1032. *Carboxylic Acid Complexes of Rhenium.*

By F. Taha and G. Wilkinson.

Interaction of rhenium trichloride and lower monocarboxylic acids in absence of air gives monomeric compounds such as $(CH_3{\cdot}CO_2H)_2ReCl_3$ in which the acid is acting as a donor ligand, together with binuclear complexes $[ReCl(O{\cdot}COR)_2]_2$ which are considered to have the bridged structure of the copper(II) carboxylates, but with terminal chlorine atoms. When carried out in dry air the reaction leads to oxygenated species of formulæ $[ReOCl(O{\cdot}COR)]_2$ and $[ReO_2(O{\cdot}COR)]_2$ which are believed to have both carboxylato- and oxo-bridges.

Interaction of rhenium pentachloride and acetic acid gives the polymeric complex $[ReCl_3(OAc)_2]_n$.

Although oxalato and some organic hydroxy-acid complexes of rhenium have been described,[1,2] no complexes of simple monocarboxylic acids appear to be known. We have investigated the interaction between acetic and other lower aliphatic carboxylic acids and rhenium trichloride and between acetic acid and rhenium pentachloride. The reactions with the trichloride take different courses when carried out in nitrogen and in dry air.

(*A*) *Chloro-carboxylates of Rhenium.*—When solutions of rhenium trichloride in the carboxylic acid (containing a little of its anhydride where available) are heated in a nitrogen atmosphere, the original red colour changes slowly to dark brown and fine orange needle-shaped crystals separate. For acetic, propionic, n- and iso-butyric, and octanoic acid the orange crystals are similar and are of the stoicheiometry $[ReCl(O{\cdot}COR)_2]_2$. The acetate is sparingly soluble in organic solvents, but the solubilities increase with the length of the alkyl chain so that the octanoate is readily soluble in benzene, chloroform, and other common solvents. Where solubility allows the molecular weights to be determined, the compounds are dimeric. The melting points decrease from $>300°$ for the acetate to 196° for the octanoate. The compounds are stable for at least three years in

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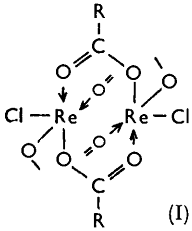
[1] Sen and Ray, *J. Indian Chem. Soc.*, 1953, **30**, 171, 181.

[2] Jezowska-Trezebiatowska *et al.*, *Bule. Acad. polon. Sci., Ser. Sci. chim., geol., geog.*, 1958, **6**, 217; 1961, **9**, 57, 65.

air; they are unaffected by cold dilute mineral acids but hot alkaline solutions decompose them, giving hydrated black rhenium dioxide.


(I)

There are no reliable infrared criteria for distinguishing between dichelate and bridging carboxylato-groups, but all the compounds have strong bands in the same regions as when bridging carboxylate groups are known to be present, *e.g.*, in chromium(II), copper(II), and basic beryllium acetates,[3] molybdenum(II) acetate and other carboxylates,[4] an olefin–rhodium bridged acetate complex,[5] etc. We have so far been unable to establish valid criteria for rhenium compounds to distinguish between bridging and non-bridging chlorine atoms in the far-infrared region. However, chemical evidence very strongly supports the view that these complexes have the copper(II) acetate structure [6] (I) with four bridging carboxylato-groups and with a terminal chlorine on each rhenium atom. This evidence is as follows.

