

RUTHENIUM(II) ISOCYANIDE COMPLEXES CONTAINING TIN OR MERCURY

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SUMMARY

The complex $trans\text{-RuCl}_2(\text{CNET})_4$ has been reinvestigated, and the new complexes $trans\text{-Ru}(\text{SnCl}_3)_2(\text{CNET})_4$ and $\text{RuCl}_2(\text{CNET})_4 \cdot \text{HgCl}_2$ have been characterised. The structures proposed for these compounds are based mainly on their vibrational (IR and Raman) spectra.

INTRODUCTION

The compounds $\text{RuX}_2(\text{CNR})_4$ ($\text{X} = \text{Cl, Br, I, CN}$; $\text{R} = \text{alkyl or aryl group}$)¹⁻³ have been known for some years, but since their original preparation and characterisation they have not been studied. I now report a reinvestigation of the compound $\text{RuCl}_2(\text{CNET})_4$, and in particular its reactions with stannous and mercuric chlorides.

Malatesta and co-workers reported¹ that $\text{RuCl}_2(\text{CNET})_4$ exists in two forms, one yellow and the other blue, and it was suggested that these are *cis* and *trans* isomers. Vibrational spectra now reveal that the yellow form is the *trans* isomer. With stannous chloride, this compound forms a 1/2 adduct, herein formulated as $trans\text{-Ru}(\text{SnCl}_3)_2\text{-}(\text{CNET})_4$, and with mercuric chloride a 1/1 adduct, $\text{RuCl}_2(\text{CNET})_4 \cdot \text{HgCl}_2$.

RESULTS AND DISCUSSION

Selected IR and Raman data are given in Table 1, with suggested assignments for some of the frequencies. The results of the conductivity measurements are listed in Table 2.

All three compounds studied here show $\nu(\text{NC})$ absorptions in the region 2260–2164 cm^{-1} , *i.e.* at frequencies which are higher than that found in free ethyl isocyanide (2151 cm^{-1})⁴. In complexes of metals in normal oxidation states, it is thought that isocyanide ligands act as good σ -donors but rather weak π -acceptors⁵, and a rise in $\nu(\text{NC})$ on co-ordination is good evidence for this. However, in complexes of the cyanide ion, CN^- , it has been suggested that the rise in $\nu(\text{CN})$ which occurs on co-ordination is due in part to a decrease in C–N repulsion brought about by the loss of the lone pair on carbon^{6,7}. Perhaps a similar effect is involved in isocyanide complexes, thereby masking any reduction in the C–N bond order caused by π back-bonding.

TABLE 1
INFRARED AND RAMAN DATA (cm^{-1})^a

<i>trans</i> -RuCl ₂ (CNEt) ₄				<i>trans</i> -Ru(SnCl ₃) ₂ (CNEt) ₄			
IR		Raman		IR		Raman	
Mull ^b	CHCl ₃	Solid ^c	CHCl ₃	Mull ^b	CHCl ₃	Solid ^c	CHCl ₃
^e	^e	2219(10)	2235(10)pol	^e	^e	2241(2)	2240(1)pol
^e	^e	2168(7)	2194(9)dp	^e	^e	2214(1.5)	2210(0.5)dp
2164 vs	2180 vs	^e	^e	2200 vs	2189 vs	^e	^e
564 m				556 vs			
532 ms				526 ms			
311 s							
305 sh							
		279(1.5)		~ 325 vs (br)		342(7)	
						322(2)	
						168(10)	168(10)pol

^a v = very, s = strong, m = medium, w = weak, (sh) = shoulder, (br) = broad, pol = polarised dp = depolarised. Relative intensities of Raman lines are given in parentheses. ^b Nujol mull. ^c Crystals. ^d Crystals ex CH₂Cl₂ solution. ^e Not observed.

