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Chloronitrile Complexes of Ru(III) and Ru(IV) and their Reactivity towards several Ligands

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Two new series of anionic organonitrile compounds are described. Complexes of type I: tetraethylammonium pentachloro(nitrile)ruthenate(IV) {$(NEt_4)[RuCl_5(RCN)]$; R = Me, Ph} were prepared by the reaction of commercial '$RuCl_3 \cdot 3H_2O$' with the appropriate nitrile in the presence of NEt_4Cl. Complexes of type II: tetraethylammonium tetrachlorobis(nitrile)ruthenate(III) {$(NEt_4)[RuCl_4(RCN)_2]$; R = Me, Ph, o*-MePh,* m*-MePh, $CH_2{:}CH$, $CH_2{:}CH \cdot CH_2$} were prepared by the reaction of '$RuCl_3 \cdot 3H_2O$' with excess of appropriate nitrile in methanol, in the presence of a stoichiometric amount of NEt_4Cl (1/1). These complexes were also obtained when starting with a new ruthenium anionic complex $[Ru_2Cl_7(OH)_3]^{2-}$ in the appropriate nitrile.*

The exceedingly labile nitriles of the complexes of type I have been substituted by N,N-dimethylformamide (DMF). Reactions of the complexes of type II with pyridine (Py) and diphenylmethylphosphine (PPh_2Me) produce the compounds $(NEt_4)[RuCl_4Py_2]$ (IIG) and $RuCl_2(RCN)_2(PPh_2Me)_2$, R = o*-MePh (IVA), respectively.*

Introduction

The chemistry of metal–nitrile complexes was reviewed by Walton in 1965 [1], and since that time there has been considerable interest in such complexes. That organonitriles are of interest as ligands is not surprising in view of the facts that the R–C≡N: group is isoelectronic with molecular nitrogen and that organonitrile complexes can serve as convenient precursors for a wide variety of coordination compounds.

We have recently observed [2] that reaction between commercial '$RuCl_3 \cdot 3H_2O$' and certain organonitriles RCN (R = Me, Ph, *o*-MePh, $CH_2{:}CH \cdot CH_2$, *etc.*) results in different types of complexes according to the nature of the organonitrile ligand and of the solvent used in the reaction. Starting with the neutral complexes $Ru_2OCl_6(RCN)_4$, or *mer*-$RuCl_3(RCN)_3$, R = *m*-MePh, we have now observed the substitution of nitrile by chloride:

$$Ru_2OCl_6(RCN)_4 + 4\,NEt_4Cl \xrightarrow{CH_2Cl_2} (NEt_4)[Ru^{IV}Cl_5(RCN)] + \ldots \qquad (1)$$

$$RuCl_3(RCN)_3 + NEt_4Cl \xrightarrow{CH_2Cl_2} (NEt_4)[Ru^{III}Cl_4(RCN)_2] + RCN \qquad (2)$$

However, the yields of anionic complexes in reactions (1) and (2) were not high; the same compounds were obtained with much better yields, starting with commercial '$RuCl_3 \cdot 3H_2O$' and a new anionic chlorocomplex of ruthenium.

We describe here the preparation and some reactions of these organonitrile complexes, $[RuCl_5(RCN)]^-$ and $[RuCl_4(RCN)_2]^-$ and of the new dimeric chlorospecies $[Ru_2Cl_7(OH)_3]^{2-}$.

Experimental

Instrumental

Analytical data for all compounds discussed are given in Table I. The infrared spectra were obtained with a Polytec FIR 30 interferometer for the 50–400 cm^{-1} range and with a Beckman IR 12 spectrophotometer for the 400–4000 cm^{-1} range. The complexes were respectively sampled as polyethylene and KBr pellets. The Raman spectra were recorded (on a PHi Coderg) using the rotating disc technique [3].

UV–visible spectra were obtained with a Beckman ACTA III spectrophotometer with optional reflectance sphere, as CH_2Cl_2 or MeOH solutions and solid sample.

Magnetic susceptibility measurements were performed with a Faraday Magnetic balance, and electrical conductivity with a Perkin RC 18 conductimeter.

TABLE I. Analytical Data[a] and Physical Properties of the Complexes.