(*a*) If the butyrates are boiled in benzene with silver thiocyanate, the chlorine atoms can be readily replaced to give the brown complexes $[Re(NCS)(O{\cdot}CO{\cdot}C_3H_7)_2]_2$. The infrared spectra of these compounds have a strong band at 2035 cm.$^{-1}$ due to the C–N stretch of the thiocyanato-group. For various transition-metal complexes it has been shown that terminal thiocyanato-groups absorb in the range 2070—2130 cm.$^{-1}$, while bridging thiocyanato-groups absorb at somewhat higher frequencies,[7a] so that the low value found in the rhenium complexes is consistent with a terminal thiocyanato-group. Although the observed frequency is closer to the region for ionic thiocyanates, the rhenium complex gives non-conducting solutions in nitrobenzene and in acetone. The number of fairly strong bands in both the chloro- and the thiocyanato-complexes in the 650—900 cm.$^{-1}$ region and the weakness of the diagnostic C–S frequencies, which enable a distinction between N-bonded and S-bonded thiocyanato-groups to be made,[7b,c] make the issue somewhat inconclusive here. However, in the 690—720 region the close similarity of the spectra of the chloro- and the thiocyanato-complex spectra suggests that the thiocyanate group is bound through nitrogen. This point is not pertinent to the present argument, however, which is that the group is a terminal one.

(*b*) The soluble chloro-complexes in aqueous acetone solution react at once on the addition of silver perchlorate or silver sulphate to give silver chloride and blue solutions. On using the butyrate, a sparingly water-soluble, blue-green sulphate, $[Re_2(H_2O)_2(O{\cdot}CO{\cdot}C_3H_7)_4]SO_4$, has been isolated which, in addition to the usual infrared acetate bands, has strong absorption due to co-ordinated water at 3400 and 1625 cm.$^{-1}$, as well as to sulphate. This shows that the terminal chlorine atoms can be replaced by water molecules, to give a dipositive cation in which the carboxylato-bridges are retained.

(*c*) The chloro-compounds do not react with *p*-toluidine, dry pyridine, or triphenylphosphine in refluxing benzene in absence of air, which suggests that the compounds are not chloride-bridged. With the same reagents in the same conditions in air, however, the orange carboxylates react quite rapidly, giving initially green solutions which later become yellow-brown. These reactions have not been further investigated at present.

The carboxylates are diamagnetic both in the solid state (bulk-susceptibility measurement by the Gouy method) and in solution in organic solvents (by the nuclear magnetic resonance method [8]). In the proposed structure the rhenium atom can be regarded as being in the III oxidation state (d^4) by analogy with the copper(II) carboxylates, but

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[3] For discussion, references, and assignments see Nakamoto, " Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York and London, 1963, pp. 197 *et seq.*

[4] Bannister and Wilkinson, *Chem. and Ind.*, 1960, 319, and unpublished work.

[5] Chatt and Venanzi, *J.*, 1957, 4735.

[6] van Niekerk and Schoening, *Acta Cryst.*, 1953, **6**, 227.

[7] (*a*) Chatt and Duncanson, *Nature*, 1956, **178**, 997; Chatt, Vallerino, and Venanzi, *J.*, 1957, 2496; (*b*) Lewis, Nyholm, and Smith, *J.*, 1961, 4590; (*c*) Turco and Pecile, *Nature*, 1961, **191**, 66.

[8] Evans, *J.*, 1959, 2003.

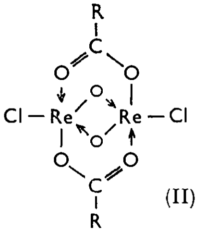
whether one regards the geometry as being square-pyramidal or octahedral, doubtless distorted in either case, is a matter of opinion; it is, however, not necessary to invoke metal–metal bonding to account for the diamagnetism.

(*B*) *Carboxylic Acid Complexes of Rhenium Trichloride.*—From the dark brown solutions remaining after the separation of the orange chloro-carboxylates, brown solids of the stoicheiometry $(R{\cdot}CO_2H)_2ReCl_3$ can be isolated. These products cannot be obtained as well-defined crystals, but they are readily soluble in polar organic solvents, giving red-brown solutions. They give non-conducting solutions in acetone and nitrobenzene, and isopiestic molecular weights in acetone indicate monomeric species. The infrared spectra show the presence of hydroxyl groups and the carbonyl stretching frequencies are lowered by *ca.* 10 cm.$^{-1}$ relative to that in the parent acid. These complexes thus appear to be carboxylic acid complexes similar to those that have been prepared from other metal halides and whose infrared spectra have been studied in detail.[9] Although various ester–donor complexes of metal halides have been prepared,[10] we have been unable to isolate any such complexes of rhenium trichloride. When rhenium trichloride is refluxed with ethyl acetate and similar esters the colour of the solution changes from red to purple, but on removal of the excess of ester only rather intractable oils remain which could not be crystallised, even after repeated washing with petroleum, and whose analyses are unsatisfactory. Attempts to esterify the carboxylic acid complexes have also failed.

