and that $[f_{BH_n^+\cdot(H_2O)_n} f_{ROH}]/f_{R^+}f_B \cong 1$ (in addition since there is evidence that $f_{ROH}/f_B = 1$ for this region of acidity,[3a,8] $f_{BH_n^+\cdot(H_2O)_n} \cong f_{R^+}$).

In the region 60–75% H_2SO_4, H_O was obtained[7] for two primary amines, 2,6-dinitro-4-methylaniline and 2,4-dinitroaniline, of closely similar behavior and a tertiary amine, N,N-dimethyl-2,4,6-trinitroaniline, whose behavior has been recognized as "divergent."[8] These results are illustrated in Fig. 2 in which again ($H_R - H_O$) is plotted *vs.* log a_{H_2O}.

The plots of Fig. 2 lead to curved rather than linear relationships. However, this result is perhaps expected in terms of the above interpretation in view of the limited availability of "excess" water molecules for hydrogen bonding with the anilinium ions. It appears significant that the curve for the tertiary amine rapidly approaches an approximately unit slope, whereas the slope for the primary amines is distinctly greater than unity throughout this region of acidity. The former behavior is consistent with earlier evidence suggesting that the single proton of the conjugate acid of a *tert.* amine is relatively poorly solvated by hydrogen bonding.[5b] It is well known[8] that in the region of no excess water molecules (83–100% sulfuric acid) H_R differs quite generally from H_O by log a_{H_2O}.

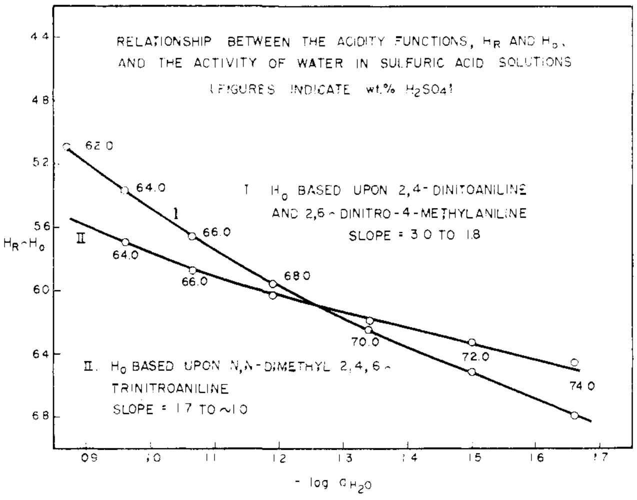

Fig. 2.

Similar plots of ($H_R - H_O$) *vs.* log a_{H_2O} in the acidity region below 40% H_2SO_4 are curved with slopes distinctly larger than 3 or 4. These results suggest that with an abundance of available water molecules, additional hydrogen bonding (and perhaps other 3a) interactions of weak and variable strengths occur (with $BH^+_n\cdot(H_2O)_n$, ROH, and B) thus invalidating the activity coefficient relationship proposed above.

The present proposals have important consequences concerning acidity function theory and prompt additional investigation and review of previously accepted concepts. It is of interest to note that Bell's recent interpretation (along rather similar lines) of the H_O function in terms of the $H_9O_4^+$ ion, apparently imposes the conditions:[2] $f_{ArNH_3^+}/f_{H_9O_4^+} \cong 1$. In terms of the present evidence, it appears that the $H_9O_4^+$ ion ($H_3O^+\cdot(H_2O)_3$), must be further solvated to a weaker extent by hydrogen bonding interactions of similar strength and degree to those involved with the $ArNH_3^+$ ions.

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[8] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

SYNTHESIS OF VANADIUM HEXACARBONYL

Sir:

Some properties and the structure of the vanadium hexacarbonyl have been described.[1] The existence of this compound demonstrates, for the first time, that a transitional element with atomic number lower than 24 is able to form a true carbonyl. Here we describe the synthesis of the $V(CO)_6$ as well as the preparation of salts of $[V(CO)_6]^-$ anion.

