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Nitrile Complexes of Rhodium(III)

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The preparation and characterisation of trans-$[RhX_2(RCN)_4]^+$ *(X = Cl or Br; R = Me, Et,* n-*Pr, Ph,* $PhCH_2$*) and* $[RhCl_3(RCN)_2]_n$ *(R = Me,* i-*Pr,* $PhCH_2$*) are reported and* $[RhCl_3(RCN)_3]$ *(R = Et,* n-*Pr,* i-*Pr,* $PhCH_2$*) has been shown to have the 1,2,4-configuration.*

Introduction

Catsikis and Good recently described rhodium(III)/acetonitrile complexes of the type $[RhCl_4(CH_3CN)_2]^-$, 1,2,3- and 1,2,4-$[RhCl_3(CH_3CN)_3]$.[1] This prompts us to report our results on $[RhCl_3(RCN)_3]$ (R ≠ Me) and the previously unreported complexes $[RhCl_3(RCN)_2]_n$ and *trans*-$[RhX_2(RCN)_4]^+$.

Results and Discussion

Complexes of the type 1,2,4-$[RhCl_3(RCN)_3]$, (R = C^2H_3, Et, *n*-Pr, *i*-Pr, Ph, $PhCH_2$). Dissolution of hydrous rhodium trichloride in a nitrile gives as the major product $[RhCl_3(RCN)_3]$. On the basis of electronic and far infrared spectra, Johnson and Walton[2] suggested that these complexes had the 1,2,4-configuration while later work by Walton[3] suggested the 1,2,3-configuration. For acetonitrile, both isomers have recently been prepared and completely characterised;[1] the data obtained for the acetonitrile complexes are in complete accord with our findings. However, we find that the previously described preparative methods for $[RhCl_3(RCN)_3]$ (R ≠ Me)[2,3] give only the 1,2,4-isomer. The analytical results are shown in Table 1 and n.m.r. provides an unambiguous assignment of their stereo-chemistry. Thus the complexes containing nitriles which possess α-hydrogens usually show a 2:1 splitting of this resonance (see Table I) consistent with C_{2v} local symmetry in the coordination sphere of the metal. The electronic spectra of all the complexes in Table I show maximal absorption at 426±4 nm and it therefore seems probable that the complexes with nitriles, which do not contain α-hydrogens, also have the 1,2,4-configuration. Furthermore, this value for the absorption maximum agrees closely with that found for 1,2,4-$[RhCl_3L_3]$ (L = py[4] or CH_3CN[1]) but is significantly different to the values found for 1,2,3-$[RhCl_3L_3]$.

Infrared spectra (*ca.* 2300 cm^{-1}) are of little use for determining the stereochemistry of these complexes since only one band due to $\nu(C{\equiv}N)$ is observed, except when R = Me. In this case, two bands are observed at 2330 and 2305 cm^{-1}, which have previously been assigned to a combination band and $\nu(C{\equiv}N)$ respectively.[2] However, this assignment must be reversed since we find that the infrared spectrum of 1,2,4-$[RhCl_3(C^2H_3CN)_3]$ shows only one band at 2330 cm^{-1}, clearly due to $\nu(C{\equiv}N)$.

Far infrared spectra have been used to lend support to the above stereochemical assignments[1] and we find that the Raman spectrum also provides useful information. Group theory predicts three rhodium-chlorine stretching modes $(2a_1+b_1)$ for molecules with C_{2v} symmetry. The Raman spectrum of 1,2,4-$[RhCl_3(CH_3CN)_3]$ in solution shows three strong bands due to $\nu(Rh{-}Cl)$ at 357, 313 and 304 cm^{-1}. The last two show a depolarisation ratio of 0.48 and so can be assigned to the $2a_1$ stretching modes.

Dissolution of hydrous rhodium tribromide in acetonitrile has been reported to give *cis*-$[RhBr_3(H_2O)(CH_3CN)_2]$[5] whereas we find that, on carrying out the above reaction in the presence of triethyl orthoformate, the non-electrolyte $[RhBr_3(CH_3CN)_3] . H_2O$ is obtained. In this case it is difficult to assign a configuration since, although the electronic spectrum is consistent with a 1,2,4-configuration (λ_{max} 480 nm), the n.m.r. spectrum shows the presence of only one peak at 7.16 τ. It was impossible to obtain a Raman spectrum due to strong absorption of the exciting radiation and little could be deduced from the i.r. spectrum alone.