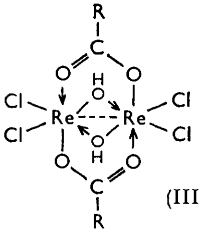
The carboxylic acid complexes are diamagnetic and their structure presumably has trigonal-bipyramidal rhenium(III) with equatorial chlorine atoms.

(*C*) *Chloro-oxo- and Oxo-carboxylate Complexes of Rhenium.*—When solutions of rhenium trichloride in carboxylic acids are refluxed in a slow stream of dry air or oxygen, the red solutions become orange, and purple needle-shaped crystals separate. For n- and iso-butyric and octanoic acid two complexes, one purple and one orange, can be fairly readily separated. The solubilities of the respective acetate and propionate complexes are similar and we have been unable to separate these compounds cleanly. The purple compounds have the stoicheiometry $[ReOCl(O{\cdot}COR)]_2$ and the orange $[ReO_2(O{\cdot}COR)]_2$.

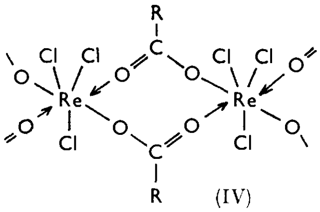
Chloro-oxo-complexes. These compounds are dimeric and diamagnetic, and give non-conducting solutions in acetone. The infrared spectra have carboxylate bands in the same regions as those of the chloro-carboxylates discussed above. It is suggested that the oxygen atoms occupy bridge positions as in (II), the structure being similar to that of the chloro-carboxylates, again with terminal chlorine atoms. Both here and for the oxo-complexes below, we have no information to suggest whether the oxo(or carboxylato)-groups are *trans*, as shown (II), or are *cis* to each other.



(II)



(III)



(IV)

Evidence for the presence of bridging oxo-groups is obtained from their protonation; the complexes dissolve in aqueous air-free mineral acids to give blue solutions. Reaction of the isobutyrate with hydrochloric acid in acetone leads to a blue, water-insoluble diamagnetic complex of stoicheiometry $[Re(OH)Cl_2(O{\cdot}CO{\cdot}C_3H_7)]_2$. The latter gives non-conducting solutions in nitrobenzene and its infrared spectrum shows the usual carboxylate bands with an additional strong O–H stretching frequency at 3380 cm.$^{-1}$. The most reasonable structure appears to be (III). While it is often difficult to decide on realistic

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[9] Zackrisson and Lindqvist, *J. Inorg. Nuclear Chem.*, 1969, **17**, 69.

[10] See, *e.g.*, Cassimati and Susz, *Helv. Chim. Acta*, 1960, **43**, 852.

oxidation states in certain complexes, the present one would appear formally to have rhenium(V), seven-co-ordinate with a metal–metal bond, or rhenium(IV) with spin-pairing between the two rhenium atoms to account for the diamagnetism. The problem in assigning oxidation states in this complex is rather similar to that in the hydrogen chloride or methyl iodide adducts of square-planar platinum(II), rhodium(I), or iridium(I) complexes to give octahedral species with the metals formally in an oxidation state two higher.[11]

Di-oxo-complexes. After removal of the purple crystals from the n- or iso-butyric acid reaction mixtures, the orange solutions deposit crystals of composition $[ReO_2(O{\cdot}CO{\cdot}C_3H_7)]_2$; a small quantity of the corresponding octanoate was also isolated. These compounds are again diamagnetic and non-conducting in nitrobenzene. In addition to the usual carboxylate bands, there is an additional very strong band at *ca.* 935 cm.$^{-1}$, indicating the presence of an Re=O bond. The compounds, unlike the chloro-oxo-compounds, are unaffected by cold, dilute mineral acids, but on several minutes' boiling they give blue solutions. They are also reduced by acetone to greenish solutions. The structure hence appears to be one similar to (II), involving bridging carboxylato- and oxo-groups but with a terminal Re=O bond. Since a metal–metal bond or spin-pairing must be postulated to accommodate the diamagnetism, we have formally a compound of rhenium(V).

