314. *Researches on Residual Affinity and Co-ordination. Part XXXIX. Complex Ruthenium Derivatives containing Nitric Oxide and Polypyridyls.*

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This communication records an application of polypyridyls to the study of co-ordinated ruthenium derivatives containing also a nitroso-group. Complex compounds containing 2 : 2′-dipyridyl, 2 : 6-di-2′-pyridylpyridine (2 : 2′ : 2″-tripyridyl) and 6 : 6′-di-2″-pyridyl-2 : 2′-dipyridyl (2 : 2′ : 2″ : 2‴-tetrapyridyl) have now been prepared.

With potassium nitrosoruthenium pentachloride, 2 : 2′-dipyridyl behaves as a chelate group and yields the internal metal complex $\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl_3}}\mathrm{dipy}\right]$ and the double salt $\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl}}\mathrm{2dipy}\right]\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl_5}}\right]$. An extrusion of nuclear chlorine is effected by the tridentate base 2 : 2′ : 2″-tripyridyl, resulting in the formation of two complex salts each with a univalent cation, $\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl_2}}\mathrm{tripy}\right]\mathrm{Cl},3\tfrac{1}{2}\mathrm{H_2O}$ and $\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl_2}}\mathrm{tripy}\right]_2\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl_5}}\right]$.

A further chlorine atom is extruded when the quadridentate tetramine 2 : 2′ : 2″ : 2‴-tetrapyridyl is introduced into the molecule of potassium nitrosoruthenium pentachloride, so that the two salts thus produced each contain a bivalent cation, $\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl}}\mathrm{tetrpy}\right]\mathrm{Cl_2,5H_2O}$ and $\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl}}\mathrm{tetrpy}\right]\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl_5}}\right]$.

In acid solution the foregoing three polypyridyls furnish the corresponding nitrosoruthenium pentachlorides, $(\mathrm{dipy\,H})_2\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl_5}}\right]\mathrm{,H_2O}$, $\mathrm{trpy\,H_2}\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl_5}}\right]$ and $\mathrm{tetrpy\,H_2}\left[\mathrm{Ru}^{\mathrm{NO}}_{\mathrm{Cl_5}}\right]$.

THE complex nitroso-compounds of ruthenium include several of the longest known and most stable derivatives of this element. Potassium nitrosoruthenium pentachloride, $K_2[ONRuCl_5]$, was first obtained by Claus (*Annalen*, 1845, **56**, 257; 1846, **59**, 234), who, however, did not recognise the presence of nitric oxide in the molecule. Later, Joly (*Compt. rend.*, 1888, **107**, 994; 1889, **108**, 946) gave the correct composition of this salt and subsequently (*ibid.*, 1890, **111**, 970) prepared a group of ammine derivatives which were represented as $\left[{}^{\mathrm{ON}}_{\mathrm{HO}}\mathrm{Ru4NH_3}\right]X_2$, $\left[{}^{\mathrm{ON}}_{\mathrm{X}}\mathrm{Ru4NH_3}\right]X_2$ and $\left[{}^{\mathrm{H_2O}}_{\mathrm{ON}}\mathrm{Ru4NH_3}\right]X_3$ by Werner (*Ber.*, 1907, **40**, 2616). The corresponding ethylenediamine salts (Werner and Smirnoff, *Helv. Chim. Acta*, 1920, **3**, 737) and some pyridine derivatives (Charonnat, *Compt. rend.*, 1924, **178**, 1423; 1930, **191**, 1453; *Ann. Chim.*, 1931, **16**, 123) have also been prepared. More recently, the polypyridyls have become available in the study of co-ordination compounds, and their application to the ruthenium series is described below.

1. 2 : 2′-*Dipyridyl Compounds.*—Following on a preliminary reference (Presidential Address, J., 1935, 569), it has been found that 2 : 2′-dipyridyl (dipy) and potassium nitrosoruthenium pentachloride in equimolecular proportion yield two products depending on experimental conditions. With gentle warming, sage-green crystals of the *complex* (I; X = Cl) are formed, whereas from boiling solutions an orange-brown *salt* (II) is deposited. The former compound is slightly soluble in acetone, from which it separates in dark brown needles. This colour change suggests the existence of *cis*- and *trans*-isomerism, which is to be anticipated since six-co-ordinated ruthenium salts are usually octahedral in structure (J., 1936, 173). With a larger proportion of the diamine to potassium nitrosoruthenium pentachloride, a deep yellow-brown solution is obtained which does not yield a crystalline chloride, but the further addition of this potassium salt gives the complex orange-brown derivative (II).