Simple and easily available vanadium compounds such as anhydrous VCl_3, $VOCl_3$, V(III) acetylacetonate are caused to react at 80–150° with a metal–amine reducing system and with pressurized carbon monoxide. Using Mg + Zn and excess of pyridine as reducing agent, the carbonylation of vanadium compounds occurs easily at 120–140° with consumption of about the theoretical amount of carbon monoxide. This method for the "reducing carbonylation" of transitional elements was reported previously[2] for a high yield synthesis of $Cr(CO)_6$ and was proved to be operative also to prepare other metal carbonyls, especially $Mo(CO)_6$. It is noteworthy that the carbonylation of vanadium compounds does not afford free $V(CO)_6$ directly as it normally occurs in the $Cr(CO)_6$ synthesis. Actually the reduction of vanadium goes further, the metal being present in the carbonylation products principally in the −1 state as $[V(CO)_6]^-$. In fact, working up the reaction mixture, aqueous solutions can be obtained from which the salts: $Ni(o\text{-fen})_3[V(CO)_6]_2$ as well as Na.2 dioxane $[V(CO)_6]$ can be isolated. Moreover the vanadium hexacarbonyl is obtained in fairly good yields (40–50%) when the residue from evaporating the liquid phase of the reaction mixture is acidified and ether extracted. An evidence for an intermediate hydrocarbonyl lies in the rapid evolution of hydrogen observed during the concentration of the ethereal layer.

Thus the carbonylation products are suitable for preparing either the $V(CO)_6$ or the salts of the anion $[V(CO)_6]^-$. The latter also can be obtained by the reaction of the hexacarbonyl with Lewis bases such as di-*n*-butyl ether, dioxane, pyridine, methanol, acetone, according to the scheme

$$3V(CO)_6 + nB \longrightarrow V(B)_n[V(CO)_6]_2 + 6CO$$

The vanadium hexacarbonyl is a volatile, air sensitive, blue-green substance which decomposes at 60–70° (capillary sealed under N_2). In the solid state, it is paramagnetic for 1 electron and has a crystal

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[1] G. Natta, R. Ercoli, F. Calderazzo, A. Alberola, P. Corradini and G. Allegra, *Rend. Accad. Naz. Lincei*, [8] **27**, 107 (1959).

[2] G. Natta, R. Ercoli, F. Calderazzo and A. Rabizzoni, THIS JOURNAL, **79**, 3611 (1957); R. Ercoli, F. Calderazzo, G. Bernardi, *Gazz. Chim.*, **89**, 809 (1959).

structure strictly similar to that of the hexacarbonyls of the 6th group metals.[1]

These results, which indicate that the carbonyl is mononuclear, were confirmed recently[3] in view of the more recent report of a diamagnetic divanadium dodecacarbonyl.[4]

Experimental.—An oscillating stainless steel autoclave of 510 ml. capacity is charged with 9.9 g. of anhydrous VCl_3, 220 g. of dry pyridine and 16.0 g. of 1:2.7 by weight mixture of magnesium and zinc powders, previously activated by addition of 2 g. of iodine. The reactants in the autoclave are vigorously stirred in order to keep the solid materials loosely dispersed, then carbon monoxide is added up to 135 atm. The autoclave is warmed up to 135° and maintained at this temperature for 8 hours while the pressure drops from 208 atm. to 160 atm.

After cooling, gases are vented and the reaction mixture is transferred under nitrogen atmosphere, with pyridine of washings, in a decantation flask. After one day the supernatant liquid is separated and cold-evaporated to a solid mass at a pressure of about 1 mm. Then 200 ml. of water and 400 ml. of very pure diethyl ether are added to the solid residue, which is then cooled and acidified under the hood with 300 ml. of 4 *N* HCl with intermittent shaking. The ether layer is removed as soon as possible, washed with diluted HCl and water, dried overnight on $MgSO_4$ and vacuum-evaporated. From the concentrated brown solution, hydrogen is evolved. The crystalline residue by sublimation at 15 mm. and 40–50° gives moist vanadium hexacarbonyl which is dried under nitrogen on P_2O_5 and resublimed (yield 5.3 g., 38%). Care must be taken during the ether evaporation and sublimation to avoid losses of compound by volatilization or by ignition.

Anal. Calcd. for $V(CO)_6$: V, 23.26; CO, 76.74. Found: V, 23.42; CO, 76.20.

(3) G. Natta, R. Ercoli, F. Calderazzo, R. Cini, P. Corradini, paper submitted to the Editor of *Chemistry and Industry*.

(4) R. L. Pruett and J. E. Wyman, *Chem. and Ind.*, 119 (1960).

(5) Fellowship of Juan March Foundation, Madrid, Spain.