(*D*) *Interaction of Rhenium Pentachloride and Acetic Acid.*—Heating rhenium pentachloride in acetic acid containing some anhydride affords a black crystalline compound having the composition $ReCl_3(OAc)_2$. This substance is highly insoluble, even in acetone, and we have been unable to obtain its molecular weight. It is diamagnetic and has infrared bands in the same region as the other acetate complexes. It can be formulated as (IV), where rhenium(V) is seven-co-ordinate. An acetatomolybdenum trichloride complex of the same stoicheiometry as the rhenium one has been described, but this is soluble, with reaction, in many polar solvents.[12]

EXPERIMENTAL

Microanalyses and molecular weights were by the Microanalytical Laboratory, Imperial College. Rhenium was determined either gravimetrically as nitron perrhenate or spectrophotometrically by using furil α-dioxime after conversion of the metal in the complexes into perrhenate. Bulk-susceptibility measurements were made by the Gouy method. Rhenium (Johnson, Matthey and Co. Ltd.) was converted into the pentachloride, and the latter thermally decomposed to the trichloride. Petroleum refers to light petroleum of b. p. 30—40°.

Interaction of Rhenium Trichloride and Carboxylic Acids in Nitrogen.—(I) *Acetic acid.* A solution of rhenium trichloride (2·5 g.) in glacial acetic acid (25 ml.) containing acetic anhydride (*ca.* 1 ml.) was heated under reflux just below the b. p. for 4—5 days in a nitogen atmosphere. The red solution became brown and crystals separated. After cooling, the orange needles of *chlororhenium*(III)-*μ-tetra-acetato-chlororhenium*(III) were removed, washed by decantation from less dense, insoluble, black material with acetone, then with petroleum, and dried *in vacuo* (*ca.* 0·25 g., *ca.* 10% based on $ReCl_3$) (Found: C, 14·1; H, 1·7; Cl, 10·4; O, 19·1; Re, 55·9. $C_8H_{12}Cl_2O_8Re_2$ requires C, 14·1; H, 1·8; Cl, 10·4; O, 18·8; Re, 54·9%). The compound is thermally stable and does not melt below 300°. It is insoluble in acetone, chloroform, dichloromethane, benzene, alcohol, and ether as well as in cold dilute or concentrated hydrochloric or sulphuric acid. It is decomposed by hot concentrated nitric acid and by hot aqueous sodium hydroxide.

The dark solution remaining after removal of the chloro-acetate was filtered and evaporated *in vacuo*. The residue was washed repeatedly with petroleum, and the black product, dried *in vacuo*, was *trichlorodi*(*acetic acid*)*rhenium*(III) (1·5 g., *ca.* 45% based on $ReCl_3$) [Found: C, 11·0; H, 1·9; Cl, 25·4; O, 16·0; Re, 45·9%; *M* (isopiestic in acetone, with azobenzene reference), 400. $C_4H_8Cl_3O_4Re$ requires C, 11·6; H, 1·9; Cl, 25·8; O, 15·5; Re, 45·1%; *M*, 412·8]. The compound is soluble in acetone, alcohol, chloroform, and acetic acid but is insoluble in benzene, carbon tetrachloride, ether, and water.

The following preparations were done similarly, except as otherwise stated.

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[11] See, *e.g.*, Chatt and Shaw, *J.*, 1962, 5075.

[12] Larson, *J. Amer. Chem. Soc.*, 1960, **82**, 1223.

