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.

DEPARTMENT OF INDUSTRIAL CHEMISTRY R. ERCOLI
POLYTECHNIC INSTITUTE OF MILAN F. CALDERAZZO
MILAN, ITALY A. ALBEROLA[5]

RECEIVED MARCH 21, 1960

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 ($\sim$224, sh), 1050 (108), 1150 (90), $\sim$1600 ($\sim$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 $\sim$600 cm.$^{-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 $[(C_6H_5)_3P]_2NiBr_2 \cdot tert\text{-}C_4H_9Br$ 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

(1) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(2) F. A. Cotton and R. Francis, THIS JOURNAL, **82**, June 20, (1960); *ibid.*, in press.

(3) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).

(4) F. A. Cotton and D. M. L. Goodgame, to be published.

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

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

(7) F. A. Cotton and D. M. L. Goodgame, *ibid.*, in press.

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

(9) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959).

(10) Y. Matsunaga, *Can. J. Chem.*, **38**, 621 (1960).

(11) W. Reppe and W. J. Schweckendiek, *Ann.*, **560**, 104 (1948).

(12) K. Yamamoto, *Bull. Soc. Chem. Japan*, **27**, 501 (1954).

these exaltations in the moment to changes in the bond angles in $[(C_6H_5)_3P]_2NiBr_2$, such that they become more nearly tetrahedral. This explanation is entirely untenable since (a) although the bond angles in $[(C_6H_5)_3P]_2NiBr_2$ have not been reported, those in $[(C_6H_5)_3P]_2NiCl_2$ are reported by Venanzi to be very near to 109°,[13] and (b) regardless of the exact bond angles, the vast difference in the two kinds of ligands may be expected to cause a quenching of most of the considerable orbital moment expected in a tetrahedral nickel(II) complex with true T_d symmetry. We believe that the most likely explanation of Matsunaga's results is that under the conditions (long heating) required for formation of the "solvates," quaternization of the phosphine occurs so that the compounds are actually $[(C_6H_5)_3\text{-}(tert\text{-}C_4H_9)P][(C_6H_5)_3PNiBr_3]$ and $[(C_6H_5)_4P]_2[NiBr_4]$. In fact, Reppe and Schweckendiek imply that a compound analogous to the former can be prepared from $[(C_6H_5)_3P(C_4H_9?)]Br$, $(C_6H_5)_3P$ and $NiBr_2$.

Our investigations of this class of compounds are continuing. We thank the U. S. Atomic Energy Commission for financial support under Contract No. AT(30-1)-1965.

---

(13) L. M. Venanzi, *J. Inorg. Nucl. Chem.*, **8**, 141 (1958).

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS
F. A. COTTON
D. M. L. GOODGAME

RECEIVED APRIL 25, 1960

A NEW HEXABORANE

Sir:

Recent studies of the mass spectra of the boranes indicate the probable existence of a hexaborane with a minimum of twelve hydrogen atoms. The compound may be the hexaborane-12 originally described but subsequently withdrawn by Stock.[1] The presence of hexaborane-12 might account for the erroneous vapor pressure measurements attributed to hexaborane-10.[2] Specifically, Stock reported the vapor pressure of hexaborane-10 as 7.2 mm. at 0° whereas we found it to be 11.85 mm.[3]

The two hexaboranes differ widely in thermal stability; at room temperature B_6H_{10} is fairly stable,[3] whereas the new hexaborane decomposes very rapidly—hence making its identity elusive until now. Actually it was not until we observed a discrepancy in vapor pressure values and the reasonable stability of purified hexaborane-10 as contrasted to previous reports that we realized there was an unknown compound accounting for these differences.

To determine the identity of this unknown compound, we prepared a sample for mass spectroscopic analysis by subjecting diborane to an electric discharge[4] and then making a gross separation of products by pumping the more volatile compounds from the sample. The sample was maintained cold until introduced into a CEC Model 21-103 mass spectrometer for analysis, which revealed the presence of the new hexaborane. The severe heat treatment used in our previous work[3] for purifying hexaborane-10 would have completely destroyed this new hexaborane.

