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POLYNUCLEAR ISOCYANIDE COMPLEXES OF RHENIUM

P. ROMITI, M. FRENI and G. D'ALFONSO

Centro del C.N.R., Istituto di Chimica Generale e Inorganica, Via G. Venezian 21, 20133 Milano (Italy)

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Summary

The new polynuclear isocyanide iodo complexes $Re_3(CNC_6H_{11})_6I_6$, $Re_3(CNC_6H_{11})_3I_6$ and $Re_3(CNC_6H_{11})_3I_9$, and the new bromo complexes $Re(CNC_6H_{11})_4Br_2$ and $Re_2O_2(CNC_6H_{11})_4Br_4$ have been synthesized and characterized by analysis and by the infrared spectra and magnetic properties.

Introduction

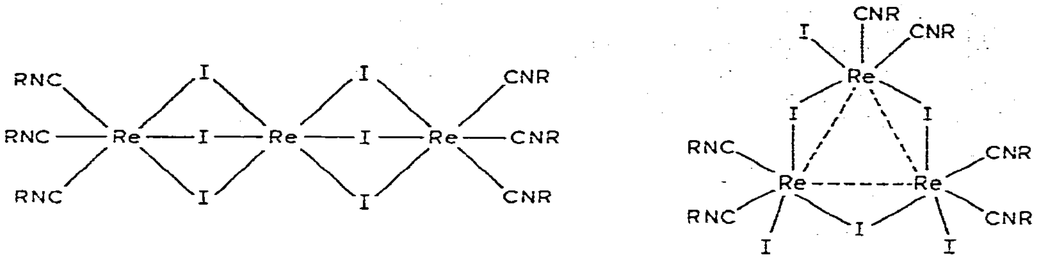
Many metal complexes containing organic isocyanides have been isolated, [1,2], but the only known compounds of rhenium are the *p*-tolyl isocyanide complexes, which are all mononuclear [3,4]. In this paper we describe new compounds, obtained by reaction of the halogenorhenium compounds ReX_6^{2-} and Re_3X_9 (X = I, Br) with cyclohexylisocyanide (CNR, $R = C_6H_{11}$), some of which are polynuclear.

Results and discussion

When potassium hexaiodorhenate(IV) is treated with an excess of cyclohexylisocyanide in ethanol at room temperature, a violet, crystalline non electrolyte, the paramagnetic compound I is formed. This is a derivative of rhenium(II), in accord with the magnetic susceptibility measurements (see Table 1).

The IR spectrum, in dichloromethane, shows two bands in the C—N stretching region, at 2220m and 2170(br) cm^{-1}. The relation of these values to those for isocyanide (2160 cm^{-1}) is in accord with the relatively low oxidation number of rhenium. The molecular weight agrees with that calculated for the trimer: $Re_3(CNR)_6I_6$ (I), possible structures for which are shown in Fig. 1.

These structures have iodine bridges between the rhenium atoms and both agree well with the IR spectrum and the magnetic susceptibility measurements. The rhenium atoms are hexacoordinated in structure a, but pentacoordinated (or heptacoordinated, if metal—metal bonds are present) in structure b, which



(Ia)

(Ib)

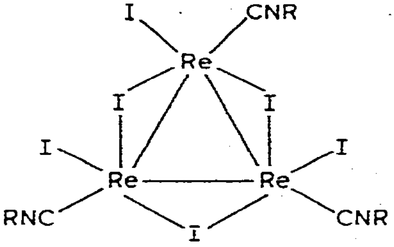
Fig. 1. Proposed structures of compound I.

contains three monomeric units $Re(CNR)_2I_2$ linked by iodine bridges.

In order to confirm or to rule out the trimeric structure for compound I, we treated Re_3I_9 with RNC in dichloromethane. Addition of ethanol gave a violet crystalline solid, which from its analysis and molecular weight corresponds to the trimer $Re_3(CNR)_3I_6$ (II), whose possible structure is shown in Fig. 2.

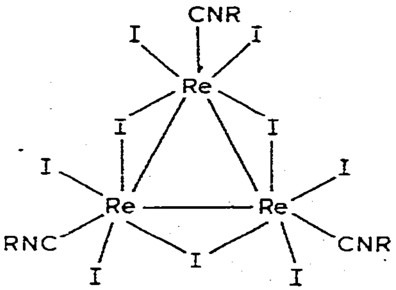
This structure contains metal—metal bonds and iodine bridges. Comparison of this complex with compound Ib excludes the presence of a metal—metal bond in Ib. The IR spectrum of compound II shows a strong band in the N—C stretching region, at 2195 cm^{-1}. The molar magnetic susceptibility of compound II (see Table 1) is consistent with that calculated for only one unpaired electron, delocalized over three rhenium atoms, while the three rhenium(II) atoms should, in the absence of any interaction between them, give the magnetic susceptibility corresponding with three unpaired electrons. The same reaction in ethanol yields an insoluble, violet, crystalline, diamagnetic compound with the stoichiometry $Re(CNR)I_3$ (III), corresponding to a known type [5].

In this case, however, we were also able to determine the molecular weight in chloroform, finding it to be trimeric. Its possible structure (Fig. 3) is similar to that of $Re_3(PEtPh_2)_3Cl_9$ [6], which is a triangular cluster of heptacoordinated rhenium atoms, with iodine atoms in bridging and terminal positions. The IR spectrum in nujol shows a strong band in the C—N stretching region at 2205 cm^{-1}. This value, compared with that of isocyanide (2160 cm^{-1}) and with those of rhenium(II) compounds previously described (2170 cm^{-1} (I), 2190



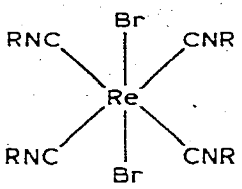
(II)

Fig. 2. Proposed structure of compound II.