(II) *Propionic acid.* 2·5 g. of trichloride, 25 ml. of acid, and 1 ml. of anhydride were used. The orange crystals of *chlororhenium*(III)-*μ-tetrapropionatochlororhenium*(III), after collection by centrifugation, were washed with acetone (1 ml.) and several times with petroleum 0·4 g., *ca.* 12% based on $ReCl_3$) (Found: C, 19·4; H, 2·1; O, 17·2. $C_{12}H_{20}Cl_2O_8Re_2$ requires C, 19·5; H, 2·7; O, 17·4%). The compound darkens above 245° in air. It is sparingly soluble in acetone (*ca.* 10 g./l. at 25°) but is insoluble in benzene, chloroform, ether, and dichloromethane.

The supernatant solution, on filtration and evaporation, left a black residue which was washed with petroleum and dried, giving *trichlorodi(propionic acid)rhenium*(III) (1·5 g., *ca.* 45% based on $ReCl_3$) (Found: C, 14·0; H, 2·6; O, 14·6. $C_6H_{12}Cl_3O_4Re$ requires C, 16·3; H, 2·7; O, 14·5%), soluble in acetone, chloroform, alcohol, and ether but insoluble in benzene and carbon tetrachloride.

(III) *n-Butyric acid.* 2·5 g. of rhenium trichloride were used. Crystals up to 1 cm. long were obtained. They were washed with petroleum and recrystallised from dichloromethane, giving *chlororhenium*(III)-*μ-tetra-n-butyrato-chlororhenium*(III) (1·1 g., *ca.* 35% based on $ReCl_3$) as orange needles, m. p. 215° (Found: C, 24·4; H, 3·6; O, 16·7. $C_{16}H_{28}Cl_2O_8Re_2$ requires C, 24·3; H, 3·5; O, 16·2%). The compound is soluble in acetone, chloroform, dichloromethane, tetrahydrofuran, and hot chlorobenzene but is sparingly soluble in cold benzene and is insoluble in carbon tetrachloride.

Evaporation of the filtered supernatant liquid left dark brown *trichlorodi(butyric acid)-rhenium*(III) (*ca.* 1·6 g.), m. p. 112° (Found: C, 18·5; H, 2·6; O, 15·8. $C_8H_{16}Cl_3O_4Re$ requires C, 20·4; H, 3·1; O, 13·4%). The compound is soluble in acetone, alcohol, and chloroform.

(IV) *Isobutyric acid.* 2·5 g. of rhenium trichloride was used, in the absence of acid anhydride. After 4 days' heating the solution was cooled and the product recrystallised from dichloromethane as orange needles of *chlororhenium*(III)-*μ-tetra-isobutyrato-chlororhenium*(III) (1·1 g., *ca.* 35% based on $ReCl_3$), m. p. 220° [Found: C, 24·8; H, 3·9; O, 16·6%; *M* (ebullioscopic in chlorobenzene), 740. $C_{16}H_{28}Cl_2O_8Re_2$ requires C, 24·3; H, 3·5; O, 16·2%; *M*, 728].

(V) *Octanoic acid.* In absence of acid anhydride. On cooling after 3 days' heating, the product was collected and crystallised from dichloromethane as orange leaflets of *chlororhenium*(III)-*μ-tetraoctanoato-chlororhenium*(III) (1·1 g., *ca.* 25% based on $ReCl_3$), m. p., 196° [Found: C, 38·0; H, 5·9; Cl, 7·4; O, 12·7%; *M* (ebullioscopic and isopiestic in benzene), 1100. $C_{32}H_{60}Cl_2O_8Re_2$ requires C, 37·8; H, 5·9; Cl, 7·0; O, 12·6%; *M*, 1016], readily soluble in acetone, benzene, alcohol, and tetrahydrofuran, but insoluble in petroleum and carbon tetrachloride.

