this type of behavior were observed. We wish to report the results of these findings, along with the investigation of the hydrogen chloride and hydrogen perchlorate compounds.

Experimental Section

Materials.—The triphenylphosphine oxide was obtained from M and T Chemicals, Inc., and used as received. Rhenium(V) chloride was prepared by a modification of the method of Hurd and Brimm[3] and β-rhenium(IV) chloride was obtained from Shattuck Chemical Co. Indium perchlorate octahydrate was obtained from Alfa Inorganics. Baker and Adamson 70% perchloric acid was used as received, while hydrogen chloride was generated by the action of sulfuric acid on sodium chloride.

Analyses.—The carbon and hydrogen analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. The chloride content was determined by the gravimetric method of Beamish.[4]

Physical Measurements.—Infrared spectra were obtained as Nujol mulls or KBr pellets on a Perkin-Elmer 521 spectrophotometer. Visible spectra were obtained on a Beckman DK-2A spectrophotometer in methylene chloride.

Preparation of the Compounds. $\{[(C_6H_5)_3PO]_2H\}_2Re_2Cl_9$.—Rhenium(V) chloride, 0.66 g (1.8 mmol), was dissolved in 25 ml of acetone giving a dark green solution. To this was added triphenylphosphine oxide, 2.38 g (8.4 mmol), in 15 ml of acetone. The solution was allowed to stand capped in a drybox, and after 2 days the solution contained dark violet crystals. The product was isolated by filtration, washed with acetone, and dried to give 0.72 g (76.5%) of product. It was recrystallized from acetone–ether. *Anal.* Calcd for $C_{72}H_{62}O_4P_4Re_2Cl_9$: C, 47.87; H, 3.46; Cl, 17.66. Found: C, 48.14; H, 3.62; Cl, 16.93. The molar conductivity determined in acetonitrile was 258 ohm^{-1} cm^2. The visible spectrum was the same as that obtained previously for the $Re_2Cl_9^{2-}$ ion.[5]

The same compound was made in an analogous fashion from β-$ReCl_4$. This conclusion was based on elemental analyses and infrared and visible spectra. In both cases, the anion was reduced to the $Re_2Cl_8^{2-}$ ion upon standing in acetone.

$\{[(C_6H_5)_3PO]_2H\}ClO_4$.—To a solution of 1.50 g (5.4 mmol) of triphenylphosphine oxide in 10 ml of ethanol was added 0.54 g (3.8 mmol) of 70% $HClO_4$. After standing for 8 hr, the solution was concentrated to half the initial volume. Upon cooling, white crystals of $\{[(C_6H_5)_3PO]_2H\}ClO_4$ were obtained. The product was isolated by filtration, washed with ethanol, and dried to yield 0.30 g (16.9%) of product. It was recrystallized from ethanol. No attempt was made to maximize the yield. *Anal.* Calcd for $C_{36}H_{31}P_2O_6Cl$: C, 65.81; H, 4.76. Found: C, 65.38; H, 4.75.

$(C_6H_5)_3PO \cdot HCl$.—Hydrogen chloride was bubbled through a solution of 2.0 g (7.2 mmol) of triphenylphosphine oxide dissolved in 25 ml of ethanol for 2 hr. The solution was allowed to evaporate slowly until crystals formed. The solid was isolated by filtration, washed with diethyl ether, and dried. The white solid weighed 0.75 g (33.2%). No attempt was made to increase the yield. *Anal.* Calcd for $C_{18}H_{16}POCl$: C, 68.69; H, 5.12. Found: C, 67.96; H, 5.37. The melting point is 112–114°, which is in agreement with that obtained by Hadzi.[6]