With 2 : 2′-dipyridyl, potassium nitrosoruthenium pentabromide and the corresponding iodide yield respectively brown complexes having the empirical formulæ (I; X = Br) and (I; X = I). In acid solution, 2 : 2′-dipyridyl and potassium nitrosoruthenium pentachloride give deep reddish-purple crystals of the *salt* (III).

$[\mathrm{ONRuX_3\,dipy}]$ (I; X = Cl, Br or I.)

$[\mathrm{ONRuCl\,2dipy}][\mathrm{ONRuCl_5}]$ (II.)

$(\mathrm{dipy\,H})_2[\mathrm{ONRuCl_5}]\mathrm{,H_2O}$ (III.)

2. 2 : 2′ : 2″-*Tripyridyl Compounds.*—In an aqueous medium potassium nitrosoruthenium pentachloride and 2 : 2′ : 2″-tripyridyl (tripy) give a mixture of the brown insoluble salt (IV) and the soluble *chloride* (V). In acid solution, however, lilac crystals of the sparingly soluble nitrosoruthenium pentachloride (VI) are obtained.

$[\mathrm{ONRuCl_2\,tripy}]_2[\mathrm{ONRuCl_5}]$ (IV.)

$[\mathrm{ONRuCl_2\,tripy}]\mathrm{Cl,3\tfrac{1}{2}H_2O}$ (V.)

$\mathrm{tripy\,H_2}[\mathrm{ONRuCl_5}]\mathrm{,H_2O}$ (VI.)

3. 2 : 2′ : 2″ : 2‴-*Tetrapyridyl Compounds.*—In aqueous-alcoholic solution the tetramine (tetrpy) and potassium nitrosoruthenium pentachloride furnish a readily soluble brown chloride (VII), which on further addition of the potassium salt yields a brown insoluble nitrosoruthenium pentachloride (VIII). In acid solution, the insoluble purple salt (IX) is readily formed on mixing solutions of its generators.

$[\mathrm{ONRuCl\,tetrpy}]\mathrm{Cl_2,5H_2O}$ (VII.)

$[\mathrm{ONRuCl\,tetrpy}][\mathrm{ONRuCl_5}]$ (VIII.)

$\mathrm{tetrpy\,H_2}[\mathrm{ONRuCl_5}]$ (IX.)

The preparation and properties of the foregoing complex ruthenium derivatives illustrate in a striking manner the characteristic co-ordinating power associated with the three polypyridyls which have now been combined with nitrosoruthenium halides. The chelate diamine, 2 : 2′-dipyridyl, occupies normally two positions in a co-ordination complex, so that with one molecular proportion of this base the non-ionised complex (I) is formed. The introduction of a second molecule of 2 : 2′-dipyridyl into the nucleus leads to extrusion of two chlorine atoms so that a bivalent cation is produced as in the complex salt (II). With the tridentate base, 2 : 2′ : 2″-tripyridyl, the formation of a non-ionised complex is no longer possible if the three associating foci of the triamine replace three chlorine atoms. Accordingly, one chlorine atom is extruded from the cationic complex, yielding the water-soluble complex salt (V). Displacement of a further atom of chlorine from the co-ordination complex takes place with the quadridentate base, 2 : 2′ : 2″ : 2‴-tetrapyridyl, which occupies four positions in the cationic complex of the soluble chloride and of the insoluble salt (VIII).

Nitric oxide combines with salts of the iron, ruthenium and osmium triad to form compounds which frequently possess remarkable stability. At least three modes of formulation are in vogue for these nitroso-derivatives, which may be exemplified by (X), (XI), and (XII) for trichloronitroso-2 : 2′-dipyridylruthenium.

$$[\mathrm{O{=}N{-}RuCl_3\,dipy}] \qquad [\overset{+}{\mathrm{O}}{\equiv}\overset{+}{\mathrm{N}}{-}\overset{=}{\mathrm{Ru}}\mathrm{Cl_3\,dipy}] \qquad [\mathrm{O}{=}\overset{+}{\mathrm{N}}{=}\overset{-}{\mathrm{Ru}}\mathrm{Cl_3\,dipy}]$$

(X.) (XI.) (XII.)