Thiocyanatorhenium(III)-*μ-tetrabutyratothiocyanatorhenium*(III).—A solution of the chloro-n-butyrate (0·8 g.) in benzene (20 ml.) was refluxed for 5 hr. under nitrogen with dry silver thiocyanate (8 g.). The orange solution became dark brown; after filtration under nitrogen and evaporation *in vacuo*, the dark brown solid *compound* remaining was crystallised from dichloromethane (Found: C, 23·2; H, 3·1; N, 3·7. $C_{18}H_{28}N_2O_8Re_2S_2$ requires C, 25·8; H, 3·4; N, 3·7%). It is insoluble in water but soluble in acetone and in benzene.

The isobutyrate was made on a smaller scale (0·2 g.) for infrared study.

Aquarhenium(III)-*μ-tetra-n-butyrato-aquarhenium*(III) *Sulphate.*—Equimolar amounts of chlororhenium(III)-μ-tetrabutyrato-chlororhenium(III) (0·470 g.) in acetone (6 ml.), and silver sulphate (0·185 g.) in distilled water (30 ml.), were mixed in a nitrogen atmosphere. Silver chloride was precipitated and after filtration the blue solution was evaporated *in vacuo* until a greenish-blue crystalline powder separated. This *salt* was collected by centrifugation and dried at 100° *in vacuo* overnight (Found: C, 22·2; H, 3·8; O, 25·7. $C_{16}H_{32}O_{14}Re_2S$ requires C, 22·5; H, 3·8; O, 26·3%).

Interaction of Rhenium Trichloride and Carboxylic Acids in Air.—(I) *Isobutyric acid.* Rhenium trichloride (2 g.) was heated with isobutyric acid (25 ml.) for 4 days at just below the b. p. and a slow stream of dry air was passed through the solution. Purple needles slowly separated from an orange solution which was filtered hot. The crystals were recrystallised from chloroform and dried *in vacuo*, giving *chlororhenium*(IV)-*μ-dioxo-μ-di-isobutyrato-chlororhenium*(IV) (*ca.* 0·5 g., 23% based on $ReCl_3$), m. p. 305° (Found: C, 14·9; H, 2·4; Cl, 11·3; O, 14·4; Re, 57·3. $C_8H_{14}Cl_2O_6Re_2$ requires C, 14·8; H, 2·2; Cl, 10·9; O, 14·8; Re, 57·3%)]. The crystals deposited from the reaction mixture are usually pure, but may contain some of the orange dioxo-compound (below); the latter is insoluble in alcohol but the purple complex is moderately soluble and is readily separated. The compound is also moderately soluble in acetone; it is slightly soluble in cold chloroform and dichloromethane but insoluble in benzene, carbon tetrachloride, and nitrobenzene. It is unaffected by prolonged exposure to air and is unaffected by cold water but is decomposed by boiling water, or by bases, to rhenium dioxide. On treatment with mineral acids, it slowly dissolves, giving blue solutions.

From the original filtrate, on cooling, orange crystals were obtained which were recrystallised from hot butyric acid, washed with petroleum until acid-free, and dried *in vacuo*, giving *oxorhenium*(V)-*μ-dioxo-di-isobutyrato-oxorhenium*(V) (*ca.* 0·4 g.) (Found: C, 15·7; H, 2·6; O, 20·3; Cl, nil. $C_8H_{14}O_8Re_2$ requires C, 15·7; H, 2·3; O, 20·9%), slightly soluble in chloroform and dichloromethane and sparingly soluble in cold, but moderately soluble in hot benzene. It is soluble in acetone but reacts therewith to give a greenish solution. Boiling water gives hydrated rhenium dioxide.

(II) *n-Butyric acid.* Procedure as above gave *chlororhenium*(IV)-*μ-dioxo-μ-di-n-butyrato-chlororhenium*(IV) (0·5 g.), purple, m. p. 210° (Found: C, 15·3; H, 2·7; O, 15·8%). The solubilities are similar to those of the isobutyrate. The filtrate afforded *oxorhenium*(V)-*μ-dioxo-μ-di-n-butyrato-oxorhenium*(V), which recrystallised from n-butyric acid as orange crystals (0·4 g., 22% based on $ReCl_3$), m. p. 260° [Found: C, 16·1; H, 2·8; O, 20·2; *M* (ebullioscopic in benzene), 610. $C_8H_{14}O_8Re_2$ requires C, 15·7; H, 2·3; O, 20·9%; *M*, 594]. Solubilities were similar to those of the corresponding isobutyrate.