Results and Discussion

Recently it was shown that rhenium(V) chloride and water react as follows[7]

$$7ReCl_5 + 12H_2O \longrightarrow 2Re_2Cl_9^{2-} + 3ReO_4^- + 17HCl + 7H^+$$

The water serves as an agent for the dimerization of the rhenium and for the formation of an acid solution necessary for the formation of the cation $[(C_6H_5)_3PO]_2H^+$. In the present work, water can come from two sources. It may be an impurity in the acetone or may be produced from the condensation of acetone, which has been shown to occur in the presence of rhenium(V) chloride.[8] Since no other solvents have been found in which rhenium(V) chloride and triphenylphosphine oxide react, this reaction again illustrates the unique character of acetone. Rhenium(V) chloride was shown to react differently from $MoCl_5$, $TaCl_5$, or $NbCl_5$, where oxygen abstraction from the triphenylphosphine oxide takes place.[9]

During a study of the coordination chemistry of indium, a second compound containing the cation was observed. When solid $In(ClO_4)_3 \cdot 8H_2O$ was exposed to moist air, it turned to a semiliquid. The reaction of this material with triphenylphosphine oxide in ethanol did not lead to the desired product $\{In[(C_6H_5)_3PO]_4\}(ClO_4)_3$[10] but to $\{[(C_6H_5)_3PO]_2H\}ClO_4$. It is felt that, upon standing, the $In(ClO_4)_3 \cdot 8H_2O$ reacts further with water to form perchloric acid and some unknown indium species, with the subsequent reaction of perchloric acid with triphenylphosphine oxide. This was shown to be the case, since the utilization of new, solid $In(ClO_4)_3 \cdot 8H_2O$ led to the isolation of the anticipated indium complex, while the reaction of perchloric acid and triphenylphosphine oxide resulted in the isolation of $\{[(C_6H_5)_3PO]_2H\}ClO_4$.

As Hadzi[6] had reported formation of $\{[(C_6H_5)_3PO]_2H\}Cl$ and its infrared spectrum, we attempted to reproduce it for comparison of the infrared spectrum to the compounds described in this paper. Numerous attempts to produce the complex were unsuccessful. These included varying the mole ratio of hydrogen chloride to triphenylphosphine oxide, as well as the amount of water present in the ethanol. Only $(C_6H_5)_3PO \cdot HCl$ was isolated, and its infrared spectrum and elemental analyses were invariant after 1 year. We are unable to account for this difference.

The infrared spectra of the salts are indicative of a hydrogen-bonded cation with a broad band in the area of 1000–800 cm^{-1}. In the hydrogen-bonding region, these spectra compare favorably with those obtained for $[(antipyrine)_2H]ClO_4$[11] and the protonic complexes of $HAuCl_4$.[2] The spectrum of $(C_6H_5)_3PO \cdot HCl$ is identical with that obtained by Hadzi for $\{[(C_6H_5)_3PO]_2H\}Cl$. In the case of the perchlorate salt the presence of noncoordinated ClO_4^- is indicated. The features are otherwise routine.

We believe that these results indicate that the formation of the cation is more widespread than previously thought, and its existence should be possible in an acid solution which contains a bulky noncoordinating anion.

---

(3) L. C. Hurd and E. Brimm, *Inorg. Syn.*, **1**, 180 (1939).

(4) F. E. Beamish, *Ind. Eng. Chem., Anal. Ed.*, **5**, 348 (1933).

(5) F. Bonati and F. A. Cotton, *Inorg. Chem.*, **6**, 1353 (1967).

(6) D. Hadzi, *J. Chem. Soc.*, 5128 (1962).

(7) E. A. Allen, N. P. Johnson, D. T. Rosevear, and W. Wilkinson, *Inorg. Nucl. Chem. Lett.*, **5**, 239 (1969).

(8) H. Gehrke, Jr., and G. Eastland, *Inorg. Chem.*, **9**, 2722 (1970).

(9) A. D. Beveridge and H. C. Clark, *Halogen Chem.*, **3**, 179 (1967).

(10) A. J. Carty and D. G. Tuck, *J. Chem. Soc.*, 6012 (1964).

(11) P. Ramamruthy, V. V. Savant, and C. C. Patel, *Indian J. Chem.*, **7**, 917 (1969).

