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## Liquid Hydrogen Chloride as an Ionizing Solvent. Part XIII.<sup>1</sup> Reactions of TetracarbonyInickel and TricarbonyInitrosylcobalt

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The reactions of tetracarbonylnickel and tricarbonylnitrosylcobalt in liquid hydrogen chloride with the halogens, nitrosyl chloride, and phosphorus pentafluoride are described. Two new compounds, tetrachlorotricarbonyldinickel and dichlorodinitrosylnickel, were prepared and isolated. The structure of these compounds is discussed in terms of their i.r. spectra and magnetic properties.

TETRACARBONYLNICKEL and tricarbonylnitrosylcobalt dissolve in liquid hydrogen chloride, without evolution of carbon monoxide, to give conducting solutions. The molar conductivity of a 0.25M-solution of tetracarbonylnickel is 0.0026 cm.<sup>2</sup> ohm<sup>-1</sup> mole<sup>-1</sup> and that of a 0.5Msolution of tricarbonylnitrosylcobalt is 0.0116 cm.<sup>2</sup> ohm<sup>-1</sup> mole<sup>-1</sup>. These are much lower than the observed molar conductivity of 0.442 cm.<sup>2</sup> ohm<sup>-1</sup> mole<sup>-1</sup> for a 0.5M-solution of pentacarbonyliron in the solvent.<sup>2</sup> The titrations of tetracarbonylnickel and tricarbonylnitrosylcobalt against phosphorous pentafluoride show a break at a molar ratio of ca. 1.0:1.0, which indicates adduct rather than salt formation, and suggests that tetracarbonylnickel and tricarbonylnitrosylcobalt are not strong enough bases in liquid hydrogen chloride for phosphorous pentafluoride to disproportionate. Solids could not be isolated on removal of the excess of solvent and phosphorous pentafluoride. Reaction of tetracarbonylnickel with boron trichloride also did not yield a solid product.

Tetracarbonylnickel reacts with chlorine in the solvent, and when all volatile substances are removed at low temperatures a compound can be isolated of empirical formula Ni<sub>2</sub>(CO)<sub>3</sub>Cl<sub>4</sub>. A tetracarbonylnickel solution reacts with bromine to give nickel dibromide and with nitrosyl chloride to give a compound of empirical formula Ni(NO)<sub>2</sub>Cl<sub>2</sub>. A tricarbonylnitrosylcobalt solution reacts with both chlorine and nitrosyl chloride to give cobaltic chloride. Salts of the type isolated <sup>2</sup> from the reactions of pentacarbonyliron in the solvent were not found.

The i.r. spectrum (cf. Table 1) obtained shows that in  $Ni_2(CO)_3Cl_4$  the carbonyl groups in the compound are present only in bridging positions. The presence of one single band and a doublet in the frequency region where bridging carbonyls absorb suggests that the structure is of  $C_{2v}$  symmetry (I). This structure is analogous to that of  $Fe_2(CO)_9$  where the same number of bands in the bridging carbonyl region has been observed by Greenwood et al.3 The diamagnetism has been confirmed experimentally. This dimeric structure would have the nickel atoms in the formal oxidation state of +2.

A tetramer in which the nickel atoms are at the corners of a tetrahedron could also be postulated, but this

<sup>1</sup> Part XII, M. E. Peach, Canad. J. Chem., in the press.

<sup>2</sup> Z. Iqbal and T. C. Waddington, J. Chem. Soc. (A), 1968, 2958.

<sup>3</sup> K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood,

Chem. Comm., 1968, 593.
 <sup>4</sup> J. Lewis, R. J. Irving, and G. Wilkinson, J. Inorg. Nuclear Chem., 1958, 7, 32, 38.

structure would have only one carbonyl bridging frequency. The bridging frequency at 1690 cm.<sup>-1</sup> is rather low compared with most observed frequencies of this type. Greenwood et al.<sup>3</sup> have, however, observed



a bridging frequency at 1750 cm.<sup>-1</sup> in the anionic species  $[Fe_{2}(CO)_{e}H]^{-}$ . This suggests that the presence of the chloride ligands in the carbonylnickel halide shifts the bridging carbonyl frequency to lower wavenumbers.

The i.r. spectrum of Ni(NO)<sub>2</sub>Cl<sub>2</sub>, with nitrosyl frequencies well above 1800 cm.-1, shows that NO+ is probably present as a ligand.<sup>4</sup> The presence of two NO frequencies (cf. Table 1) and the low stability of the compound indicate that it is analogous to Pd(NO)<sub>2</sub>Cl<sub>2</sub>.<sup>5,6</sup> The structure would then be tetrahedral with nickel present in the formal oxidation state 0 and the compound would be diamagnetic. An octahedrally coordinated polymeric structure of the trans-form (II)



can also be postulated. Such a structure would be paramagnetic with nickel in the formal oxidation state of +2 and would have only one NO frequency. The e.s.r. spectrum of the solid measured at room temperature shows a weak, broad, signal which is probably due to decomposition to the paramagnetic and more stable polymeric compound Ni(NO)Cl<sub>2</sub>.7 This is supported by the fact that an aged sample of Ni(NO)<sub>2</sub>Cl<sub>2</sub> gave a much <sup>5</sup> W. P. Griffith, J. Lewis, and G. Wilkinson, J. Chem. Soc.,

1959, 1775.
W. Manchot and A. Waldmuller, Ber., 1926, 59, 2363.