Compound		C		H		N		Colour	MP °C	μ_{eff} BM	Λ_M Ω^{-1} [c] mol^{-1} cm^{-2}
		Fd	(Calc)	Fd	(Calc)	Fd	(Calc)				
IA	$(NEt_4)[RuCl_5(MeCN)]$	26.8	(26.71)	5.3	(5.12)	6.6	(6.23)	red-brown	178–180[e]	–	–
IB	$(NEt_4)[RuCl_5(PhCN)]$	35.0	(35.20)	4.8	(4.89)	6.0	(5.48)	red-brown	65–67 [e]	2.3	–
IC	$(NEt_4)[RuCl_5(DMF)]$	25.8	(26.45)	5.9	(5.85)	5.9	(5.61)	brown	160–162[e]	–	–
IIA	$(NEt_4)[RuCl_4(MeCN)_2]$	31.4	(31.64)	5.8	(5.71)	9.5	(9.23)	yellow	220–225[e]	1.7	66
IIB	$(NEt_4)[RuCl_4(PhCN)_2] \cdot 0.5H_2O$[b]	44.7	(44.88)	5.4	(5.27)	7.3	(7.14)	yellow	190–195[e]	1.9	65
IIC	$(NEt_4)[RuCl_4(o\text{-}MePhCN)_2]$	47.7	(47.43)	5.9	(5.60)	6.8	(6.91)	yellow	200–210[e]	1.9	88
IID	$(NEt_4)[RuCl_4(m\text{-}MePhCN)_2] \cdot H_2O$[b]	46.2	(46.70)	5.8	(5.84)	7.2	(6.83)	orange	210–215[e]	–	97
IIE	$(NEt_4)[RuCl_4(CH_2{:}CH \cdot CN)_2]$	35.1	(35.07)	5.3	(5.43)	8.8	(8.76)	orange	150–155[e]	1.9	71
IIF	$(NEt_4)[RuCl_4(CH_2{:}CH \cdot CH_2 \cdot CN)_2]$	38.2	(37.86)	6.0	(5.91)	8.4	(8.28)	orange	160–165[e]	1.7	68
IIG	$(NEt_4)[RuCl_4Py_2]$	40.3	(40.67)	5.7	(5.65)	8.3	(7.91)	yellow	270–275[e]	–	–
IIIA	'$(NEt_4)_2[Ru_2Cl_7(OH)_3]$'	24.4	(25.20)	5.6	(5.64)	3.7	(3.68)	brown	165–170[e]	0.0	142
IIIB	'$(AsPh_4)_2[Ru_2Cl_7(OH)_3]$'	45.5	(45.68)	3.4	(3.67)	19.6[d]	(19.57)	brown	160–165[e]	0.0	156
IVA	$RuCl_2(o\text{-}MePhCN)_2(PPh_2Me)_2$	62.1	(62.55)	5.1	(4.96)	3.6	(3.47)	yellow-green	169	0.0	–

[a] Microanalyses for C, H, N were performed by the Service Central de Microanalyses of CNRS. [b] For these compounds, the water of crystallization was detected in the infrared by the frequencies νOH at ~3480 cm^{-1} and δHOH at ~1620 cm^{-1}. [c] Molar conductivity measurements at 25 °C in ~10^{-3} M $MeNO_2$. [d] Chlorine analysis. [e] Decomposition point.

TABLE II. Selected Infrared (IR) and Raman (R) Spectral Data (cm^{-1}).

Compound	ν(CN)	Other bands[a]
IA	2250w, 2303m, 2316m	412w, 361sh, 331sh, *305s,l, 281s*
IB	2230w, 2273s	410w, 362sh, 330s,l, *313sh, 278sh*
IC	1623[b]	
IIA	2298m (IR)	*325vs,l,* 245s, 167s, 151sh
IIB	– 2274s (R)	387s, 332vs, *299vs,* 280sh, 148m
IIC	– 2266s (R)	400s, 333s, *290vs,l,* 148m
IID	–	402m, 338s, *297vs,* 288sh, 151m
IIE	2260m (IR), 2271s (R)	404m, 373w, 314s,l, *290sh,* 254sh, 155m
IIF	– 2311s (R)	395w,l, 348s, 318vs, *287vs,* 258s, 171m
IIG	–	*337vs, 312vs,* 280w, 265w, 236vs, 177m
IIIA	–	417w, 405w, 368sh, *339vs, 309vs, 287sh*
IIIB	–	403w, 362sh, 345vs, *304s, 282sh*
IVA	2218sh, 2236vs	406s,l, 354m, 340s, 325sh, *290s,* 251m

[a] vs = very strong; s = strong; m = medium; w = weak; sh = shoulder; l = large. ν(RuCl) bands are in italics. [b] vibration ν(CO) of DMF [free ν(CO) 1700 cm^{-1}].

