

Complexes of Pyridine Bases with Rhodium

REDOX BEHAVIOUR AND ANTIBACTERIAL ACTIVITY

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The ability of pyridine and similar nitrogenous heterocyclic bases to bind to metal ions has been known for many years. Complexes of the platinum metals with such bases were studied in considerable detail in the early days of coordination chemistry. For example, the compound *trans*-dichlorotetra-pyridinerhodium(III) chloride was made by S. M. Jorgensen in 1885.

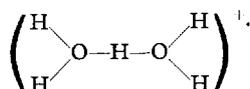
In the development of the Werner theory of stereochemistry, one of the outstanding series of compounds was that involving rhodium(III) with chloride and pyridine ligands. By the end of the 1930s, as a result of the work of Delepine and of Poulenc, the known compounds included $[\text{Rhpy}_3\text{Cl}_4]^-$ (*cis* and *trans*), $[\text{Rhpy}_3\text{Cl}_3]$ (*cis* and *trans*) and $[\text{Rhpy}_4\text{Cl}_2]^+$, with most of the analogous bromo-compounds. The classical work is admirably summarised in the recent book by Griffith (1).

Many extensions to the available range of compounds have been made in recent years, and complexes involving the chelating ligands 2,2'-bipyridyl and 1,10-phenanthroline have been studied. However, the main interest in this type of compound has shifted in recent years towards their redox properties, particularly in connection with catalytic possibilities. It is the purpose of this short review to point out some novel and interesting facets of this branch of platinum metal chemistry that have emerged during the past few years.

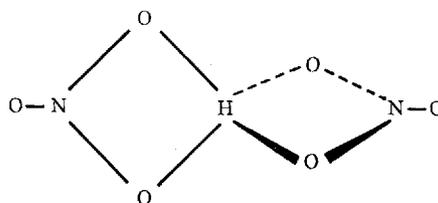
Acid Adducts

A new crystalline solid is obtained from *trans* $[\text{Rhpy}_4\text{Br}_2]\text{Br}\cdot 6\text{H}_2\text{O}$ in the presence of

excess hydrobromic acid. It has the composition *trans* $[\text{Rhpy}_4\text{Br}_2]\text{Br}\cdot\text{HBr}\cdot 2\text{H}_2\text{O}$, and its infra-red spectrum and thermogravimetric properties strongly support its formulation as *trans* $[\text{Rhpy}_4\text{Br}_2](\text{H}_5\text{O}_2)\text{Br}_2$. The $(\text{H}_5\text{O}_2)^+$ cation is stabilised within the crystal lattice and apparently contains a very short, probably symmetrical, hydrogen bond,

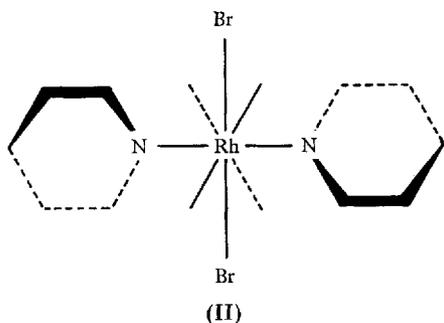


In the same way, several "adducts", which contain two compounds stable in their own right, exist among these pyridine-rhodium complexes. Perhaps the most striking case concerns the nitric acid adduct, discovered by Poulenc, of formula *trans* $[\text{Rhpy}_4\text{Br}_2]\text{NO}_3\cdot\text{HNO}_3$. As a result of spectroscopic work and of conductivity studies in dichloromethane, where the compound is a 1:1 electrolyte, it was reformulated as a salt of a new anion $[\text{Rhpy}_4\text{Br}_2][\text{H}(\text{NO}_3)_2]$. This hydrogen dinitrate species (isoelectronic with $[\text{H}(\text{CO}_3)_2]^{2-}$, observed in sodium sesquicarbonate $\text{Na}_2\text{CO}_3\cdot\text{NaHCO}_3\cdot 2\text{H}_2\text{O}$ by neutron diffraction) turns out to have several possible conformations.



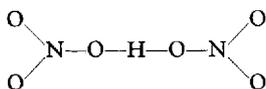
(1)

The approximate conformation of the hydrogen dinitrate ion in its *trans* $[\text{Rhpy}_4\text{Br}_2]^+$ salt



The ion $\text{trans}[\text{Rhpy}_4\text{Br}_2]^+$ in its hydrogen dinitrate salt, viewed along a C_2 axis in the direction $C_4 \rightarrow N \rightarrow Rh \rightarrow N \text{-----} C_4$

Two have already been observed in crystalline lattices; the linear conformation

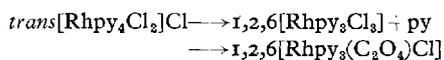


is stabilised (2) as its tetraphenylarsonium salt, whereas the conformation of the ion in the rhodium complex salt (3) is shown in (I).

Stereochemical Developments

A further point of significance arises from the crystal structure of this nitric acid adduct. This is that the complex ions exist as four-bladed propellers (II), this shape being a compromise between the steric requirements of the α -hydrogens of the pyridine ligands and the planar overall geometry which would give the strongest rhodium-nitrogen bonds. A number of synthetic observations may be rationalised on this basis.

