561. *Metal Carbonyl Compounds. Part II.** *Some Carbonyl Compounds of Ruthenium.*

By R. J. Irving.

Ruthenium carbonyl iodide has been shown to be a halogen-bridged polymer. The compound reacts with a number of ligands, namely, pyridine, dipyridyl, acetonitrile, aniline, *p*-toluidine, ammonia, and methyldiphenylarsine, to form stable octahedral complexes of Ru(II) of the type $RuL_2(CO)_2I_2$ (L = monodentate ligand), which are non-ionic and diamagnetic.

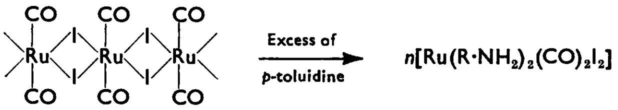
The ochre-red compound $Ru(CO)_2I_2$, first described by Manchot and König [1] in 1924, is the most stable and easily prepared carbonyl compound of ruthenium. It is insoluble in the common solvents, does not decompose below 250°, and is only slowly attacked by strong acid or alkali. By contrast, the corresponding iron compound is soluble in organic solvents and is decomposed by water. The structure of dicarbonyldi-iodoiron is unknown but the instability and other properties are consistent with the apparent co-ordination number of four.

Co-ordination number four is virtually unknown for ruthenium and this, together with the marked insolubility and inertness of the compound, suggests that ruthenium carbonyl iodide is a polymer. This insolubility precludes the common methods of molecular-weight determination. In an attempt to determine the molecular weight by the rate of evaporation at low pressures,[2] the vapour pressure at 130° was shown to be less than 10^{-6} mm. Hg, very much lower than expected for the monomer.

Polymer formation could involve either iodine or carbonyl bridges and, with two bridges between each pair of ruthenium atoms, the usual co-ordination number six for ruthenium would be attained.

Brimm and his co-workers [3] have shown that bridging carbonyl groups in iron enneacarbonyl have an absorption at 1828 cm.$^{-1}$ while the terminal carbonyl groups absorb in the region 2000—2100 cm.$^{-1}$. Dicarbonyldi-iodoruthenium(II) absorbs at 1995 and 2050 cm.$^{-1}$, and the monomeric compound $Ru(AsPh_2Me)_2(CO)_2I_2$, which certainly contains terminal carbonyl, absorbs at 1988 and 2042 cm.$^{-1}$. The most likely structure for the dicarbonyldi-iodoruthenium(II) polymer is (I).

(I)



$n[Ru(R{\cdot}NH_2)_2(CO)_2I_2]$ (II)

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* Part I, *J.*, 1956, 1860. The series title has been changed from " The Chemistry of the Transition Elements " there used.

[1] Manchot and König, *Ber.*, 1924, **57**, 2130.

[2] Bradley, Evans, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1946, *A*, **186**, 368.

[3] Brimm, Lynch, and Sesny, *J. Amer. Chem. Soc.*, 1954, **76**, 3831.

The carbonyl iodide was found to be diamagnetic and this supports the idea of a polynuclear structure with two bridges between each pair of ruthenium atoms.

Gleu and his co-workers[4] have examined a number of octahedral complexes of ruthenium and found the bivalent ones diamagnetic and the tervalent paramagnetic, as predicted by theory.

The monomeric form of the carbonyl iodide, if planar, should have one unpaired electron, and, if tetrahedral (sp^3 hybridisation), should have four unpaired electrons. Carbonyl compounds apparently always use inner orbitals for bonding, so the possibility of d^3s hybridisation with resulting diamagnetism * would have to be considered were it not for the weight of evidence in support of the octahedral di-iodo-bridge structure.

The action of amines such as *p*-toluidine on halogen-bridged compounds is known to result in rupture of the bridges giving mononuclear derivatives,[5] and compound (II) has been obtained by this reaction.

The usual method of rupturing halogen bridges is to allow the compound to react with the amine in a solvent such as benzene. Because of the insolubility of ruthenium carbonyl iodide it was convenient to use the ligand itself as solvent. Thus, the carbonyl iodide dissolved in hot aniline, and orange crystals of $Ru(NH_2Ph)_2(CO)_2I_2$ separated on cooling.

