

resulting in low electron density along the platinum-chloride bonds.^{8,8,9}

Besides the extensive evidence that six π -electrons are favored in aromatic systems, there are two experimental observations that indicate that the $6p_z$ orbital might be involved in pd^2 hybridization of platinum in **1**. (1) Whereas **2** and **3** are conveniently recrystallized from water, **1** is quite insoluble. Although dimethyl sulfoxide is a superior solvent for most of these neutral complexes, **1** is not even very soluble in that solvent. Since solvation probably involves bonding through the empty p_z orbital in square complexes, these observations suggest that in the bipyridyl complex, **1**, the p_z orbital is not available for bonding to solvent—a necessary consequence of the formation of hybrid pd^2 orbitals.¹¹ (2) An example of the solvolysis of **1** has been reported¹²; the rate constant for hydrolysis of **1** is smaller than that of **3** by a factor of four. Such a solvolysis result would be expected if the p_z orbital were not available for bonding with an incoming nucleophile¹⁶ as pd^2 hybridization would require. If this is correct it might mean that the initial interaction of dithiooxamide with platinum(II) complexes is electrophilic,^{1b,1c} and, in fact, **1** may turn out to be diagnostically useful in distinguishing between electrophilic and nucleophilic reagents for displacement in square complexes.

Acknowledgment.—We thank the U. S. Public Health Service for a grant, No. RG-9294, in support of this research, and the National Science Foundation for a grant for P. A. C. under the Undergraduate Research Participation Program.

(8) A third possibility for π -bonding is that a single d orbital (d_{xz} or d_{yz}) on platinum might overlap with the p_z orbitals on both nitrogens.

(9) Displacement of chloride by pyridine in the tripyridyl complex, **4**, has been observed¹⁰ to be 10^3 times faster than in the saturated diethylenetriamine complex. Although strain has been suggested as an explanation, aromaticity could also account for the large rate increase.

(10) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

(11) An alternative explanation of the solubility relations would involve a high lattice energy due to close packing of the planar bipyridyl complex. This possibility was pointed out to us by Professor K. N. Trueblood.

(12) Reference 10; the result is in the text, top of p. 4203, second column.

CONTRIBUTION No. 1498

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA

PAUL HAAKE
PATRICIA A. CRONIN

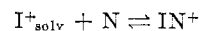
RECEIVED MARCH 11, 1963

Crystal Field Theory of Halogen Cations

Sir:

Pasternack and Piper have discussed the way in which the energies of various states of the iodine cation would be modified by the approach of a single negatively charged "ligand."¹ They point out, in particular, that the $^1\Sigma$ level would fall below the $^3\Pi$ states when Δ reaches about 5000 cm.^{-1} . This is of interest since it shows how the energy levels would be modified during reaction with a nucleophile (N).

(1) R. F. Pasternack and T. S. Piper, *Inorg. Chem.*, **2**, 429 (1963).



Thus the electrons are ultimately constrained to pair, leaving a vacant p-orbital which is then suitable for covalent bonding.

It has been suggested² that the iodine cation is unlikely to be symmetrically solvated, but rather that solvent molecules should interact strongly in the xy -plane, and weakly along the z -axis, for an ion having the configuration $4p_x, 4p_y, 4p_z$. If one ignores possible covalent interactions this is equivalent to a positive axial field and will lead to a $^3\Sigma$ ground state and three $^3\Pi$ excited states. Although crude, this model does seem to accommodate the spectral and magnetic results quite well² and there seems to be no compelling reason for abandoning it at present.

(2) J. Arotzky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 11 (1961); J. Arotzky and M. C. R. Symons, *Quart. Rev. (London)*, **16**, 282 (1962).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF LEICESTER
LEICESTER, ENGLAND

J. AROTZKY
M. C. R. SYMONS

RECEIVED MAY 3, 1963

Preparation of Silane from Silica

Sir:

The direct hydrogenation of silica to silane has been reported to require either high temperatures (1000 – 1200°) or high pressures (400 – 900 atmospheres)¹ and is therefore not easily adapted to laboratory preparations.

We have found that silane can be synthesized at 200° , either under vacuum or in an inert atmosphere, by simply heating a mixture of silica and lithium aluminum hydride. Yields averaging 10% silane, based upon hydride, have been obtained in this reaction. The only recognized impurity, detected by infrared spectra of product samples, was ether, which was an impurity in the lithium aluminum hydride. High purity material was obtained by vacuum fractionation of the mixture through a trap cooled by a Freon-12 slush at -155° , at which temperature the ether is effectively removed. In another preparation we removed nearly all the ether ahead of time by simply preheating the reactants at a lower temperature prior to collecting the products.

In a typical experiment 1 g. (16.6 mmoles) of silica gel, previously dried at 160° for 16 hr., and 0.15 g. (3.9 mmoles) of lithium aluminum hydride were placed in a Pyrex glass tube where they were mixed by shaking. The tube was evacuated, then heated to 170° with an oil bath. Vapors emanating from the reactor were collected in a trap cooled to -196° with liquid nitrogen. The collected material, identified by infrared analysis to be ether containing a trace of silane, was discarded. The reactor tube was then heated slowly to 200° , and the condensable vapors were again collected. As the

(1) H. L. Jackson, F. D. Marsh, and E. L. Muettterties, *Inorg. Chem.*, **2**, 43 (1963).

heating progressed, the pressure in the system rose, thereby indicating formation of hydrogen by decomposition of hydride. When the pressure in the system reached 20 mm., the stopcock to the pump was opened and the system was quickly pumped down to less than 1 mm. This was repeated as necessary. The pumping time was purposely made short in order to minimize loss of silane, which has an appreciable vapor pressure at -196° . When hydrogen evolution ceased, the product was measured to be 6.3 cc. (STP) of gas (0.3 mmole) and was identified as silane by its infrared spectrum. A trace ($<1\%$) of ether contaminant was readily removed by fractionation at -155° . The calculated yield of silane based upon hydride was 7.1%.