(III) *Octanoic acid.* Similar reaction gave purple leaflets of *chlororhenium*(IV)-*μ-dioxo-μ-dioctanoato-chlororhenium*(IV) (0·1 g., 4·5% based on $ReCl_3$), m. p. 155° (Found: C, 25·9; H, 4·4; O, 12·7. $C_{16}H_{30}Cl_2O_6Re_2$ requires C, 25·2; H, 3·9; O, 12·6%), very soluble in acetone, chloroform, dichloromethane, and benzene but insoluble in petroleum; it is best crystallised from chloroform. In air the compound slowly decomposes to a black sticky mass; orange leaflets of the dioxo-compound were isolated but in quantities too small for analysis.

Dichlororhenium(V)-*μ-dihydroxo-μ-di-isobutyrato-dichlororhenium*(V).—To a solution of chlororhenium(IV)-μ-dioxo-μ-di-isobutyrato-chlororhenium(IV) (0·2 g.) in acetone (10 ml.) was added concentrated hydrochloric acid (5 ml.). The purple acetone solution became blue and, on removal of acetone under vacuum, blue crystals separated. These were centrifuged, washed several times with water, and crystallised from acetone; drying *in vacuo* at 100° gave the *dihydroxo-compound* (0·1 g.) (Found: C, 13·5; H, 2·8; O, 15·9. $C_{16}H_{30}Cl_4O_{10}Re_2$ requires C, 13·3; H, 2·2; O, 13·3%). It is sparingly soluble in benzene but readily soluble in acetone, alcohol, and chloroform. It gives a non-conducting solution in nitrobenzene.

In a similar manner, *dichlororhenium*(V)-*μ-dihydroxo-μ-n-butyrato-dichlororhenium*(V) (Found: Cl, 18·2; O, 13·8%), was prepared.

Interaction of Rhenium Pentachloride and Acetic Acid.—Rhenium pentachloride (2 g.) was refluxed with glacial acetic acid (25 ml.) containing acetic anhydride (1 ml.) for 2 days under nitrogen. The black solution was evaporated and the residue crystallised from hot chloroform, giving *trichlorodiacetatorhenium*(V) (1·5 g., *ca.* 65% based on $ReCl_5$) (Found: C, 12·0; H, 1·8; O, 15·8; Re, 23·6. $C_4H_6Cl_3O_4Re$ requires C, 11·7; H, 1·5; O, 15·6; Re, 23·6%). The compound does not melt below 280°. It is unaffected by water or cold dilute hydrochloric or sulphuric acid, but is decomposed by boiling aqueous sodium hydroxide to give hydrated rhenium oxide. It is insoluble in acetone, benzene, and carbon tetrachloride but is sparingly soluble in nitrobenzene and hot chloroform.

Infrared Spectra.—Spectra were taken in Nujol and hexachlorobutadiene mulls, on a Perkin–Elmer model 21 spectrometer with sodium chloride optics, and were as follows:

$[ReCl(OAc)_2]_2$: 2960, 2924w (CH str.); 1456vs, 1385vs (CO_2); 1425sh, 1345s (CH_3 def.); 1040s, 1020m (CH_3 rock); 945w, 680vs (CO_2 def.).

$[ReCl(O{\cdot}CO{\cdot}C_2H_5)_2]_2$: 2990, 2940, 2890m; 1470vs, 1375vs; 1438, 1304s; 1085s, 1015m, 975w, 935s, 885w, 850s, 800s, 680m, 650s.

$[ReCl(O{\cdot}CO{\cdot}C_3H_7\text{-n})_2]_2$: 3000, 2955, 2885m; 1470vs, 1375vs; 1450s, 1305s, 1267s, 1200s, 1092s, 1037m, 955sh, 933m, 887s, 861s, 797vs, 765m, 723s, 650vs.