The pyridine compound appears analogous to $Fe\ py_2(CO)_2I_2$, described by Hieber and Bader.[6] There is one important difference in properties. The ruthenium compound is stable in the presence of a large excess of pyridine, while the iron compound rapidly forms $[Fe\ py_4]I_2$. This suggests that the iron is four co-ordinate, *i.e.*, indicates a structure $[Fe(CO)_2py_2]I_2$.

The derivatives of ruthenium carbonyl iodide are stable in light and air and do not decompose below 200°. On stronger heating, iodine is liberated and decomposition to ruthenium dioxide is complete at 500°. Sodium hydroxide solution causes slow decomposition, ultimately with the quantitative formation of sodium iodide and hydrated ruthenium oxide. Nitric acid and hot concentrated sulphuric acid liberate iodine or form iodic acid.

With the exception of the ammonia derivative the compounds are insoluble in water. In aqueous solution the ammonia derivative is hydrolysed slowly at room temperature and rapidly on heating, especially in the presence of acid.

All the derivatives are non-electrolytes in nitrobenzene solution. Conductivities were determined in M/2000-solution because of the sparing solubilities. Values for the molar conductivities varied from 0·23 mho in the case of the tertiary arsine derivative to 4·3 mho for the acetonitrile compound. The conductivity of the former in M/1000-solution was 0·22 mho.

The conductivity of an M/1000-aqueous solution of the amine increased over a period of several months reaching a maximum value of 207 mhos, consistently with the existence of three ions in solution, and in this aged solution all the iodine could be precipitated with silver nitrate. Attempts to isolate the hydrolysis product were unsuccessful.

The tertiary arsine compound $Ru(AsPh_2Me)_2(CO)_2I_2$ is the only one soluble to any extent in organic solvents and a cryoscopic determination of its molecular weight in benzene showed it to be mononuclear.

The derivatives of ruthenium carbonyl iodide reported in this paper are all diamagnetic.

Five geometrical isomers are possible for octahedral complexes of the type $Ma_2b_2c_2$. This type of compound is rare and, owing to the difficulty of assigning a structure to a non-ionic octahedral complex, the configuration of no $Ma_2b_2c_2$ compound is known with any degree of reliability. In spite of preparations under differing conditions, only one isomer for each of the compounds described has been observed. Both the pyridine and the dipyridyl compound had a dipole moment of 8 D, suggesting that in the former the pyridine groups are *cis* to each other but not permitting assignment of the positions of the other groups.

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* The author thanks the referees for reminding him of this possibility.

[4] Gleu, Breuel, and Rehm, *Z. anorg. Chem.*, 1938, **235**, 201; Gleu and Cuntze, *ibid.*, 1938, **237**, 187; Gleu and Breuel, *ibid.*, p. 326.

[5] Chatt, *J.*, 1951, 652.

[6] Hieber and Bader, *Ber.*, 1930, **63**, 1405.

EXPERIMENTAL

Dicarbonyldi-iodoruthenium(II).—This was prepared by Manchot and König's method [1] (Found: I, 61·8; Ru, 24·7. Calc. for $C_2O_2I_2Ru$: I, 61·7; Ru, 24·7%). It is diamagnetic: $\chi_g = -0{\cdot}11 \times 10^{-6}$ at 25°.

*Di-(*p*-toluidine)dicarbonyldi-iodoruthenium*(II).—Ruthenium carbonyl iodide (0·4 g.) was fused at 100° with *p*-toluidine (5 g.) until a clear orange melt was obtained. Excess of *p*-toluidine was removed *in vacuo* at 100°. The *compound* was obtained as a yellow powder, sparingly soluble in benzene, acetone, and alcohol, and insoluble in water. It was also prepared by refluxing ruthenium carbonyl iodide for several days with a benzene solution of *p*-toluidine (Found: I, 41·4; Ru, 16·7. $C_{16}H_{18}O_2N_2I_2Ru$ requires I, 41·2; Ru, 16·6%).