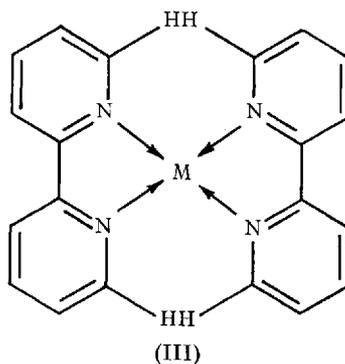
The *trans* di-iodo complex readily loses pyridine (presumably because the bulky iodide ligands compress the propeller increasing the non-bonded interactions between pyridine ligands). It has not yet proved possible to obtain complexes of the type $[\text{RhL}_4\text{X}_2]^+$, where L is a 2-substituted pyridine (e.g. α -picoline or pyridine-2-aldehyde). One pyridine is rather readily lost even from the dichloro-complexes, as in (4)



This last oxalato-product shows an unusual property, synergic solubility. Insoluble in

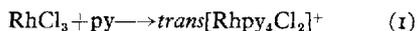
pure water and insoluble in neat pyridine, it is yet quite soluble in their 1:1 mixture.

Very recently, great interest has centred on the complexes of the type $[\text{M}(\text{AA})_2\text{X}_2]^+$, where $\text{M} = \text{Co}^{\text{III}}, \text{Rh}^{\text{III}}, \text{or Ir}^{\text{III}}$, AA is 2,2'-bipyridyl or 1,10-phenanthroline, and $\text{X} = \text{Cl}$ or Br . As a result of studies of X-ray isomorphism, far infra-red spectra, electronic spectra, N.M.R. and optical resolution, they have now (5) been formulated as *cis*-isomers. The inaccessibility of the *trans*-isomer is commonly attributed to steric hindrance between α -hydrogens in (III), though it should be noted that the species $[\text{M}(\text{AA})_2]^{2+}$ where $\text{M} = \text{Pd}$ or Pt , certainly exist, where the stereochemistry of the MN_4 unit is likely to be planar.



Catalysis and Inhibition

Much work on complexes of nitrogenous ligands with rhodium has been stimulated by the possibility that useful catalytic properties might be achieved. Delepine in 1929 recorded that the aqueous reaction (1)



was remarkably catalysed by ethanol, and in 1953, extended this observation to many other organic species containing the group

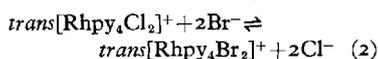


This particular hydrogen atom a of ethanol, in other reactions of platinum metal compounds, may serve as a two-electron reductant, and it therefore seemed likely that the catalytic species in Delepine's case was

either a rhodium(I) complex or a hydrido-complex of rhodium(III). The reaction was studied kinetically and preparatively, and a large number of 2-electron reducing agents (e.g. hypophosphite, hydrazine, and ethanol) were found useful (6). Most of the reduced species of rhodium described in the literature (often said to involve rhodium(II)) are either complexes of rhodium(III) whose formation had been catalysed by the two-electron "reducing" agents employed, or hydridorhodium(III) complexes.

One of the most spectacular catalysts for reaction (1) was molecular hydrogen, effective at one atmosphere and ambient temperature (6). It was further found that the homogeneous hydrogenation of olefins could be achieved in this system.

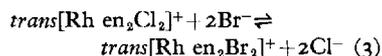
This appeared then to be a fairly readily understood (although novel) area of rhodium chemistry. The catalytic species (containing Rh^I or $\text{Rh}^{III}\text{-H}$) were apparently formed by the interaction of rhodium(III) with two electron reducing agents, including hydrogen. However, this is certainly not the whole story, as shown by work on halogen exchange in aqueous solution (reaction 2).



An apparent inhibition period when these experiments were done under the usual aerobic conditions disappears when they are repeated under an atmosphere of water vapour only. The inhibition is by molecular oxygen. Indeed, in the total absence of

oxygen, the exchange occurs too fast to follow by conventional techniques.

This finding strongly indicates that the *trans*-tetrapyridine-rhodium(III) moiety has unexpected redox properties. The corresponding very slow exchange in



is quite unaffected by oxygen. The observation of this ready reaction of oxygen with whatever reduced species of rhodium is present in aqueous solutions of the tetrapyridine complexes has also led to the characterisation of new compounds, containing the unit $\text{L}_5\text{Rh}^{III}\text{-O}_2^{(-)}\text{-Rh}^{III}\text{L}_5$. The blue salts $[\text{ClL}_4\text{RhO}_2\text{RhL}_4\text{Cl}]\text{Y}_3$, where $\text{L} = \text{py}$ or γ -picoline and $\text{Y} = \text{ClO}_4^-$ or BF_4^- , have been characterised, as have similar compounds where $\text{L} = \text{NH}_3$.