Moderately intense IR bands between 570 and 520 cm^{-1} have been assigned to the RuCN bending modes; this is the region in which $\delta(\text{CoCN})$ vibrations were assigned by Boorman *et al.* in some cobalt(I) and cobalt(II) isocyanide complexes⁸. No absorptions were observed in the Raman spectra in this region.

The vibrational spectra of yellow RuCl₂(CNEt)₄ in the $\nu(\text{NC})$ region clearly support a *trans* configuration for the molecule, with D_{4h} point group symmetry. Thus the number of bands observed, both in solution and in the solid state, are as predicted by simple point group theory, and the IR and Raman spectra are mutually exclusive in this region, indicating a centro-symmetric structure for the compound. Furthermore, Raman polarisation data enable the three $\nu(\text{NC})$ lines to be unequivocally assigned to the A_{1g} , B_{1g} and E_u symmetry species as given in Table 1. A strong IR absorption at 311 cm^{-1} in this compound is assigned to $\nu_{\text{asym}}(\text{ClRuCl})$; the corresponding symmetric vibration may give rise to the Raman line at 279 cm^{-1} .

The 1/2 adduct of *trans*-RuCl₂(CNEt)₄ with SnCl₂ has strong absorptions in its IR and Raman spectra in the range 345–320 cm^{-1} , which are characteristic of $\nu(\text{Sn}-\text{Cl})$ vibrations in the SnCl₃ group^{9,10}. In addition, the similarity of its spectra in the $\nu(\text{NC})$ region to those of *trans*-RuCl₂(CNEt)₄ suggests that it should be formulated as *trans*-Ru(SnCl₃)₂(CNEt)₄. The presence of the *trans*-SnRuSn moiety in this compound is supported by a Raman band at 168 cm^{-1} (which is polarised in CHCl₃ solution) of remarkably high intensity (it is the strongest band in the spectrum). This

RuCl ₂ (CNEt) ₄ ·HgCl ₂				Assignment
IR		Raman		
Solid ^d	CHCl ₃	Solid ^c	CHCl ₃	
2255 w	~2256 w	2258(7)	2160(10)pol	$\left. \begin{array}{l} A_{1g} \\ B_{1g} \\ E_u \\ A_1 \end{array} \right\} \nu(\text{NC})$
2204 vs	~2212 (sh)	2225(10)	2228(8)dp	
	2205 vs			
~2175 (sh)	2194 (sh)	2198 (sh)	~2185(5)(br)	
~565 (sh)	2177 (sh)	2170(6.5)		$\left. \begin{array}{l} \\ \\ \end{array} \right\} \delta(\text{RuCN})$
556 m (sh)				
542 vs				
		284(8)		$\left. \begin{array}{l} \\ \\ \end{array} \right\} \nu(\text{RuCl})$ $\left. \begin{array}{l} \\ \\ \end{array} \right\} \nu(\text{SnCl})$ $\left. \begin{array}{l} \\ \\ \end{array} \right\} ? \nu(\text{HgCl})$ $\left. \begin{array}{l} \\ \\ \end{array} \right\} \nu_{\text{sym}}(\text{SnRuSn})$

TABLE 2

CONDUCTIVITY DATA (NITROMETHANE SOLUTION; T = 298° K)

Compound	Concn. (10 ⁻³ M)	10 ⁶ κ (ohm ⁻¹ ·cm ⁻¹) (±0.5)
<i>trans</i> -RuCl ₂ (CNEt) ₄	1.01	1.0
<i>trans</i> -Ru(SnCl ₃) ₂ (CNEt) ₄	1.00	0.0
RuCl ₂ (CNEt) ₄ ·HgCl ₂	0.99	75.4

absorption is assigned to $\nu_{\text{sym}}(\text{SnRuSn})$: it is well known that metal-metal bonds give rise to very strong Raman lines¹¹.