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A NEW TYPE OF TETRAHEDRAL COMPLEX OF NICKEL(II)

Sir:

Recently, several kinds of authentic tetrahedral complexes of nickel(II) have been prepared and/or recognized: those of the kind $[NiX_4]^{-2}$ (X = Cl,[1,2,3] Br,[1,2] I,[1] NCS[4]) and those of the kind $[NiL_2X_2]^0$ (L = $(C_6H_5)_3P$, X = Cl, Br, I[5]; L = $(C_6H_5)_3PO$, X = Cl, Br, I[6]; L = $(C_6H_5)_3AsO$, X = Cl, Br[7]). We report here the preparation and characterization of two members of a new class of tetrahedral Ni(II) compounds. The new species, of the general type $[LNiX_3]^{-1}$, where L is a neutral ligand and X an anionic ligand, occur in the compounds $[(C_2H_5)_4N][(C_6H_5)_3PNiBr_3]$ and $[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PNiI_3]$.

$[(C_2H_5)_4N][(C_6H_5)_3PNiBr_3]$ is a green, crystalline solid which separates on cooling a stoichiometric mixture of $[(C_2H_5)_4N]Br$, $(C_6H_5)_3P$ and $NiBr_2$ in hot butanol. [*Anal.* Calcd. for $C_{26}H_{35}Br_3NNiP$: C, 45.19; H, 5.11; N, 2.03; Ni, 8.49; P, 4.48. Found: C, 44.80; H, 4.98; N, 2.07; Ni, 8.61; P, 4.74.] A millimolar solution in nitromethane has a molar conductance of 80 ohm.$^{-1}$. The solid has an effective magnetic moment of 3.66 B.M. at 300°K. The visible spectrum of a nitromethane solution has these absorption bands[8]: 386 (3040), 635 (240), 675 (~224, sh), 1050 (108), 1150 (90), ~1600 (~40, very broad). The first band is almost certainly a charge transfer band. The remaining ones would appear to be due to *d-d* transitions, but cannot be accommodated on the energy level diagram given by Liehr and Ballhausen[9] for nickel(II) in fields of T_d symmetry. This observation is in agreement with a considerable body of spectral data we have collected on complexes of the type L_2NiX_2 and L_2CoX_2 which show that the relatively simple energy level pattern for a regular tetrahedral complex of T_d symmetry, $[NiX_4]^{-2}$, is considerably perturbed on replacing some X's by phosphines.

$[(n\text{-}C_4H_9)_4N][(C_6H_5)_3PNiI_3]$ is a very deep red crystalline compound obtained from a butanol solution of $[(n\text{-}C_4H_9)_4N]I$, $(C_6H_5)_3P$ and NiI_2 in stoichiometric proportions by evaporation in vacuum to a very small volume. [*Anal.* Calcd. for $C_{34}H_{51}I_3NNiP$: C, 43.25; H, 5.44; N, 1.48; P, 3.28. Found: C, 42.92; H, 5.01; N, 1.64; P, 3.04.] The solid has an effective magnetic moment of 3.46 B.M. at 300°K. The visible spectrum in benzene has these absorption bands: 765 (450), 1095 (233). There is very strong absorption below ~600 cm.$^{-1}$. A millimolar solution in nitromethane has a molar conductance of 72 ohm.$^{-1}$.

We believe that these compounds are the first tetrahedral nickel(II) complex anions of their type to be recognized. We note, however, that they may not be the first to have been prepared, although we had no reason to doubt that they were at the time this work was done. Quite recently, a note by Matsunaga[10] called attention to the existence of compounds he formulates as $[(C_6H_5)_3P]_2NiBr_2\cdot$*tert*-$C_4H_9Br$ and $[(C_6H_5)_3P]_2NiBr_2\cdot 2C_6H_5Br$. (Other similar compounds which were *written* as solvates of bis-(triphenylphosphine)-nickel(II) bromide have been mentioned by Reppe and Schweckendiek[11] and by Yamamoto.[12]) However, Matsunaga states that the two compounds he mentions have magnetic moments of 3.4 and 3.8 B.M., respectively, as compared with a moment of 3.2 B.M. he reports for $[(C_6H_5)_3P]_2NiBr_2$. He attributes

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(5) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

(6) F. A. Cotton and D. M. L. Goodgame, THIS JOURNAL, **82**, in press (1960).

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(8) Band positions in mμ with molar extinction coefficients given in parentheses; sh = shoulder.

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