CONTRIBUTION FROM THE CENTRO DI STABILITÁ E
REATTIVITÁ DI COMPOSTI DI COORDINAZIONE,
CNR, ISTITUTO DI CHIMICA GENERALE,
UNIVERSITÁ DI PADOVA, PADUA, ITALY

The Reaction of Hydrogen Cyanide with Bis[1,4-bis(diphenylphosphino)butane]nickel(0)

BY C. CORAIN,* P. RIGO, AND G. FAVERO

Received November 6, 1970

Recently it has been reported that the Ni(0) complexes $Ni(P(OC_2H_5)_3)_4$ and $Ni(P(C_6H_5)_2(CH_2)_2P$-

$(C_6H_5)_2)_2$ react with strong nonaqueous acids in various solvents to give hydrido complexes of the type NiL_4H^+.[1,2] In addition, the observation that $Ni(P(OC_2H_5)_3)_4$ reacts with HCN in benzene to give $NiH(P(OC_2H_5)_3)_3CN$ is reported in a patent specification.[3] These papers prompt us to describe the reaction of HCN with $Ni(dpb)_2$ (dpb = 1,4-bis(diphenylphosphino)butane) in which the oxidation reaction pattern seems to be quite different from that shown by related compounds.[1-4]

Experimental Section

All operations were carried out in an atmosphere of argon, the solvents were dried by conventional methods, and $Ni(dpb)_2$ was prepared as described previously.[5] Infrared spectra were recorded on a Perkin-Elmer 357 and absorption in the visible region was measured by an Optica CF4 instrument. HCN was thoroughly degassed and saturated with argon.

A three-necked flask (50 or 100 ml) was fitted with a gas-tight rubber cap, a stirrer, and a device which enabled solid samples to be added under an inert atmosphere. In this device the complex (0.1–0.5 mmol) was placed in a Teflon cylindric container, where the compound could be thoroughly degassed. The appropriate volume of argon-saturated solution of HCN in benzene (1–2 *M*) and pure benzene was introduced by means of the rubber cap and a suitable syringe. An infrared spectrum taken at this stage could be used later as a reference. The complex was then added to the flask and stirred vigorously until it had dissolved. The presence of HCN seemed to facilitate solution. Samples for ir analysis were carefully sucked from reaction mixtures by means of stainless steel and glass syringes and transferred to a cell with NaCl windows of suitable path length. As the reaction proceeded, however, a precipitate was formed and Millipore filtering equipment, previously filled with argon, was used to obtain a perfectly clear solution for analysis. The use of this technique enabled the infrared spectrum of the solid products to be recorded immediately after that of the filtrate.

The reaction products were recognized as $[(Ni^ICN(dpb)_{1.5}]_2$[6] and $[Ni^{II}(CN)_2(dpb)]_2$[7] from their characteristic infrared and visible spectra. The latter product often appeared to be contaminated with the pentacoordinated species.[7] The spectrophotometric determination of the concentration of $Ni(CN)_2(dpb)_2$ was carried out by adding a suitable excess of dpb to the solution containing the Ni(II) complexes at the end of the reaction. $[Ni(CN)_2dpb]_2$ present is transformed into the pentacoordinated species (Figure 2).[7]

The presence of hydrogen and hydrogenated products of benzene was investigated by means of a Hewlett-Packard 5750 gas chromatograph. A Poropak Q or molecular sieve column, 2 m long, was used for gases while for the liquids a 2-m long column filled with β,β'-oxydipropionitrile on Chromosorb Q (15%) was employed. The possibility that products with high boiling temperatures were present led to the use of a column filled with dinonyl phthalate on Chromosorb at 150°, but none was detected. The benzene used for chromatographic experiments was very pure and practically free from cyclohexane. DCN was prepared from DCl and dry KCN in D_2O.

