = mass of solvate dissolved (mg), and V = volume of solution (ml). Hence the difference between the apparent formula weight and the (unsolvated) formula weight gives the amount of solvation.

A related experiment, quantitatively precipitating $[Rh(py)_4Cl_2]ClO_4$ from a solution of $[Rh(py)_4Cl_2]Cl_2,nH_2O$ gave $n = 4{\cdot}6$ (*cf.* usual values of 5 from elemental analyses, with a few values of $n = 6$).

We thank Dr. J. A. Creighton for help with Raman experiments, and Dr. B. T. Heaton for comments.

[2/1642 *Received*, 11*th July*, 1972]