In the oldest formulation (X), nitric oxide is considered to be combined with ruthenium as in organic nitrosyl derivatives, but according to more modern views concerning the mode of attachment of nitric oxide in metallic complexes the alternative arrangements (XI) and (XII) are possible, the effective atomic number in both instances being that of xenon, 54. In the former, one electron from nitrogen is donated electrovalently to ruthenium, and two more electrons from nitrogen constitute a co-ordinate link with ruthenium, which thereby becomes effectively bivalent. This view receives experimental support from the fact recorded below that with excess of dipyridyl the complex under discussion is in part converted into tris-2 : 2′-dipyridylruthenous dichloride.

In formula (XII) one electron from nitrogen is again donated electrovalently to ruthenium and the combination is completed by two ordinary covalent bonds. This arrangement (XII) attributes to ruthenium a principal valency of four, as in the older formulation (X), but there is no experimental evidence of the formation of any quadrivalent ruthenium derivative after displacement of nitric oxide from such nitroso-ruthenium compounds under non-oxidising conditions. These practical considerations support the electronic arrangement suggested by formula (XI) rather than those of formulæ (X) and (XII). A mesomeride of the forms (XI) and (XII) would, however, react as if it contained tervalent ruthenium (compare Milward, Wardlaw, and Way, this vol., p. 233).

EXPERIMENTAL.

Potassium nitrosoruthenium pentachloride, $K_2[NORuCl_5]$, obtained according to the method described by Werner and Smirnoff (*loc. cit.*), was used in preparing potassium nitroso-ruthenium pentabromide and pentaiodide (see Dufet, *Bull. Soc. chim.*, 1891, **14**, 206).

Trichloronitroso-2 : 2′-*dipyridylruthenium* (I, X = Cl).—Potassium nitrosoruthenium pentachloride (1·9 g.) and 2 : 2′-dipyridyl (0·8 g.) in water (50 c.c.) were warmed (40—50°) until green leaflets separated. This product was rapidly collected, washed with water and dried (Found: Ru, 25·9; Cl, 26·6. $C_{10}H_8ON_3Cl_3Ru$ requires Ru, 25·8; Cl, 27·0%). This *salt* was slightly soluble in hot acetone, from which it separated in brown crystals (Found: N, 10·7; Cl, 26·5. Calc.: N, 10·7; Cl, 27·0%) of the same composition. Both the green and the brown form of this salt dissolved slowly in aqueous 2 : 2′-dipyridyl but evaporation of the solution gave only a small quantity of the complex $[\mathrm{Ru\ 3dipy}]Cl_2,6H_2O$ of bivalent ruthenium and a very soluble dark brown product which could not be crystallised, but which yielded the following red-brown salt with aqueous potassium nitrosoruthenium pentachloride.

Chloronitrosobis-2 : 2′-*dipyridylruthenium Nitrosoruthenium Pentachloride* (II).—When nitrosoruthenium pentachloride (1·9 g.) in water (50 c.c.) was slowly added to a boiling aqueous-alcoholic solution of 2 : 2′-dipyridyl (0·8 g.), insoluble red-brown crystals of the complex *salt* separated (Found : Ru, 25·8; N, 10·8; Cl, 27·1. $C_{20}H_{16}O_2N_6Cl_6Ru_2$ requires Ru, 25·8; N, 10·7; Cl, 27·0%). This product, which was slightly soluble in acetone, was also formed when the aqueous solution containing potassium nitrosoruthenium pentachloride (1·9 g.) and 2 : 2′-dipyridyl (1·6 g.) was treated with a further proportion of the potassium salt. This complex nitrosochloride dissolved slowly with some decomposition in aqueous 2 : 2′-dipyridyl and the solution so formed gave the original salt on addition of a solution of the potassium salt.

Tribromonitroso-2 : 2′-*dipyridylruthenium* (I, X = Br) was prepared in a similar manner to the corresponding chloro-derivative from potassium nitrosoruthenium pentabromide (3·0 g.) and 2 : 2′-dipyridyl (0·8 g.). This brown product was crystallised from hot acetone (Soxhlet), but in this instance only one form was obtained (Found : Ru, 19·5; Br, 45·5. $C_{10}H_8ON_3Br_3Ru$ requires Ru, 19·3; Br, 45·4%).

Tri-iodonitroso-2 : 2′-*dipyridylruthenium* (I, X = I) was obtained as in the foregoing experiment from potassium nitrosoruthenium pentaiodide (2·2 g.) and 2 : 2′-dipyridyl (0·4 g.). It formed brown, almost black, crystals from hot acetone (Soxhlet) but again only one form was distinguished (Found: Ru, 15·5; N, 6·6; I, 57·3. $C_{10}H_8ON_3I_3Ru$ requires Ru, 15·2; N, 6·3; I, 57·0%).