Preparation of the Complexes

Complexes of type I: (NEt_4)[$RuCl_5(RCN)$]

A solution of '$RuCl_3 \cdot 3H_2O$' (300 mg) in the appropriate nitrile (20 ml) with NEt_4Cl (180 mg, ~1.2 mmol) was heated under reflux. After *ca.* 4 hr, the red solution was filtered and the compound precipitated by addition of a large excess of diethylether. It was filtered, washed with diethylether and dried *in vacuo* (yields 50–70%).

Complexes of type II: (NEt_4)[$RuCl_4(RCN)_2$]

These reactions were carried out by two different procedures.

a) A solution of '$RuCl_3 \cdot 3H_2O$' (300 mg) in a mixture of 20 ml methanol and 10 ml of appropriate nitrile, with a stoichiometric amount of NEt_4Cl (180 mg, ~1.2 mmol) was heated under reflux, until a yellow solution was obtained. Addition of diethylether (~20 ml) precipitates the product, which was recrystallized from a dichloromethane–diethylether solution (yields 60–75%).

b) Complex IIIA (300 mg, ~0.4 mmol) dissolved in 20 ml of the appropriate nitrile, was stirred and heated under reflux, until the solution became clear and a yellow product precipitated. The solid was filtered, washed with diethylether and dried *in vacuo* (yields 60–75%).

Complex IIIA

All steps of this preparation were carried out in air. A solution of '$RuCl_3 \cdot 3H_2O$' (1 g) in HCl 12 N (40 ml) is heated to 90 °C for 10 hr. The solution is allowed to cool; ~1 g of NEt_4Cl in 20 ml H_2O is added, together with a few drops of mercury and shaken, at ambient temperature, until a blue-green solution is obtained. The solution is filtered to eliminate the mercury salt and heated to reduce the volume of the solvent by one half: the solution becomes red. This solution, when cooled, deposits brown-red micro-crystals. The compound is filtered and dried under vacuum (1 g, yield 65%). The compound is soluble in water and acetonitrile at ambient temperature, but it decomposes into undetermined products. However, this compound is very stable in solution in nitromethane.

Results and Discussion

Complexes of Ru(IV)

The preparation of complexes of type I: tetraethylammonium pentachloro(nitrile) ruthenate(IV) {(NEt_4)[$RuCl_5(RCN)$]; R = Me, Ph} has resulted from the reaction of '$RuCl_3 \cdot 3H_2O$ in the presence of NEt_4Cl (1/1), with the appropriate nitrile. The nitrile in these complexes is extremely labile, and by recrystallization of these compounds in a DMF–diethylether mixture the nitrile ligand is substituted by DMF.

The infrared spectra of the organonitrile complexes (see Table II) show a strong band, at 2316 cm^{-1} for R = Me and at 2273 cm^{-1} for R = Ph, confirming the presence of the coordinated nitrile and indicating bonding through the nitrogen lone pair [1]. For the two complexes, in the KBr pellets but not in nujol mulls, we observe bands of weak intensity corresponding to the free ligand. This seems to confirm the extreme lability of nitrile, which is displaced in the solid state by Br^-. For the aceto-

TABLE III. Electronic Spectra[a] and Reflectance Data (nm).

Compound	Solvent	Electronic Spectra	Reflectance[b,d]
IA	CH_2Cl_2	252, 304sh, 380–408(7700), 486(3500), 742(70)	258, 292, *380–405 l*, 495sh, 575sh, 733
IB	CH_2Cl_2	246, 304sh, 378–412(5200), 480(3100), 738sh(70)	257, 300, *375–430 l*, 500sh, 570sh, 730
IC	CH_2Cl_2	391–425(max.), 487	255, 297, *380–430 l*, 490sh, 575sh, 725
IIA	MeOH	242, 294, 381(4300), 391(4400), 451(630)	255, 301, *391*, *406*, 465, 575sh
IIB	MeOH	283, 289, 298, 397(4290), 409(4400), 478(570)	260, 290sh, 310, *407*, *423*, 493, 582sh
IIC	MeOH	282, 290, 298, 397(4250), 409(4500), 477(640)	260, 290sh, 317, *412*, *427*, 493 575sh
IID	MeOH	282, 289, 299, 396(4450), 409(4680), 476(650)	265, 291sh, 305, *405*, *420*, 482 575sh
IIE	MeOH	251, 295, 398(5100), 410(5400), 479(660)	257, 305, *405*, *420*, 485, 580sh
IIF	MeOH	244, 300, 390(4500), 404(4730), 470(600)	255, 305, *400*, *415*, 481, 580sh
IIG	c	–	252, 290sh, 318, *366*, *382*, 433, 485sh
IIIA	$MeNO_2$	398(4430), 443(6000)	255, 290, 355sh, *395–435 l*, 505sh, 580sh
IIIB	$MeNO_2$	405(5800), 442(6500), 494(3300)	262, 295, *395–450 l*, 500sh, 575sh
IVA	CH_2Cl_2	337(15100), 391(12300)	260, 270sh, *338*, *402*, 577sh