Results and Discussion

A comparison of the infrared spectra of the reaction products in solution with those of independently prepared compounds shows that the addition of HCN to a solution of $Ni(dpb)_2$ in benzene initially leads to the formation of $[NiCN(dpb)_{1.5}]_2$[6] ($\nu_{CN} = 2100\ cm^{-1}$) followed by the production of $[Ni(CN)_2(dpb)]_2$[7] ($\nu_{CN} = 2115\ cm^{-1}$). The infrared spectrum of a benzene reacting solution after a few minutes at 20° is shown in Figure 1. In the region 2000–2200 cm^{-1} three bands appear, *i.e.*, 2100, 2085 (ν_{CN} of free HCN), and 2065 cm^{-1}. The clear reddish yellow solution soon deposits yellow crystals and the ir bands at 2100 and 2065 cm^{-1} lose intensity while a weak shoulder appears at 2115 cm^{-1}. The color of the solution gradually becomes darker and the yellow solid can be identified as $[Ni(CN)_2(dpb)]_2$. The band at 2065 cm^{-1} does not arise from an Ni–H stretching mode since the reaction with DCN only moves the absorption to 1830 cm^{-1} (ν_{CN} of DCN is 1910 cm^{-1}), and this band was attributed to coordinated HCN. However, the possibility that small quantities of hydrido species are present as intermediates cannot be ruled out. Attempts have been made to follow the reaction in an nmr tube in C_6D_6, but the reaction products are insufficiently soluble and no reliable information could be obtained.

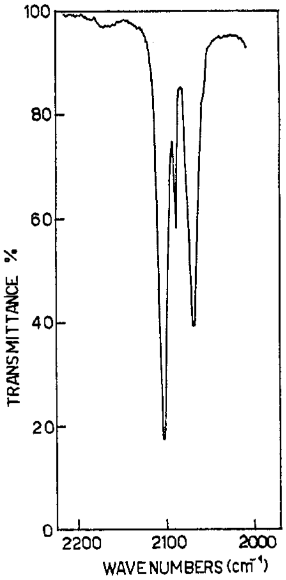

Figure 1.—Ir spectrum of a benzene solution containing $Ni(dpb)_2$ (5×10^{-2} *M*) and HCN (3×10^{-1} *M*); cell path 0.45 mm.

When the reaction was carried out in ethyl ether, the reaction products were practically insoluble and after 30 min at 20° only $[NiCN(dpb)_{1.5}]_2$ mixed with dpb was isolated; that is oxidation had only occurred as far as the Ni(I) species. However, after 30 min in benzene, a noticeable amount of Ni(II) complex was present. Little amounts of cyclohexane (recovery of hydrogen calculated for the oxidation to Ni(I) is *ca.* 5%) were detected in some experiments; however the reproducibility of this finding was rather scarce. In all experiments carried out other low-boiling hydrogenation products of benzene were absent. No H_2 was detected as a reaction product in benzene, only trace amounts were detected in ether, and no trace at all was found in dichloroethane, which was also employed as a solvent. The destiny of the HCN hydrogen atom remains therefore uncertain in the investigated reaction.

Our interpretation of the data available is that the initial reaction of HCN with $Ni(dpb)_2$ goes *via* a very reactive hydride intermediate to $[NiCN(dpb)_{1.5}]_2$ (ν_{CN} 2100 cm^{-1}). An adduct of the type $NiCN(dpb)_{1.5} \cdot HCN$[8] is then formed between HCN and the

---

(1) W. C. Drinkard, D. R. Eaton, J. P. Jesson, and R. V. Lindsey, Jr., *Inorg. Chem.*, **9**, 392 (1970).

(2) R. A. Schunn, *ibid.*, **9**, 394 (1970).

(3) W. C. Drinkard, C. Williams, Jr., R. V. Lindsey, Jr., and V. Richard, Jr., German Patent 1,808,434 (1969); *Chem. Abstr.*, **71**, 70093 (1969).

(4) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

(5) B. Corain, P. Rigo, and M. Bressan, *Chim. Ind.* (*Milan*), **51**, 386 (1969).

(6) B. Corain, M. Bressan, P. Rigo, and A. Turco, *Chem. Commun.*, 509 (1968).

(7) P. Rigo, B. Corain, and A. Turco, *Inorg. Chem.*, **7**, 1623 (1968).