As noted earlier, pyridine and nitriles produce similar ligand field splittings and the reactions of $[RhCl_3L_3]$ (L = py or RCN) are also similar. Thus, the polymeric pink compound, $[RhCl_3L_2]_n$, is produced on refluxing an acetone solution of 1,2,4-$[RhCl_3L_3]$, and 1,2,3-$[RhCl_3L_3]$ readily isomerises to the more thermodynamically stable 1,2,4-isomer on heating. Indeed, even when carrying out the reactions at *ca.* 20°, we have found it impossible to isolate 1,2,3-$[RhCl_3(RCN)_3]$ when using nitriles other than acetonitrile. The complexes $[RhCl_3(RCN)_2]_n$, which can be reconverted to 1,2,4-$[RhCl_3(RCN)_3]$ on prolonged boiling with the appropriate nitrile, are probably halogen-bridged polymers since the i.r. spectrum shows ν-

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(1) B.D. Catsikis and M.L. Good, *Inorg. Chem.*, *8*, 1095 (1969).
(2) B.F.G. Johnson and R.A. Walton, *J. Inorg. Nucl. Chem.*, *28*, 1901 (1966).
(3) R.A. Walton, *Canad. J. Chem.*, *46*, 2347 (1968).
(4) R.D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1224 (1964).
(5) B.D. Catsikis and M.L. Good, *Inorg. Chem.*, *10*, 1522 (1971).

Table I. Analytical and Spectroscopic data for complexes of the type 1,2,4-[$RhX_3(RCN)_3$].

R	X	λ_{max}(nm)	$\tau\alpha$-CH_2 [a]	Found (%) C	H	N	Required (%) C	H	N
Et	Cl	422	7.00(2) 7.04(1)	28.0	4.1	10.6	27.6	4.1	10.7 [b]
n-Pr	Cl	429	7.08(2) 7.12(1)	34.5	5.0	10.0	34.6	5.1	10.1
i-Pr	Cl	425	6.18	34.1	5.0	10.3	34.6	5.1	10.1
Ph	Cl	426	—	48.4	3.0	8.2	48.6	2.9	8.1
$PhCH_2$	Cl	425	5.25(2) 5.81(1)	52.0	3.7	7.3	51.4	3.8	7.5

[a] In $CDCl_3$ solution. Figures in brackets are relative intensities. [b] These figures correspond to [$RhCl_3(EtCN)_3$] . H_2O. Water of crystallisation was indicated by a broad i.r. absorption band at 3500 cm.$^{-1}$ It proved impossible to obtain an anhydrous product even by addition of triethylorthoformate to the reaction mixture.

Table II. Analytical and Spectroscopic data for complexes of the type *trans*-[$RhX_2(RCN)_4$]Y.

R	X	Y	max(nm)	Λ [a]	ν(C≡N) [b]	Found (%) C	H	N	Required (%) C	H	N
Me	Cl	Cl	410	96	2330	21.7	2.8	12.3 [d]	22.0	2.8	12.8
Me	ClO_4	Cl	410	96	2330	23.5	2.8	17.1	24.0	3.0	17.5
Me	ClO_4	ClO_4	441	97	2350	18.2	2.5	10.2	18.25	2.3	10.6
Et	ClO_4	NO_3	410	—	2320	25.1	3.75	9.7	25.5	3.6	9.9 [c]
n-Pr	ClO_4	Cl	415	—	2325	34.6	5.1	10.1	34.9	5.1	10.2
Ph	ClO_4	Br	415	—	2300	49.0	2.9	8.2	48.5	3.2	8.4
$PhCH_2$	Cl	Cl	415	—	2320	51.8	3.65	7.4	51.8	3.8	7.55

[a] conductance of 10^{-3}*M* solution in acetonitrile (ohm^{-1} cm^{-2} mole^{-1}) at 25°: [b] cm.$^{-1}$ measured as nujol mulls. [c] These figures correspond to *trans*-[$RhCl_2(EtCN)_4$]ClO_4 . $4H_2O$. [d] Found, Cl, 24.4; Required, Cl, 24.3%.

