coupling in the halogen, an effect which would not be expected in the pseudohalides bound to the metal through the light donor nitrogen.

A third interesting question concerns the inductive effect of the nonbonded group VI atom on the energy of charge transfer from the nitrogen of the pseudohalide to the metal. As expected, this energy falls in the sequence NCO, NCS, NCSe, but the magnitude of the effect is quite surprising. The average difference between isocyanate and isothiocyanate bands of the same metal is 10 kK, which is greater than the difference between chloride and bromide or bromide and iodide.[3] Where it can be estimated, the difference between isothiocyanate and isoselenocyanate is much smaller, about 2–3 kK.

The present work, therefore, confirms the previous generalization[1] that the lowest energy allowed transitions of metal thiocyanates bound through nitrogen are primarily ligand-to-metal charge-transfer type and also extends the generalization to isocyanates and isoselenocyanates.

Experimental Section

The tetra- and hexapseudohalide complexes were prepared as tetramethyl-, tetraethyl-, or tetra-*n*-butylammonium salts by the methods described by Forster and Goodgame.[1] Satisfactory analyses were obtained.

Spectra were measured in dichloromethane solution on a Unicam SP700. No excess ligand was added since tetraalkylammonium pseudohalides are rather insoluble in this very weakly coordinating solvent. However, it is to be expected that solvolysis of nitrogen-bonded pseudohalide complexes will be less pronounced than that of the corresponding halides.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SOUTHERN ILLINOIS UNIVERSITY, CARBONDALE, ILLINOIS

Synthesis and Properties of a Nitrogen-Containing Phosphorus(V) Monobasic Acid, Hydroxypentaphenylcyclotriphosphazatriene

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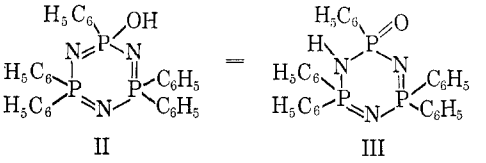
In the course of kinetic studies of base-catalyzed hydrolysis of chloropentaphenylcyclotriphosphazatriene (I), a stable white solid, hydroxypentaphenylcyclotriphosphazatriene (II), was isolated. The physical properties and chemical behavior of this compound proved sufficiently interesting to warrant its detailed description.

Compound II is readily prepared by the action of water on I dissolved in pyridine. Its infrared spectrum exhibits a weak, broad band at 2653 cm^{-1}, attributed to an O–H stretching frequency, and a strong band at 950 cm^{-1}, attributed to a P–OH stretch.[1] Bands attributed to the P=N—P linkage are found at 1233 (s) and 1205 (s) cm^{-1}. The corresponding P=N—P bands in $(C_6H_5)_5ClP_3N_3$ are found at 1205, 1189 (s doublet), and 1165 (s) cm^{-1}. A band at 1122 (m) cm^{-1} is assigned to a phenyl vibration coupled with P–C stretching. The spectrum of II also contains phenyl bands at 1590 (w), 1485 (w), 1440 (s), 740 (s), and 689 (s) cm^{-1}. These data indicate a phosphazene structure and suggest that, if indeed there is an equilibrium between tautomeric forms II and III, it strongly favors II. It is possible that tautomerization to III is kinetically unfavorable.



II = III (1)

In contrast to chloropentaphenylcyclotriphosphazatriene, complete hydrolysis of hexachlorocyclotriphosphazatriene in neutral or weakly basic solution yields trimetaphosphimic acid (trimetaphosphimate in strongly basic solution) rather than hexahydroxycyclotriphosphazatriene.[2] It is evident that hydrolysis is accompanied by tautomerization and the phosphimate is the more stable species. The structures of the partially hydrolyzed hexachlorocyclotriphosphazatriene, $Cl_4(OH)_2P_3N_3$ and $Cl_2(OH)_4P_3N_3$, are not known with certainty.[3,4] Both of these compounds are thought to be phosphazenes, but there is limited evidence to support this claim.[3] Both compounds are transformed to metaphosphimic acid in a moist atmosphere.