(8) Examples of coordination of HCN to metal atoms can be found in the following references: (a) M. F. A. Dove and J. G. Hallet, *J. Chem. Soc.*, 1204 (1969); (b) J. F. Guttemberger, *Chem. Ber.*, **101**, 403 (1968); (c) K. Kawai and I. Kanesaka, *Spectrochim. Acta, Part A*, **25**, 1265 (1965).

Ni(I) complex (ν_{CN} 2065 and 2100 cm^{-1}) followed by the slow formation of the final products, $[Ni(CN)_2(dpb)]_2$ (ν_{CN} 2115 cm^{-1}) and $Ni(CN)_2(dpb)_2$ (ν_{CN} 2100 cm^{-1}).[7] The formation of small amounts of the pentacoordinated species of Ni(II) which displays the ν_{CN} band at 2100 cm^{-1} does not complicate the assignment of the strong band at 2100 cm^{-1} to Ni(I) species, because the intensity of this band was very high, whereas the Ni(II) complex is sparingly soluble in benzene even in the presence of an excess of HCN. Moreover it is reasonable to suppose that both $[NiCN(dpb)_{1.5}]_2$ and $NiCN(dpb)_{1.5} \cdot HCN$ display a 2100-cm^{-1} ν_{CN} band, as experiments performed on some Ni(II) complexes, for example on $Ni(CN)_2(P(C_3H_7)_3)_2$,[9] show that quite similar adducts are formed and the ν_{CN} due to the CN coordinated directly to the metal is unaffected by the coordination of HCN.

The reaction between $Ni(dpb)_2$ and HCN was also followed in dichloroethane, and the ir pattern was similar to that observed in benzene, but the relatively good solubility of the pentacoordinated Ni(II) species complicated the assignment of the band at 2100 cm^{-1}.

Absorption spectra in the visible region were also taken during the reaction in dichloroethane and are consistent with the interpretation of the infrared spectrum. A few minutes after $Ni(dpb)_2$ had been added to an HCN solution at 20°, the visible spectrum (Figure 2) closely resembled that of a solution containing $[NiCN(dpb)_{1.5}]_2$ at the same initial concentration of $Ni(dpb)_2$ in the presence of the identical concentration of HCN. The final products were found to correspond to a mixture of $[Ni(CN)_2(dpb)]_2$ and the pentacoordinated species, which are known to exist in equilibrium.[7] Spectrophotometric determination of the total amount of Ni(II) complexes showed that 95% of the Ni(0) complex has been oxidized to Ni(II) species.

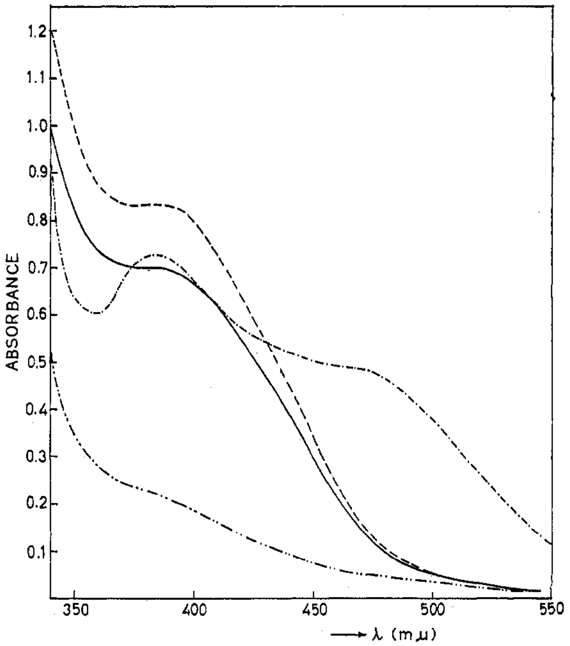

Figure 2.—Visible spectra of reaction solutions: ——, $[Ni(dpb)_2] = 4.8 \times 10^{-4}$ *M*, $[HCN] = 6.2 \times 10^{-2}$ *M*; -··-··-··-, t_∞; -·-·-·-, t_∞ after addition of dpb (*ca.* 1.2×10^{-2} *M*); ------, $[[NiCN(dpb)_{1.5}]_2] = 4.8 \times 10^{-4}$ *M*, $[HCN] = 6.2 \times 10^{-2}$ *M*. Cell path 0.5 cm.