(C≡N) in the usual place (*ca.* 60-70 cm^{-1} higher than in the free ligand) for coordinated nitriles.

However, one notable difference is that whereas the reactions of pyridine-rhodium(III) complexes are catalysed by 2-electron reducing agents and inhibited by the presence of di-oxygen,[6] no such effects are observed in the nitrile series.

Complexes of the type trans-[*Rh*X_2(*RCN*)$_4$]$^+$, (X = Cl, or Br; R = Me, Et, *n*-Pr, Ph, $PhCH_2$). The preparation of *trans*-[$RhCl_2(MeCN)_4$]Y (Y = ClO_4 or NO_3) is readily accomplished by the addition of AgY (1 mol) to a solution of 1,2,4-[$RhCl_3(MeCN)_3$] in acetonitrile. Complexes containing other nitriles are more readily prepared by heating a solution of *trans*-[$RhCl_2(MeCN)_4$]$^+$ in the appropriate nitrile whereupon acetonitrile is displaced and can be distilled off. The analysis, conductance and electronic spectra support the formulation [$RhCl_2L_4$]Y, (see Table II). Unfortunately they were insufficiently soluble in nonpolar solvents for n.m.r. measurements and attempts to prepare more organic soluble complexes, by replacement of perchlorate with chloride, resulted in the displacement of coordinated nitrile and formation of 1,2 4-[$RhCl_3L_3$] and *trans*-[$RhCl_4L_2$]$^-$.

Support for the *trans*-configuration comes from vibrational spectra. Thus the Raman spectra of [$RhX_2(MeCN)_4$]ClO_4 (X = Cl or Br) are very similar except for bands associated with ν(Rh–Cl) 304 cm^{-1} and ν(Rh–Br) 194 cm^{-1}. The far infrared spectra are also very similar and show only one band due to ν(Rh–X) at 367 cm^{-1} and 226 cm^{-1} respectively. The positions of these bands are very similar to those found for *trans*-[$RhX_2(py)_4$]$^+$.[7]

Coordinated nitriles in *trans*-[$RhX_2(RCN)_4$]$^+$ are labile and undergo ready displacements with pyridine and 1,10-phenanthroline to give *trans*-[$RhX_2(py)_4$]$^+$ and *cis*-[$RhX_2(phen)_2$]$^+$ respectively.

The reaction of ammonia and aliphatic amines with nitrile/platinum(II) complexes has been shown to result in the formation of amidine complexes[8] and it seems probable that the above nitrile/rhodium(III) complexes undergo similar reactions with ammonia since the i.r. spectra of the resulting yellow products did not have a band due to ν(C≡N). However, the exact nature of these products was not investigated further because they were insoluble and gave variable analytical results.

Experimental Section

^{1}H n.m.r. spectra were recorded on a Perkin Elmer R. 10 spectrometer at 60 MHz. I.r. spectra (4000-400 cm^{-1}) were measured as nujol mulls on a Perkin Elmer 457 spectrometer, and as polythene discs on a R.I.I.C. interferometer fitted with a FTS-100-7 computer (400-100 cm^{-1}). Raman spectra were measured on a Coderg spectrometer with an O.I.P. 181B He/Ne laser emitting 180mW at 6328 Å. Electronic spectra were recorded on a Unicam SP800 spectrometer using matched silica cells. Conductivities were determined using a Phillips PR 9500 conductivity bridge with a dipping cell. Nitriles were obtained from Koch-Light Ltd., and used without further purification.

1. *Preparation of Complexes of the type 1,2,4-*[*Rh*Cl_3(*RCN*)$_3$], (R = Et, *i*-Pr, *n*-Pr, Ph, $PhCH_2$). Com-

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(6) R.D. Gillard, B.T. Heaton, and D.H. Vaughan, *J. Chem. Soc.* (*A*), 1840 (1971).

(7) R.D. Gillard and B.T. Heaton, *J. Chem. Soc.* (*A*), 451 (1969).