[a] Molar extinction coefficients in parentheses. [b] Maximum intensity peaks between 300 and 500 nm are in italics. [c] Compound too slightly soluble. [d] l = large; sh = shoulder.

nitrile complex, a combination $\delta(CH_3) + \nu(CC)$ appears at 2303 cm^{-1} [1, 4]. Bands at ~300 cm^{-1}, assignable to ruthenium–chloride [ν(RuCl)] and ruthenium–nitrogen [ν(RuN)] stretching modes, were also observed.

The electronic spectra in the visible present a rather large absorption between 380 and 420 nm ($\epsilon \sim 7000$), and another at ~480 nm ($\epsilon \sim 3000$), apparently due to charge transfers. For the organonitrile complexes we also observe an absorption at ~740 nm ($\epsilon \sim 70$) (Table III).

Complexes of Ru(III)

The reaction of commercial '$RuCl_3 \cdot 3H_2O$' with excess organonitrile, in the presence of NEt_4Cl (1/1) *in methanol*, leads to complexes of type II: tetraethylammonium tetrachlorobis(nitrile)ruthenate(III) {$(NEt_4)[RuCl_4(RCN)_2]$; R = Me, Ph, *o*-MePh, *m*-MePh, $CH_2{:}CH$, $CH_2{:}CH{\cdot}CH_2$}.

These complexes, yellow or orange, are very stable in the solid state and in solution in dichloromethane, but are transformed in methanol. This transformation followed by UV–visible (Fig. 1) can be described:

$$(NEt_4)[Ru^{III}Cl_4(RCN)_2] \xrightarrow[\text{2 days}]{\text{MeOH}}$$

$$Ru^{III}Cl_3(RCN)_2MeOH \xrightarrow[\text{2 days}]{\text{MeOH}}$$

$$[Ru^{III}Cl_2(RCN)_2(MeOH)_2]\,Cl$$

The UV–visible spectra are identical to those found in the literature for $RuCl_3(RCN)_2MeOH$, R = *o*-MePh [2] and the species $RuCl_2^+$ [5, 6] in methanol and perchloric acid respectively.

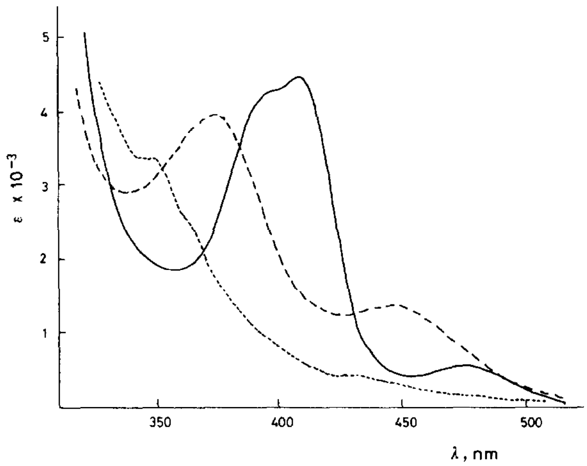

Fig. 1. Electronic spectra in MeOH of $RuCl_4(RCN)_2^-$ [——] ; after 2 days $RuCl_3(RCN)_2MeOH$ [– – –] ; after 4 days the species $RuCl_2^+$ [------].

These anionic complexes of type II react with pyridine (Py) and diphenylmethylphosphine (PPh_2Me). $(NEt_4)[RuCl_4Py_2]$, formed in hot pyridine, resulted from substitution of the two RCN by Py.

The reaction with PPh_2Me in excess in warm methanol leads essentially to a complex of Ru(II), $RuCl_2(RCN)_2(PPh_2Me)_2$, resulting this time from the substitution of two chlorides by PPh_2Me.

The compounds $(NEt_4)[RuCl_4Py_2]$ [7] and $RuCl_2(RCN)_2(PPh_2Me)_2$ (R = *o*-MePh) [1] have been isolated and characterized.