7 C. C. Addison and B. F. G. Johnson, Proc. Chem. Soc., 1962, 305.

# Inorg. Phys. Theor.

stronger e.s.r. signal with the same g value under the same conditions. The available evidence therefore supports the tetrahedral structure.

### EXPERIMENTAL

Handling Techniques.—The apparatus and general techniques used have been described previously.<sup>8</sup> Special care was taken in the handling of tetracarbonylnickel and a Puretha gas mask with type B respiration was used during transfer operations. The transfer of hygroscopic salts was carried out in a dry-box flushed with dry nitrogen.

Chemicals.—Tetracarbonylnickel and tricarbonylnitrosylcobalt were supplied by International Nickel Ltd. and P. J. Preparation of the Compounds.—(i) Tetrachlorotricarbonyldinickel, Ni<sub>2</sub>(CO)<sub>3</sub>Cl<sub>4</sub>. Tetracarbonylnickel (ca. 0.2 g.) was distilled into a reaction cell and kept under vacuum at  $-196^{\circ}$  (liquid nitrogen bath). Pure hydrogen chloride (ca. 2 ml.) was distilled into the cell and the temperature raised to  $-95^{\circ}$  (toluene slush bath) when the carbonyl dissolved in the solvent. The solution was frozen at  $-196^{\circ}$  and a slight excess of chlorine was distilled into the cell. The mixture was allowed to warm up to  $-95^{\circ}$ . A yellow-green solid was precipitated which slowly became yellow-brown as the volatile substances were removed by pumping at as low a temperature as possible. The isolated solid was stored in an evacuated ampoule at

	Bands in	the i.r. spectral	region (4000-	$-200 \text{ cm.}^{-1}$ )		
Assignment	$Ni(CO)_4$	Fe <sub>2</sub> (CO) <sub>9</sub> *	${\rm Ni}_2({\rm CO})_3{\rm Cl}_4$	[Fe <sub>2</sub> (CO) <sub>8</sub> H] <sup>-</sup> *	$Pd(NO)_2Cl_2$ †	$Ni(NO)_2Cl_2$
Terminal CO stretch	2058s	2082s 2026s		2045w 1997s 1923vs 1860s		
Bridging CO, $A_1 + B_2$		1845s 1833s 1825sh	1805m 1700s,sh 1690s	1778m 1750s		
NO Stretch			10005	11005	1833s	1872s
Ni–C Stretch Ni–Cl Stretch	422s		240s 215s		10105	282s 255s 230s

TABLE 1

\* See Ref. 3. † See Ref. 4.

TABLE 2

Analytical data

	Change in weight (%) on carbonyl		Required (%)				Found (%)			
Compound	Required	Found	Ni	C1	со	N	Ni	Cl	СО	Ŋ
$Ni_2(CO)_3Cl_4$	+0.6	-0.1	$34 \cdot 2$	41.3	24.5	14.0	33.6	43.3	$23 \cdot 4$	10 7
$N1(NO)_2 CI_2 \dots$	+11.5	+13.0	31.9	37.5		14.8	32.8	37.9		13.1

Sas Ltd., respectively, and purified by trap-to-trap distillation. Analar-grade bromine was used. Chlorine, boron trichloride, and nitrosyl chloride were obtained commercially and purified by fractionation in the vacuum line. Phosphorous pentafluoride was prepared by a standard method and purified by fractionation in the vacuum line.

Analyses and Physical Measurements.—Weight analyses were carried out as described previously.<sup>8</sup> Nickel was determined by atomic absorption spectrophotometer. Chloride was determined by Volhard's method. Carbon monoxide was determined by means of a gas burette after decomposition of a known weight of the compound with a known volume of water. Nitrogen was determined by the Kjeldahl–Gunning–Jodlbauer method.<sup>9</sup> I.r. spectra were recorded on Perkin-Elmer 621 and 457 double-beam spectrophotometers.

<sup>8</sup> T. C. Waddington and F. Klanberg, J. Chem. Soc., 1960, 2329.

 $-196^{\circ}$ . It decomposed slowly at 20° with evolution of carbon monoxide to give nickel dichloride. This reaction was accelerated by heating. The compound vigorously evolved carbon monoxide in the presence of water and other polar solvents. The solid was not very soluble in non-polar solvents such as carbon tetrachloride.

(ii) Dichlorodinitrosylnickel, Ni(NO)<sub>2</sub>Cl<sub>2</sub>. The same procedure used for the preparation of Ni<sub>2</sub>(CO)<sub>3</sub>Cl<sub>4</sub> was employed except that a slight excess of nitrosyl chloride was added. The reaction took place vigorously at  $-95^{\circ}$  to give a deep green solid which decomposed slowly at  $20^{\circ}$  with evolution of nitric oxide. The solid dissolved readily in water and alcohol with decomposition and the solution slowly turned blue. The solid was insoluble in non-polar solvents.

The analytical data for the compounds prepared are shown in Table 2.

#### [8/1568 Received, October 31st, 1968]

<sup>9</sup> C. R. N. Strouts, H. N. Wilson, R. T. Parry Jones, 'Chemical Analysis,' Clarendon Press, Oxford, 1962, vol. 3, p. 4.