$[ReCl(O{\cdot}CO{\cdot}C_3H_7\text{-iso})_2]_2$: 2980, 2930m; 1470vs, 1440sh, 1430vs, 1377m, 1300s, 1283sh, 1164m, 1081s, 963m, 928s, 845s, 755s, 672s.

$[ReCl(O{\cdot}CO{\cdot}C_7H_{15})_2]$ (4000—1200 cm.$^{-1}$ in CCl_4): 2995, 2910, 2850; 1468vs, 1440sh, 1420vs, 1400s, 1365m, 1340m, 1320m, 1295m, 1245.

$[Re(SCN)(O{\cdot}CO{\cdot}C_3H_7\text{-n})_2]_2$: 2980, 2930m; 2035vs (C–N); 1480vs, 1430vs, 1375vs, 1310s, 1205m, 1085s, 890m, 820w, 790sh, 760s, 650s.

$[Re(SCN)(O{\cdot}CO{\cdot}C_3H_7\text{-iso})_2]_2$: 2980, 2930m; 2040vs (C–N), 1470vs, 1440sh, 1430s, 1375s, 1290s, 1165m, 1090s, 960w, 925m, 845s, 750m, 672s.

$[Re_2(H_2O)_2(O{\cdot}CO{\cdot}C_3H_7\text{-}n)_4]SO_4$: 3400s, broad ($H_2O$); 2960, 2900m; 1625m ($H_2O$); 1470vs, 1440vs, 1313vs, 1270s, 1210s, 1160s (SO_4), 1080s, 1025s, 940m, 895s, 795s, 720w, 650s.

$ReCl_3(AcOH)_2$: 3300s, broad (O–H); 2924s, 1708s, 1476s, 1445vs, 1385vs, 1350s, 1080m, 1040m, 920s, 845s, 775s, 685s.

$[ReCl_3(n\text{-}C_3H_7{\cdot}CO_2H)_2]_n$: 3370s, broad (O–H); 2970, 2930, 2870m; 1710, 1462vs, 1415s, 1385s, 1317s, 1262s, 1200m, 1090s, 1030m, 975w, 940s, 840s, 790s, 660s.

$[ReO_2(O{\cdot}CO{\cdot}C_3H_7\text{-}n)]_2$: 3000, 2955, 2885m; 1465vs, 1385vs; 1420s, 1310s, 1290s, 1267vs, 1220s, 1205sh, 1092s, 1080w, 980s, 932vs (Re=O), 825s, 755s, 670s.

$[ReOCl(O{\cdot}CO{\cdot}C_3H_7\text{-}n)]_2$: 2950, 2924m; 1470vs, 1430vs, 1400sh, 1330m, 1305m, 1260s, 1205m, 1195m, 1099m, 1073sh, 1045w, 978m, 938s, 913s, 858s, 793m, 748sh, 723s, 650s.

$[ReOCl(O{\cdot}CO{\cdot}C_3H_7\text{-iso})]_2$: 2970, 2950m; 1480vs, 1463s, 1430vs, 1383m, 1365m, 1300s, 1170m, 1080s, 960sh, 940s, 887s, 835s, 670s.

$[ReO_2(O{\cdot}CO{\cdot}C_3H_7\text{-iso})]_2$: 2970, 2875m; 1462vs, 1440sh, 1415vs, 1335m, 1312w, 1270s, 1167m, 1095s, 976s, 935vs (Re=O), 815s; 755s, 680s.

$[ReCl_2OH(O{\cdot}CO{\cdot}C_3H_7\text{-iso})]_2$: 3380s (O–H); 2980, 2930m; 1475vs, 1451vs, 1431vs, 1377s, 1367sh, 1300s, 1285sh, 1165w, 1080vs, 925s, 840m, 760m, 675m.

$[ReCl_3(OAc)_2]_n$: 2940s, 1560s, 1455vs, 1425vs, 1396vs, 1025m, 1010m, 930w, 720s, 650s.

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