Anionic complexes of type II have magnetic moments at room temperature corresponding to ruthenium(III) spin-paired complexes, and conductivity measurements in nitromethane which are in close agreement with the values expected for a univalent electrolyte in this solvent [8].

The infrared spectra were recorded in the 4000–400 cm^{-1} range, but not all bands were assigned. One finds frequencies corresponding to vibrations characteristic of the cation NEt_4^+ and of the nitrile ligand. A *trans*-$[RuCl_4(RCN)_2]^-$ anion would be expected to have one infrared active ν(CN) stretching vibration (A_2). In fact, this ν(CN) vibration is weak (R = Me, and CH_2 = CH) or, in most cases, completely absent (Table II). The absence of a C–N stretching mode is therefore surprising, as the strong C–N stretching of free nitriles is known to increase in intensity on coordination [1]. However, it was already observed for other complexes such as Re-$(PPh_3)_2(MeCN)Cl_3$ [9], $[Pt(L)_2(NCR)(Me)]^+$, L = PPh_2Me [10], and $[Fe(p\text{-}MePhNC)(MeCN)]^{2+}$ [11], that the C–N stretching does not appear. On the contrary, Raman spectrum shows a very intense ν(CN) vibration; the shift of the C–N stretching to higher frequencies indicates that the nitriles are coordinated through the nitrogen lone pair.

For the compounds with acrylonitrile and allylcyanide, one observes only a weak displacement of the ν(CC) vibration, which indicates that there exists no interaction between the double bond C=C and the ruthenium. Bands at ~300 cm^{-1} assignable to ruthenium–chloride [ν(RuCl)] and ruthenium–nitrogen [ν(RuN)] stretching modes were observed. For the acetonitrile, acrylonitrile, and allylcyanide complexes, there appears one additional band at ~250 cm^{-1} assigned to a vibration δ(N–Ru–N) and which has been observed previously only for *trans*-nitrile complexes [12]. This observation suggests a *trans*-nitrile configuration and therefore the point group D_{4h} for these complexes. The intense band at ~300 cm^{-1} splits into two components in certain cases, which seems to indicate a decrease in symmetry due to a slight deformation of the octahedral.

The electronic spectra in the range 800–240 nm are very characteristic for the complexes of type II. The major bands observed in the visible region of the electronic spectra of these anionic complexes are probably of charge-transfer origin. Also, the two absorptions at ~400 and 410 nm ($\epsilon \sim 4300$) may be attributed to metal ← chlorine charge transfers; that observed at ~480 nm ($\epsilon \sim 600$) to a metal ← nitrile charge tranfer. These conclusions would be in accord with results obtained for other complexes of the same type: *trans*-$[RuCl_4L_2]^-$ (L = $AsPh_3$, PPh_3) [13].

While some d–d bands are probably present, it can be concluded that the intensities of the visible peaks are dominated by the charge-transfer bands.

Anionic Chlorocomplex of Ruthenium

Starting with commercial '$RuCl_3 \cdot 3H_2O$' we have prepared a new anionic chlorocomplex of ruthenium. It is less hygroscopic than '$RuCl_3 \cdot 3H_2O$' and this allows its easier manipulation. The ionic nature of this complex has been verified by a molar conductivity measurement in nitromethane; the obtained value (Table I) is compatible with that expected for a 2:1 electrolyte in this solvent [14]. The diamagnetism of this compound suggests a di- or polynuclear structure [15].

In the infrared spectrum (4000–400 cm^{-1}) one finds the frequencies corresponding to vibrations characteristic of the tetraethylammonium cation at 790, 1001, 1072, 1390, 1484 and 2980 cm^{-1}. The weak band at ~3450 cm^{-1} was assigned to the vibration νOH. Furthermore, we observe a weak absorption at ~900 cm^{-1}. The far infrared spectrum (400–50 cm^{-1}) presents four bands at ~300 cm^{-1}, assigned to the vibrations ν(RuCl) (Table II).

In the UV–visible spectra, we observe two absorptions: one at ~400 nm ($\epsilon \sim 4500$), the other at 440 nm ($\epsilon \sim 6000$); this spectrum is analogous to that of the species $(Ru_2OCl_{10})^{4-}$ studied by Clark *et al.* [16].

We have attributed a formula to the compound IIIA, based solely on these microanalyses (Table I) and by substitution of the cation NEt_4^+ by $AsPh_4^+$. This species may be written '$(NEt_4)_2[Ru_2Cl_7(OH)_3]$', but whether the species is oxo- or hydrobridged cannot be concluded. However, this complex can serve as starting material in synthetic ruthenium chemistry.

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