Dipyridinedicarbonyldi-iodoruthenium(II).—Ruthenium carbonyl iodide dissolved readily in boiling pyridine to a deep red solution from which, after filtration and cooling, the *compound* crystallised as a fine orange powder. It was recrystallised from pyridine and washed with ether (Found: C, 25·9; H, 1·7; I, 44·2; Ru, 17·9. $C_{12}H_{10}O_2N_2I_2Ru$ requires C, 25·3; H, 1·8; I, 44·6; Ru, 17·9%).

Diamminedicarbonyldi-iodoruthenium(II).—Liquid ammonia (50 ml.) was added to ruthenium carbonyl iodide (0·5 g.) and after a few minutes' stirring the deep red solution was filtered through a pre-cooled sintered-glass funnel. The brown solid remaining after evaporation of the excess of ammonia was added to boiling water (100 ml.), and the orange solution filtered and cooled as rapidly as possible to minimise contamination with hydrolysis products. Orange crystals of the *diammine* separated (Found: C, 5·5; H 1·4; N, 6·3; Ru, 22·8. $C_2H_6O_2N_2I_2Ru$ requires C, 5·4; H, 1·4; N, 6·7; Ru, 22·8%).

Dianilinedicarbonyldi-iodoruthenium(II).—Ruthenium carbonyl iodide (1·0 g.) was added to freshly distilled aniline (10 ml.) at 100°. The dark red solution was filtered and cooled as rapidly as possible. Orange crystals of the *compound* separated and were washed with benzene (Found: C, 28·9; H, 2·1; N, 4·6; Ru, 17·0. $C_{14}H_{14}O_2N_2I_2Ru$ requires C, 28·1; H, 2·4; N, 4·7; Ru, 17·0%). If the aniline solution was heated for more than a few minutes it became black and the product which separated on cooling was contaminated with a paramagnetic impurity.

Diacetonitriledicarbonyldi-iodoruthenium(II).—A boiling saturated solution of ruthenium carbonyl iodide in acetonitrile was filtered and, on cooling, orange-red crystals of the *compound* separated: it was recrystallised from acetonitrile and washed with ether (Found: I, 51·9; Ru, 20·5. $C_6H_6O_2N_2I_2Ru$ requires I, 51·4; Ru, 20·6%). On exposure to air for several weeks the compound darkened and became paramagnetic.

Bis(methyldiphenylarsine)dicarbonyldi-iodoruthenium(II).—Ruthenium carbonyl iodide (0·3 g.) was heated on a water-bath with diphenylmethylarsine (5 ml.) until a clear orange solution was obtained. Excess of the arsine was removed at 180° *in vacuo*. The orange residue was recrystallised from benzene–light petroleum. The *compound* was obtained as orange-yellow crystals, m. p. 105° [Found: C, 37·6; H, 2·8; Ru, 11·2%; *M* (cryoscopic in 1·288% benzene solution), 920. $C_{28}H_{26}O_2As_2I_2Ru$ requires C, 37·4; H, 2·9; Ru, 11·3%; *M*, 900].

Di-2-pyridyldicarbonyldi-iodoruthenium(II).—Ruthenium carbonyl iodide and di-2-pyridyl (0·6 g. of each) were refluxed with benzene (500 ml.) for 24 hr. The yellow solution was filtered and evaporated until the *compound* separated as yellow crystals: it recrystallised from benzene (Found: C, 25·4; H, 1·47; Ru, 17·7. $C_{12}H_8O_2N_2I_2Ru$ requires C, 25·4; H, 1·42; Ru, 17·9%).

Dipole Moments.—The dielectric constants of benzene solutions of the dipyridyl and pyridine derivatives were determined on an apparatus kindly made available by Dr. W. R. Moore. No claim is made for great accuracy of the measurements made on 4×10^{-4}M-solution. At 20° the dielectric constant of benzene was determined as 2·282 and of both the pyridine and dipyridyl solutions as 2·286. The dipole moments calculated from these values following Jensen's procedure [7] were 8·0 ± 0·4 D for each of the two compounds.

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[7] Jensen, *Acta Chem. Scand.*, 1949, **3**, 479.