Bacteriostatic Properties

Perhaps the strangest property of these rhodium-pyridine compounds is that they have very marked antibacterial activity. Typical results are collected in the Table. In summary, the activity increases when co-ordinated chloride is replaced by co-ordinated bromide, or when the pyridine ligand is progressively substituted with lipophilic groups (e.g. $\text{py} < 3 \text{ Mepy} < 3 \text{ Etpy} \approx 3,4\text{-diMepy}$), but decreases when polar groups are introduced (e.g. 4OHpy , $4\text{NH}_2\text{py}$). The activity is specific to the structure $\text{trans}[\text{RhL}_4\text{X}_2]\text{Y}$ (where $\text{L} = \text{pyridine}$ or a substituted pyridine, $\text{X} = \text{Cl}$ or Br , and Y is an anion such as Cl^- , Br^- , NO_3^- ,

Bacteriostasis by $\text{trans}[\text{RhL}_4\text{X}_2]\text{Y}$			
	Staph. aureus ^p	Strep. pneumoniae ^p	E coli (Strain B) ⁿ
$[\text{Rhpy}_4\text{Cl}_2]\text{Cl}$	5 ^a	2.5	> 80
$[\text{Rh}(4\text{Mepy})_4\text{Br}_2]\text{Br}$	1.25	0.32	10
$[\text{Rh}(4\text{nPrpy})_4\text{Br}_2]\text{NO}_3$	0.16	0.16	40

a. The lowest concentration ($\mu\text{g/ml}$) preventing growth n. Gram negative p. Gram positive
(Staphylococcus aureus occurs in septic infections, streptococcus pneumoniae in chest infections, and escherichia coli in the gastro-intestinal tract.)

ClO_4^-). Thus, the complex where $L = \frac{1}{2}$ en is inactive. Salts of analogous complexes of the type $\text{trans}[\text{Mpy}_4\text{Cl}_2]^+$ ($M = \text{Co}^{\text{III}}$ or Ir^{III}) are inactive. This suggests that the effect in the rhodium cases is not merely that of a cation of particular charge and shape since many complexes $[\text{Mpy}_4\text{X}_2]\text{Y}$ ($M = \text{Co}, \text{Rh}$ or Ir) are isomorphous.

The mechanism of this antibacterial action of $\text{trans}[\text{Rh}(\text{py-X})_4\text{Cl}_2]^+$ is being studied. The fact that the property is so specific to compounds of this structure offers a clue. We have already suggested that the other property which is highly specific to these particular rhodium complexes is their redox behaviour, and it seems likely that the biological activity may be related to this.

There is some evidence that this is so from observations on the culture of *Escherichia coli* with sub-lethal amounts of $\text{trans}[\text{Rhpy}_4\text{Cl}_2]^+$. Further, the rhodium(III) pyridine complexes, polarographically, have $E_{\frac{1}{2}} \sim -100$ to -200 mV, whereas the biologically inactive complexes $\text{trans}[\text{Rhen}_2\text{Cl}_2]^+$ and $\text{trans}[\text{Rhen}_2\text{Br}_2]^+$ have $E_{\frac{1}{2}} -700$ and -500 mV respectively.

The chemistry of complexes of rhodium with aromatic nitrogen donors was apparently well understood thirty years ago. In 1957, Delepine's actual samples were used in the first application of ligand field theory to rhodium complexes, and it then seemed likely that further effort in this area would be barren. Striking developments have occurred in the past five or six years, and I hope that it will be clear from the present treatment that it is not necessary to invent new ligands to obtain surprising and thought-provoking results in the chemistry of these fascinating elements.

References

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Palladium-Silver Resistor Pastes

EFFECT OF FIRING CONDITIONS ON ELECTRICAL PERFORMANCE

Complex reactions occur when silver-palladium resistor pastes are fired in the preparation of thick film circuits. Some light was shed on these in a paper by P. H. Krahl and A. F. Bogenschütz of the Research Institute of Allgemeinen Electricitätsgesellschaft, AEG-Telefunken, Ulm (*Metall*, 1968, **22**, (10), 988) and reviewed in *Platinum Metals Review*, 1968, **13**, (1), 30. The same authors have now investigated the effect of firing conditions on the electrical properties of the resistors (*Metall*, 1970, **24**, (2), 118-122).

The authors used two Du Pont pastes based on silver-palladium and silver-palladium oxide, and a three-zone kiln with independent zone control. The effects of firing time and temperature were investigated independently using controlled atmospheres of air and oxygen.

Their results show that the firing temperature, cycle and atmosphere strongly influence

the electrical properties of the resistors, mainly because of variations in the degree of oxidation of Pd and reduction of PdO, and in the degree of fusion of the glass frit vehicle in which the metal and oxide powders are dispersed. Under no single set of conditions were optimum values obtained for all of: reproducibility of resistance values, temperature coefficient of resistance, low electrical noise, and long-term stability.

The authors recommend that because it is difficult to predict the behaviour of the pastes, firing tests should always be carried out to establish the most suitable conditions. They obtained their most favourable results using a 30 to 40 minute cycle, and temperatures of 680°C and 780°C respectively for the Pd and PdO based resistors, claiming reproducible resistances with a scatter of ± 10 per cent of the mean values by rigid adherence to these conditions.

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