A comparison in the *m/e* 65–78 range of the polyisotopic mass spectrum of pure hexaborane-10[3] (cut-off at *m/e* 76) and that of the new hexaborane (labeled B_6H_{12}) contaminated by hexaborane-10 is given in Table I. Additionally, the new hexaborane spectrum is contaminated by about 3% heptaborane (assuming equal sensitivity of the dominant peaks) and a trace of octaborane. As indicated below, the peaks at *m/e* 77 and 78 are real, and are part of a parent grouping of peaks in the B_6 range that cannot be attributed to B_6H_{10}. This together with the sharp cut-off at *m/e* 78 leaves no question of the existence of another hexaborane, which may be either hexaborane-12, or possibly hexaborane-14. Precedent for the latter is found in the case of tetraborane-10 and pentaborane-11 since the mass spectra of both these compounds cut off at two mass units lower than their corresponding molecular weights.

TABLE I

COMPARISON OF POLYISOTOPIC MASS SPECTRA OF HEXABORANES

	Relative intensities			Relative intensities	
m/e	B_6H_{12}[a]	B_6H_{10}[3]	*m/e*	B_6H_{12}[a]	B_6H_{10}[3]
78	7.3	..	71	100	100
77	11.0	..	70	75.5	79.4
76	34.8	22.6	69	54.1	57.7
75	43.5	34.1	68	41.8	44.0
74	60.7	48.2	67	39.0	41.5
73	63.5	49.4	66	32.4	35.4
72	93.6	86.9	65	18.8	20.7

[a] Includes contaminants of hexaborane-10, heptaborane (*ca.* 3%), and octaborane (trace amount).

That the peaks at *m/e* 77 and 78 cannot be due to contamination by compounds other than boranes is inferred from the fact that the polyisotopic spectrum can be reduced to a monoisotopic one on the basis of $B_6H_x^+$ with only negligible residues. If effective peak heights at both *m/e* 77 and 78, or *m/e* 77 alone, were reduced by as much as 5%, negative residues would occur in the monoisotopic spectrum. The possibility that *m/e* 78 could be due entirely to contamination cannot be eliminated by this method; however, the carefully controlled experimental work leads us to believe that there is no non-borane contaminant present.

The possibility that the peaks at *m/e* 77 and 78 are due primarily to heptaborane was eliminated by "stripping" the heptaborane contribution (based on principal peaks at *m/e* 83 or 87)[5] from

---

(1) A. Stock and W. Siecke, *Ber.*, **57**, 566 (1924).

(2) A. Stock and E. Kuss, *ibid.*, **56**, 789 (1923).

(3) S. G. Gibbins and I. Shapiro, *J. Chem. Phys.*, **30**, 1483 (1959).

(4) W. V. Kotlensky and R. Schaeffer, THIS JOURNAL, **80**, 4517 (1958).

(5) In our studies we have observed repeatedly the mass spectra of two heptaboranes. One of these (principal peak at *m/e* 83) is similar to that reported recently[6]; the other has a dominant peak at *m/e* 87. Contamination by *ca.* 15% octaborane prevents a precise determination of the cut-off peak of the heptaboranes. If the octaborane is the same as that reported,[7] then the cut-off must be at least as high as *m/e* 92, corresponding to heptaborane-15. Regardless of the lack of precision associated with the mass spectrum of either heptaborane, we feel that only an extremely small error is introduced when this mass spectrum is used to strip 3% heptaborane from hexaborane-12 at *m/e* 77 and 78.

(6) R. W. Schaefer, K. H. Ludlum and S. E. Wiberley, THIS JOURNAL, **81**, 3157 (1959).

(7) I. Shapiro and B. Keilin, *ibid.*, **76**, 3864 (1954).