quite reasonable. The value of ρ_4 is closer to that for $NiBr_4^{-2}$, 4560 cm.$^{-1}$, than would have been expected if the distortion were neglected. However, it is still rather high, a fact that we must ascribe to the larger covalency of the more electronegative copper ion. The ratio ρ_2/ρ_4 is 0.9, in consonance with previous experimental determinations which suggest this ratio is considerably smaller than the value of 2 or 3 predicted by Hartree-Fock metal ion functions.[5]

The predicted splitting of the T_2 state is very large and the ground state is non-degenerate as required by the Jahn-Teller theorem. Ballhausen and Liehr[6] have correctly pointed out that even tetrahedral $CuBr_4^{-2}$ is strictly not a case to which this theorem applies since the spin-orbit splitting alone (*ca.* 1000 cm.$^{-1}$) provides a non-degenerate ground state. Comparison with the but slightly distorted $ZnBr_4^{-2}$ ion suggests that spin-orbit coupling is insufficient to stabilize the $CuBr_4^{-2}$ ion against further distortion than already is provided by the lattice.

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(5) H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).

(6) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, **4**, 190 (1960).

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RECEIVED JUNE 25, 1962

The Preparation of a Series of Compounds Containing the Pentachloroalkoxoniobate (IV) Anion

Sir:

We wish to report the preparation of a new class of niobium(IV) compounds. In particular, pyridinium pentachloromethoxoniobate(IV), $(py)_2[Nb(OCH_3)Cl_5]$, has been prepared by the electrolytic reduction of $NbCl_5$ dissolved in anhydrous methanol (saturated with anhydrous HCl), followed by the addition of a hot methanol solution of pyridinium chloride. The compound, which results after cooling for several hours, is obtained as a red-brown, spiny, crystalline agglomerate.

Anal. Calcd. for $(pyH)_2Nb(OCH_3)Cl_5$: C, 28.61; H, 3.27; Cl, 38.45; Nb, 20.13. Found: C, 28.67; H, 3.30; Cl, 38.21; Nb, 20.21.

In agreement with the formulation $Nb(OCH_3)Cl_5^{-2}$, the infrared spectrum reveals no absorption characteristic of the OH group, but does show an intense band at 1095 cm.$^{-1}$ which is not due to pyridinium ion, but is typical of the C–O stretching mode in alkoxides. Furthermore, the spectrum indicates the presence of pyridinium ion and not ligand pyridine.[1]

Magnetic studies indicate Curie–Weiss paramagnetism (Table I) and verify the presence of the niobium(IV) ion, with $4d^1$ configuration.

TABLE I

Temp., °K.	$\chi'_M \times 10^6$	θ	μ_{eff}
299	1020	61°	1.72
196	1425		
77	2700		

The compound is extremely sensitive to air, turning blue and then white. It is soluble in water and gives an immediate brown coloration and then slowly deposits a brown hydrous oxide. It is soluble with decomposition in alcohols. In dimethylformamide, solution is accompanied by a violet color which changes quickly to blue. It is insoluble in dimethyl sulfoxide and common organic solvents, such as benzene, ethers, and ketones.

By varying the organic base and the solvent, a series of methoxy, ethoxy, and isopropoxy compounds has been obtained. They are similar, except in color, to $(py)_2[Nb(OCH_3)Cl_5]$, and will be described in detail in a later publication. Further work will include an investigation of the distinct color differences in these compounds and the preparation of the analogous bromides, iodides, and thiocyanates.

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(1) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

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RECEIVED JULY 25, 1962

Mechanism of Alkylborane Isomerization[1]

Sir:

I wish to present evidence which suggests that an intramolecular bridge hydrogen tautomerism

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(1) Presented at the American Chemical Society Regional Meeting, Los Angeles, Calif., December, 1960.