Similar yields of silane were obtained by heating a mixture of silica and lithium aluminum hydride in a stream of helium gas at atmospheric pressure. The helium was passed through a heated U-tube reactor and a trap at -196° and was then vented to the atmosphere through a mercury bubbler. Ether removal was effected by first heating the reactants at 155° for 5 min. in the helium gas stream. Heating to 200° gave the desired product, silane. It is possible that higher yields could be obtained by agitating the reaction mixture.

Heating the reaction mixture above 200° liberated more hydrogen, indicating unreacted hydride, but no further yield of silane was obtained. We did not observe silane formation from heated mixtures of lithium hydride and silica or from the lithium hydride-aluminum metal-silica system. These facts suggest that the reactive species is an aluminum hydride, which is in agreement with the proposed¹ aluminum chlorohydride intermediate reported for the Al- AlCl_3 -catalyzed hydrogenation of silica.

CHEMICAL SCIENCES DEPARTMENT
DYNAMIC SCIENCE CORPORATION
SOUTH PASADENA, CALIFORNIA

H. G. WEISS
H. D. FISHER

RECEIVED MAY 20, 1963

Characterization of the Brown Molybdenyl Bisacetylacetonate

Sir:

We wish to correct our earlier report¹ of the constitution and valency of the brown molybdenyl bisacetylacetonate. Recent data have shown that this has been erroneously described as an isomer of the known yellow molybdenum(VI) compound, $\text{MoO}_2(\text{C}_6\text{H}_7\text{O}_2)_2$. It is now proposed that this is actually a molybdenum(V) complex, μ -oxo-dioxotetrakis-(2,4-pentanedionato)-dimolybdenum(V), with the simplest formula of $[(\text{C}_6\text{H}_7\text{O}_2)_2\text{Mo}=\text{O}]_2\text{O}$.

The differences between the elemental analysis for these molybdenum(VI) and molybdenum(V) complexes were so slight that it was difficult to derive an accurate formula. The molybdenum(VI) valency and

the molybdenyl structure was supported by its diamagnetism and the presence of the strong $\text{Mo}=\text{O}$ absorption (961 cm.^{-1}) in the infrared (NaCl region). There was no indication of hydroxy absorption in the infrared spectrum, thus discounting the possibility of $\text{MoO}(\text{OH})(\text{C}_6\text{H}_7\text{O}_2)_2$ or its hydroxo-bridged dimer. Unfortunately, the molecular weight and dipole moment could not be determined in solution because of rapid dissociation and apparent oxidation.

Although the visible absorption spectra of the yellow and brown molybdenyl bisacetylacetonates were found to be distinctly different, their significance was not realized until the recent publication of papers dealing with the visible absorption and magnetic susceptibility of oxopentachloromolybdate(V), $[\text{MoOCl}_5]^{2-}$, in the crystalline state and in various concentrations of HCl. In particular, the report of Haight² revealed that this green molybdenum(V) species underwent dimerization by hydrolysis in 5–6 *M* HCl solution to give a species which was postulated to be $[\text{OCl}_4\text{Mo}-\text{O}-\text{MoCl}_4\text{O}]^{4-}$. The electron paramagnetic resonance study of Gray and associates³ indicates that this species may be paramagnetic. Further dilution of the HCl solution causes disappearance of paramagnetism, and Haight² proposes the formation of new dimeric species. This effect of hydrolysis led to the suspicion that the diamagnetic, brown molybdenyl bisacetylacetonate was actually a similar molybdenum(V) complex. An investigation of the oxidation state, independent syntheses from hydrolyzed $[\text{MoOCl}_5]^{2-}$, and the absorption spectra confirmed this suspicion.

It was found possible to dissolve this compound readily and completely in 12 *N* hydrochloric acid without heating to obtain the green color characteristic of molybdenum(V). The visible absorption spectrum of this solution was identical with that reported by Haight.² Furthermore, the cerimetric titration of this solution, after chloroform extraction of liberated acetylacetonate, confirmed the Mo^{+5} oxidation state.

Two independent syntheses of the brown bisacetylacetonate from molybdenum(V) in aqueous solution and acetylacetonate were achieved. One was from the reaction of the unneutralized aqueous solution of ammonium oxopentachloromolybdate(V), $(\text{NH}_4)_2[\text{MoOCl}_5]$. The other synthesis was from a neutralized solution of molybdic oxide in concentrated hydrochloric acid, which had been reduced by molybdenum metal powder. Although the yellow molybdenyl bisacetylacetonate, $\text{MoO}_2(\text{C}_6\text{H}_7\text{O}_2)_2$, is transparent in the 350–800 $\text{m}\mu$ region, the brown molybdenyl bisacetylacetonate had definite and strong absorption. Because of solvolytic decomposition, the absorption spectrum had to be determined immediately after preparation of the solution. The methylene chloride solution gave the following peaks: 485 $\text{m}\mu$ (ϵ 6236); approximately 400 $\text{m}\mu$ (broad shoulder, ϵ 2068); 327 $\text{m}\mu$ (ϵ 9672). The charge transfer peak at 485 $\text{m}\mu$ closely corresponds to that reported to occur

(2) G. P. Haight, Jr., *J. Inorg. Nucl. Chem.*, **24**, 663 (1962).

(3) C. R. Hare, I. Bernal, and H. B. Gray, *Inorg. Chem.*, **1**, 831 (1962).

(1) M. L. Larson and F. W. Moore, *Inorg. Chem.*, **1**, 856 (1962).