

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.

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(8) A third possibility for π -bonding is that a single d orbital (d_{zz} 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

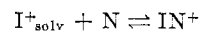
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Crystal Field Theory of Halogen Cations

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

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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).