Dichloronitroso-2 : 2′ : 2″-*tripyridylruthenium Nitrosoruthenium Pentachloride* (IV).—Potassium nitrosoruthenium pentachloride (1·9 g.) and 2 : 2′ : 2″-tripyridyl (1·1 g.) in water (50 c.c.) were stirred and warmed at 90°; dark brown crystals of the complex *salt* then separated in small yield and were washed with water and dried (Found: Ru, 25·6; Cl, 27·0. $C_{30}H_{22}O_3N_9Cl_9Ru_3$ requires Ru, 25·8; Cl, 27·0%). This salt was also formed when potassium nitrosoruthenium pentachloride was added to a solution of the following salt.

Dichloronitroso-2 : 2′ : 2″-*tripyridylruthenium Chloride* (V).—On evaporating the filtrate from the foregoing preparation brown leaflets of the water-soluble hydrated chloride separated, and were recrystallised from a little water and air-dried (Found: Ru, 18·8; N, 10·9; Cl, 19·8; H_2O, 12·7. $C_{15}H_{11}ON_4Cl_3Ru,3\frac{1}{2}H_2O$ requires Ru, 19·0; N, 10·5; Cl, 19·9; H_2O, 11·8%).

Chloronitroso-2 : 2′ : 2″ : 2‴-*tetrapyridylruthenium Chloride Pentahydrate* (VII).—Potassium nitrosoruthenium pentachloride (1·9 g.) and 2 : 2′ : 2″ : 2‴-tetrapyridyl (1·6 g.) in aqueous alcohol were stirred and warmed at 90° until the base had dissolved and the colour had changed from red to brown. Evaporation and cooling of the filtered mixture gave dark brown needles of the pentahydrated *salt*, which was purified and air-dried (Found: Ru, 16·3; N, 11·2; H_2O, 12·6. $C_{20}H_{14}ON_5Cl_3Ru,5H_2O$ requires Ru, 15·9; N, 11·0; H_2O, 12·6%).

Chloronitroso-2 : 2′ : 2″ : 2‴-*tetrapyridylruthenium Nitrosoruthenium Pentachloride* (VIII).—Potassium nitrosoruthenium pentachloride was added in excess to an aqueous solution of the foregoing salt (VII); the brown microcrystalline salt then separated and was washed with water and dried at 110° (Found: Ru, 26·0; Cl, 27·5. $C_{20}H_{14}O_2N_6Cl_6Ru_2$ requires Ru, 25·9; Cl, 27·0%).

Nitrosoruthenium Pentachlorides of Polypyridyls.—*Bis*-2 : 2′-*dipyridylnitrosoruthenium pentachloride* (III). 2 : 2′-Dipyridyl (1·5 g.) in hydrochloric acid and potassium nitrosoruthenium pentachloride (1·9 g.) in water (30 c.c.) were mixed; the complex *salt* then separated in deep purple crystals and was air-dried (Found : Ru, 15·7; Cl, 27·5. $C_{20}H_{18}ON_5Cl_5Ru,H_2O$ requires Ru, 15·8; Cl, 27·6%). This and the following two salts were decomposed into their generators with dilute aqueous potassium hydroxide or carbonate.

2 : 2′ : 2″-*Tripyridylnitrosoruthenium pentachloride* (VI) was obtained in mauve needles by mixing equimolecular proportions of 2 : 2′ : 2″-tripyridyl in hydrochloric acid and potassium nitrosoruthenium pentachloride (Found : Ru, 18·4; Cl, 31·1; H_2O, 2·9. $C_{15}H_{13}ON_4Cl_5Ru,H_2O$ requires Ru, 18·2; Cl, 31·6; H_2O, 3·2%).

2 : 2′ : 2″ : 2‴-*Tetrapyridylnitrosoruthenium pentachloride* (IX) separated in mauve crystals when equimolecular proportions of 2 : 2′ : 2″ : 2‴-tetrapyridyl in hydrochloric acid and potassium nitrosopentachloride were mixed. After 12 hours the crystals were collected, washed with water, and air-dried (Found : Ru, 16·7; Cl, 27·9. $C_{20}H_{16}ON_5Cl_5Ru$ requires Ru, 16·4; Cl, 28·5%).

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[*Received, August 25th, 1938.*]