The reactions of the Ni(I) complex $[Ni(CN)(dpb)_{1.5}]_2$ with HCN in $C_2H_4Cl_2$ and benzene were also investigated. The ir patterns in solution were found to be identical with those observed with $Ni(dpb)_2$, confirming thus that the Ni(I) complex is an intermediate in the oxidation of $Ni(dpb)_2$.

It would seem that the oxidative addition of HCN to $Ni(dpb)_2$ is rather peculiar in that no hydride species are discernible, no hydrogen is evolved, and two separated formal oxidation state changes of 1+ are observed. It may well be that very reactive hydrides such as $Ni(CN)(dpb)H$ or $Ni(dpb)_2H^+$ [3] are present in relatively low concentration.

[9] B. Corain, to be submitted for publication.

Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

The Crystal Structure of Mercury(II) Cyanonitrate

By Carol Mahon and Doyle Britton*

Received November 9, 1970

Infinite linear chains –M–CN–M–CN–M–, with disordered cyanide groups, occur in crystalline AuCN,[1] AgCN,[2] and $AgCN \cdot 2AgNO_3$;[3] chains of the type –Ag–NC–Hg–CN–Ag– occur in $Hg(CN)_2 \cdot AgNO_3 \cdot H_2O$.[4] The structure of $Hg(CN)(NO_3)$, reported here, was examined to see whether similar infinite linear chains –Hg–CN–Hg–CN–Hg– were present.

Experimental Section

Upon evaporation of a solution made up from a concentrated solution of $Hg(CN)_2$ and an equal volume of concentrated HNO_3, a mass of tetragonal and hexagonal prisms formed. The crystals were separated by hand under a microscope. A precession photograph of one of the tetragonal crystals was identical with a similar photograph from a known sample of $Hg(CN)_2$.

The infrared spectrum of the hexagonal crystals shows a C–N stretching band at 2245 cm^{-1}, indicative of a bridging cyanide group,[5] and characteristic nitrate bands. Only one report of the compound $Hg(CN)_2 \cdot Hg(NO_3)_2$ mentions a hexagonal form. In 1839 Johnston[6] described the residue after evaporation of a dilute HNO_3 solution of $(HgCN)_2O$ as "quadrangular prisms, hexagonal plates, and pearly scales." He did not appear to realize that this was a mixture, not a pure compound.

The cell dimensions of the hexagonal crystals, estimated from film data, were determined accurately by least-squares calculations from the θ angle values of 17 peaks scanned with a diffractometer using Mo Kα radiation (λ 0.7107 Å). The dimensions are $a = 5.422$ (1) Å and $c = 5.252$ (2) Å. The density from flotation in thallous formate–thallous malonate solution, 3.60 (2) g/cm^3, agrees with the density of 3.585 (2) g/cm^3 calculated assuming one unit of $Hg(CN)(NO_3)$ per cell.

Precession and oscillation photographs showed no systematic extinctions and no doubling of the *c* dimension. The film data

---

[1] *Nat. Bur. Stand.* (*U. S.*), *Circ.*, **No. 539**, **10**, 33 (1960); G. S. Zhdanov and A. E. Shugam, *Zh. Fiz. Khim.*, **19**, 519 (1945); G. S. Zhdanov and A. E. Shugam, *Acta Physicochim. U.R.S.S.*, **20**, 253 (1945).

[2] C. D. West, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **88**, 173 (1934); **90**, 555 (1935).

[3] D. Britton and J. D. Dunitz, *Acta Crystallogr.*, **19**, 815 (1965).

[4] C. Mahon and D. Britton, *Inorg. Chem.*, **10**, 586 (1971).

[5] D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

[6] J. F. W. Johnston, *Phil. Trans. Roy. Soc. London*, **129**, 113 (1839).