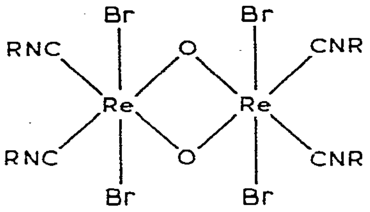
(III)

Fig. 3. Proposed structure of compound III.



(IV)

Fig. 4. Proposed structure of compound IV.



(V)

Fig. 5. Proposed structure of compound V.

cm^{-1} (II)) agrees with the higher oxidation number of the metal. The reaction of the bromo derivative (K_2ReBr_6) with cyclohexylisocyanide has been also investigated. Stirring hexabromorhenate(IV) with an excess of cyclohexylisocyanide at room temperature without a solvent gives only an orange, crystalline, paramagnetic compound of formula $Re(CNR)_4Br_2$ (IV), which is a non electrolyte.

The molecular weight determination agrees with a monomeric structure (see Table 1). The IR spectrum in nujol shows a broad band in the C—N stretching region, at 2075 cm^{-1}, with two shoulders at 2120 and 2040 cm^{-1}, The most probable structure (shown in Fig. 4) has symmetry D_{4h}, in accordance both with the IR spectrum and the magnetic susceptibility value for the rhenium(II) atom.

When hexabromorhenate(IV) is treated with cyclohexylisocyanide in ethanol a yellow-orange compound is obtained, which is a mixture of compound IV and a new paramagnetic compound of formula $ReO(CNR)_2Br_2$ (V), which is a nonelectrolyte. The molecular weight is in accordance with a dimeric structure tentatively suggested in Fig. 5.

The IR spectrum shows a strong band at 2200 cm^{-1}, which can be assigned to C—N stretching, and another strong band at 800 cm^{-1} which can be assigned to Re—O—Re stretching.

TABLE 1

ANALYTICAL DATA AND MAGNETIC SUSCEPTIBILITIES OF COMPOUNDS I—V

Compound	Colour	M.p. (°C)	μ (BM)	Analysis (found (calcd.) (%))				Mol. wt. found (calcd.)
				C	H	N	O	
$Re_3(CNR)_6I_6$ (I)	violet	112	3.27	25.35 (25.50)	3.20 (3.34)	4.23 (4.25)		2002 (1974)
$Re_3(CNR)_3I_6$ (II)	violet	103	1.68	15.01 (15.35)	1.92 (2.01)	2.67 (2.58)		1540 (1647)
$Re_3(CNR)_3I_9$ (III)	violet	106	Diamagnetic	12.17 (12.40)	1.54 (1.63)	1.99 (2.07)		2350 (2028)
$Re(CNR)_4Br_2$ (IV)	orange	158	2.54	43.09 (43.00)	5.88 (5.60)	7.18 (7.15)		Insol. (782)
$Re_2O_2(CNR)_4Br_4$ (V)	yellow	141	2.56	30.36 (29.00)	4.08 (3.80)	4.98 (4.85)	2.73 (2.76)	1225 (1160)

The differences between the iodo and the bromo derivatives described are surprising, and we cannot offer any explanation for them.

Experimental

Molecular weights in chloroform were obtained with a Mechrolab model 301-A osmometer. IR spectra were recorded on a Beckman model IR 33 spectrometer. Magnetic susceptibilities were measured on a Gouy balance at room temperature.

Hexaiodohexakis(cyclohexyl isocyanide)trirhenium (I)

Potassium hexaiodorhenate (1 g) was dissolved in ethanol (20 ml), and cyclohexyl isocyanide (1 g) was added. After stirring for 1 h at room temperature, the violet crystals of $Re_3(CNR)_6I_6$ (I) were separated. The compound is soluble in acetone, dichloromethane, chloroform, and benzene, but insoluble in other common organic solvents.

Hexaiodotris(cyclohexyl isocyanide)trirhenium (II)

Rhenium triiodide (1 g) was suspended in dichloromethane (10 ml), and treated with cyclohexyl isocyanide (0.5 g) at room temperature for 24 h. After filtration, addition of ethanol (20 ml) gave violet crystals corresponding to $Re_3(CNR)_3I_6$ (II). The product is soluble in acetone, chloroform, dichloromethane and benzene, but insoluble in other common organic solvents.

Enneaiodotris(cyclohexyl isocyanide)trirhenium (III)

Rhenium triiodide (0.5 g) was dissolved in ethanol (25 ml) and cyclohexyl isocyanide (0.5 g) was added to the solution. After stirring for 3 h at room temperature, the violet crystals of $Re_3(CNR)_3I_9$ (III) were separated. The compound is soluble in acetone, chloroform, dichloromethane and benzene, but insoluble in other common organic solvents.

Dibromotetrakis(cyclohexyl isocyanide)rhenium (IV)

Potassium hexabromorhenate (0.5 g) was treated with cyclohexyl isocyanide (1.5 ml) at room temperature for 12 h. On addition of ethanol (20 ml) and water (20 ml) orange crystals of $Re(CNR)_4Br_2$ (IV) separated. The product is soluble in acetone, chloroform and dichloromethane; but insoluble in other common organic solvents.

Tetrabromo-μ-dioxotetrakis(cyclohexyl isocyanide)dirhenium (V)

Potassium hexabromorhenate (0.5 g) in ethanol (20 ml) was treated with cyclohexyl isocyanide (0.5 g) at room temperature for 24 h. After addition of 20 ml of water and further stirring for 24 h at room temperature, orange crystals of IV separated. After filtration, the mother liquor gave yellow crystals which corresponded to $Re_2O_2(CNR)_4Br_4$ (V). The product is soluble in acetone, chloroform and dichloromethane.

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