Detailed structural conclusions about the adduct RuCl₂(CNEt)₄·HgCl₂ cannot be easily made on the basis of its vibrational spectra. However, both in the solid state and in solution, these are consistent with the four EtNC ligands being in a *cis* octahedral arrangement. Such a structure lacks a centre of symmetry, and all four $\nu(\text{NC})$ modes are both IR- and Raman-active, making unambiguous assignments of the observed frequencies impossible. Nevertheless, Raman polarisation measurements indicate that the highest frequency band (ca. 2260 cm⁻¹) is an A₁ mode.

If a *cis* octahedral configuration exists in this compound, then there are two reasonable possibilities for its structure in the solid state:

- (i). *cis*-RuCl(HgCl₃)(CNEt)₄ *i.e.* one containing an Ru-Cl bond and an HgCl₃ group bonded to ruthenium via a metal-metal bond, or

(ii). one in which an HgCl_2 group is linked to the $\text{Ru}(\text{CNet})_4$ fragment by two chlorine bridges.

Both structures have been put forward for analogous iron(II) adducts^{12,13}. Here, (ii) is preferred, because there is no intense Raman band in the range $80\text{--}200\text{ cm}^{-1}$ which would arise from the $\nu(\text{Ru}\text{--}\text{Hg})$ vibration in structure (i). However, in the absence of any crystallographic work, the postulated structure of $\text{RuCl}_2(\text{CNet})_4 \cdot \text{HgCl}_2$ in the solid state must be regarded with some doubt.

A 10^{-3} M solution of $\text{RuCl}_2(\text{CNet})_4 \cdot \text{HgCl}_2$ in nitromethane has a conductivity in the range expected¹⁴ for a 1/1 electrolyte (see Table 2) which suggests that dissociation takes place according to an equation such as



As noted above, vibrational spectra indicate that a *cis* configuration is preserved upon dissolution. Both *trans*- $\text{RuCl}_2(\text{CNet})_4$ and *trans*- $\text{Ru}(\text{SnCl}_3)_2(\text{CNet})_4$ are essentially non-electrolytes in nitromethane solution.

The formation and proposed structures of these adducts of *trans*- $\text{RuCl}_2(\text{CNet})_4$ closely parallel the corresponding iron(II) complexes^{12,13,15}. However, much more vigorous conditions are necessary to prepare the ruthenium compounds, and no evidence was found for the existence of *cis*- $\text{Ru}(\text{SnCl}_3)_2(\text{CNet})_4$. Furthermore, while *trans*- $\text{RuCl}_2(\text{CNet})_4$ appears to be stable indefinitely in solution, *trans*- $\text{FeCl}_2(\text{CNAr})_4$ ($\text{Ar} = p$ -methoxyphenyl) readily isomerises to the *cis* complex in chloroform¹². These differences in behaviour have led me to consider all the complexes of general formula *cis*- and *trans*- MA_2B_4 ($\text{M} = \text{Fe}$ or Ru ; $\text{A} = \text{Cl}$ or SnCl_3 ; $\text{B} = \text{CO}$ or isocyanide ligand) with a view to understanding the relative stabilities of the two isomers of each compound. Here the "more stable" compound is taken to be the one which will remain unchanged in solution, *i.e.* the one which does not isomerise. In Table 3 are listed the compounds involved, together with the "more stable" isomer.

The relative stability of the two isomers is governed mainly by steric and electronic effects. Models show that the *cis*- $\text{M}(\text{SnCl}_3)_2\text{B}_4$ compounds are all crowded, and on these grounds a *trans* structure would be favoured for them. Steric factors are not important for the *trans*- MA_2B_4 or *cis*- MCl_2B_4 compounds. In order to minimise competition for the π -electrons on M by CNR or CO, a *cis* configuration is preferred for all the compounds (assuming that both CNR and CO are better π -acceptors than