(8) N.C. Stephenson, *J. Inorg. Nucl. Chem.*, *24*, 801 (1962).

Table III. Analytical data for complexes of the type $[RhCl_3(RCN)_2]_n$.

	Found (%)			Required (%)		
R	C	H	N	C	H	N
Me	16.6	2.0	9.6	16.5	2.1	9.0
i-Pr	27.5	4.0	8.0	27.7	4.0	8.1
$PhCH_2$	43.5	3.0	6.2	43.3	3.15	6.3

plexes of this type were prepared by the methods described previously,[3] using triethyl orthoformate as dehydrating agent, (see Table I).

1,2,4-Trichlorotris(perdeuteroacetonitrile)rhodium(III), 1,2,4-$[RhCl_3(C^2H_3CN)_3]$. A solution of 1,2,4-$[RhCl_3(CH_3CN)_3]$in perdeuteroacetonitrile was boiled for 1 h. Concentration of this solution (25°/1mm) resulted in the formation of large orange crystals of the product. The n.m.r. spectrum in perdeuteroacetonitrile solution showed no resonance at *ca.* 7.4τ due to coordinated acetonitrile and the electronic spectrum had λ_{max} 432 nm.

1,2,4-Tribromotris(acetonitrile)rhodium(III), monohydrate, 1,2,4-$[RhBr_3(CH_3CN)_3]$ $1H_2O$. Hydrated rhodium tribromide (0.5 g) was dissolved in a mixtures of acetonitrile (50 ml) and triethylorthoformate (5 ml) and allowed to stir overnight. The solution was filtered and cautious addition of sodium-dried diethyl ether to the filtrate gave the product as orange-red crystals. (Found: C, 15.0; H, 2.55; N, 8.7. $C_6H_{11}Br_3N_3ORh$ requires C, 14.9; H, 2.3; N, 8.7%).

2. *Preparation of Complexes of the type* $[RhCl_3(RCN)_2]_n$, (R = Me, *i*-Pr, $PhCH_2$). An acetone solution of 1,2,4-$[RhCl_3(RCN)_3]$ (R = Me or *i*-Pr) set to reflux for 1 h. gave a pink precipitate of the product, which was filtered off, washed with ether and air-dried. $[RhCl_3(PhCH_2CN)_2]_n$ was prepared by refluxing a toluene solution of 1,2,4-$[RhCl_3(PhCH_2CN)_3]$ for 1 h. The analytical results obtained for these products are in Table III. Addition of the appropriate nitrile to these polymeric complexes, followed by boiling for 1 h., resulted in the reformation of 1,2,4-$[RhCl_3(RCN)_3]$.

3. *Preparation of Complexes of the type* trans-$[RhX_2(RCN)_4]Y$, (X = Cl or Br; Y = NO_3 or ClO_4; R = Me, Et, *n*-Pr, Ph, $PhCH_2$).

trans-*Dichlorotetrakis(acetonitrile)rhodium(III)perchlorate, trans-*$[RhCl_2(MeCN)_4]ClO_4$. An acetonitrile solution (10 ml) containing 1,2,4-$[RhCl_3(MeCN)_3]$ (200 mg) and silver perchlorate (125 mg) was refluxed for 1/2 h. during which time the colour changed from orange to yellow and a pale yellow precipitate formed. The precipitate was removed and repeatedly extracted with hot acetonitrile. These extracts were combined with the original filtrate and concentration produced pale yellow crystals of the product.

Trans-$[RhCl_2(MeCN)_4]NO_3$ was prepared by using silver nitrate instead of silver perchlorate. The dibromo-complex, *trans*-$[RhBr_2(CH_3CN)_4]ClO_4$, was prepared similarly starting from 1,2,4-$[RhBr_3(CH_3CN)_3]$ and silver perchlorate.

Trans-$[RhCl_2(RCN)_4]ClO_4$, (R = Et, *n*-Pr, Ph, $PhCH_2$). These complexes are best prepared by heating a slurry of *trans*-$[RhCl_2(MeCN)_4]ClO_4$ in the appropriate nitrile to 100° for 1/2 h. Cautious addition of diethyl ether to this solution produced crystals of the desired product. The analytical and spectroscopic data are given in Table II.

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