TABLE 3
RELATIVE STABILITIES OF ISOMERIC Fe^{II} AND Ru^{II} COMPLEXES

Compound	'More stable' isomer	Ref.
$\text{FeCl}_2(\text{CO})_4$	<i>cis</i> (probably)	16
$\text{FeCl}_2(\text{CNAr})_4^a$	<i>cis</i>	12
$\text{Fe}(\text{SnCl}_3)_2(\text{CO})_4$	<i>cis</i>	17
$\text{Fe}(\text{SnCl}_3)_2(\text{CNAr})_4^a$	<i>trans</i>	12
$\text{RuCl}_2(\text{CO})_4$	<i>cis</i>	18
$\text{RuCl}_2(\text{CNR})_4^a$	<i>trans</i>	This work
$\text{Ru}(\text{SnCl}_3)_2(\text{CO})_4$	<i>trans</i>	19
$\text{Ru}(\text{SnCl}_3)_2(\text{CNR})_4^a$	<i>trans</i>	This work

^a Ar = *p*-methoxyphenyl; R = ethyl.

SnCl_3). The fact that these compounds do not all adopt the *cis* structure (especially those with SnCl_3 groups) suggests that steric factors are important. However, the relatively mild conditions necessary to effect the isomerisations that occur indicate that the energy difference between any *cis-trans* pair must be small.

EXPERIMENTAL

Microanalyses were performed by Alfred Bernhardt, W. Germany. IR spectra were recorded on Perkin-Elmer 457 and RIIC FS-520 spectrometers, and Raman spectra on a Cary 81 instrument fitted with a Coherent Radiation krypton ion laser. Conductivities were measured using a Wayne Kerr Universal Bridge B 221.

Ethyl isocyanide was obtained from *N*-ethylformamide by the method of Casanova *et al.*⁴. The complex $\text{RuCl}_2(\text{CNet})_4$ was prepared as described by Malatesta and co-workers¹, needle-like crystals of the yellow form being readily obtained. (Found: C, 36.75; H, 5.3; Cl, 18.2; N, 14.35. $\text{C}_{12}\text{H}_{20}\text{Cl}_2\text{N}_4\text{Ru}$ calcd.: C, 36.7; H, 5.1; Cl, 18.1; N 14.3 %.) All attempts to obtain the blue isomer from the mother liquor failed, however.

trans-Bis(trichlorostannato)tetrakis(ethyl isocyanide)ruthenium(II)

$\text{RuCl}_2(\text{CNet})_4$ (150 mg; 0.38 mmole) and anhydrous SnCl_2 (720 mg; 3.80 mmoles) were refluxed under nitrogen in ethanol (ca. 50 ml) to give a colourless solution. After 0.5 h, this was cooled to room temperature, and the colourless crystals of *trans-Ru*(SnCl_3)₂(CNet)₄ which formed were filtered off, washed with ethanol and ether and pumped dry. Yield 200 mg (68 %). Recrystallisation was effected from chloroform by the addition of ether with cooling. (Found: C, 18.8; H, 2.7; Cl, 27.4; N, 7.4. $\text{C}_{12}\text{H}_{20}\text{Cl}_6\text{N}_4\text{RuSn}_2$ calcd.: C, 18.7; H, 2.6; Cl, 27.6; N, 7.3 %.)

trans-Dichlorotetrakis(ethyl isocyanide)ruthenium(II) adduct with mercuric chloride.

$\text{RuCl}_2(\text{CNet})_4$ (400 mg; 1.01 mmoles) and HgCl_2 (800 mg; 2.94 mmoles) were refluxed together under nitrogen in 20 ml 2-methoxyethanol for 10 min. The now very pale yellow solution was cooled to room temperature (when it was almost colourless) and filtered. Addition of ether to the filtrate gave colourless crystals of $\text{RuCl}_2(\text{CNet})_4 \cdot \text{HgCl}_2$; yield 485 mg (72 %). It was recrystallised from dichloromethane/ether. (Found: C, 21.9; H, 3.2; Cl, 21.6; N, 8.4. $\text{C}_{12}\text{H}_{20}\text{Cl}_4\text{HgN}_4\text{Ru}$ calcd.: C, 21.7; H, 3.0; Cl, 21.4; N, 8.4 %.)

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