The base-catalyzed hydrolysis of a 2,6-dichlorocyclotetraphosphazatriene polymer, $(C_6H_5)_6Cl_2P_4N_4$, yielded a stable dihydroxy derivative $(C_6H_5)_6(OH)_2P_4N_4$, mp 272°.[5] The behavior of the dihydroxy derivative is like that of compound II in that its infrared spectrum contains a band at 2620 cm^{-1} characteristic of the O–H stretch and it reacts with $(C_6H_5)_6Cl_2P_4N_4$ to give a polymer and hydrogen chloride. The latter behavior is similar to that described for the reaction of I and II to give the bridged compound IV, *vide infra*.

Compound II is a very weak acid with a pK_a of 9.92 in 77 vol. % ethanol. Table I[6–9] shows that it is a much

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weaker acid than diphenylphosphinic acid (pK_a = 4.44) or phenylphosphonic acid (pK_a = 4.41). This difference in acidity is of the same magnitude as the difference between phenol and benzoic acid. (See Table I.) The weaker acid properties of $(C_6H_5)_5(OH)P_3N_3$ and phenol may be attributed in part to the lack of resonance stabilization of the anion. Whereas the anions of both benzoic acid and diphenylphosphinic acid are stabilized by delocalization of the negative charge over two oxygen atoms, there is no possibility for such delocalization with the anion of phenol or $(C_6H_5)_5(OH)P_3N_3$.

TABLE I
pK_a VALUES FOR PHOSPHORUS(V) ACIDS

Acid	pK_a 77% C_2H_5OH[a]	pK_a 75% C_2H_5OH[b]	pK_a H_2O
$(C_6H_5)_5(OH)P_3N_3$ (II)	9.92 ± 0.08	...	...
$(C_6H_5)_2POOH$	4.44 ± 0.08	4.10 ± 0.05[c]	...
$C_6H_5PO(OH)_2$	4.41 ± 0.08	3.96 ± 0.05	1.83[d]
C_6H_5OH[f]	...	...	9.98[e]
C_6H_5COOH[e]	6.79 ± 0.08	6.28 ± 0.05	4.17[e]

[a] pH values were taken at 24 ± 1° at the midpoint of the potentiometric titrations of 10^{-3} M solutions, and pK_a values were computed with the equation: $pK_a = pH - \log [([A^-] + [H^-])/([HA] - [H^+])]$. See ref 6. [b] See ref 7. [c] A value of 4.24 in 80% ethanol was reported in ref 8. [d] See ref 9. [e] See ref 6. [f] Inserted for comparison.

Compound II is sparingly soluble in chloroform and ethanol and insoluble in water. The apparent molecular weight of $(C_6H_5)_5(OH)P_3N_3$ measured in chloroform was greater than that for the monomeric species (537) but less than that for the dimeric species. It was dependent upon concentration. The results of the molecular weight studies are summarized in Table II. Solubility limitations prevented the determination of apparent molecular weights at higher concentrations.

TABLE II
APPARENT MOLECULAR WEIGHT AND DIMERIZATION CONSTANT, K_D, OF $(C_6H_5)_5(OH)P_3N_3$ IN CHLOROFORM AT 37°

$(C_6H_5)_5(OH)P_3N_3$ concn, $M \times 10^3$	0.95	1.88	3.53	3.66	5.66	8.33
Apparent mol wt	570	630	680	680	740	770
$10^{-2}K_D$, M^{-1} [a]	...	1.6	1.8	1.7	2.3	2.4

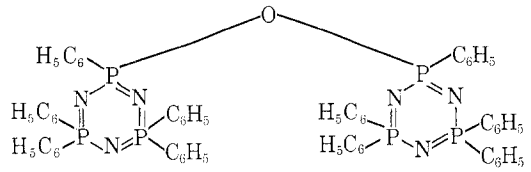
[a] Calculated with the aid of eq 2; estimated error in K_D values is $\pm 0.7 \times 10^2$.

On the assumption that the only two solute species in chloroform solution were the dimer and the monomer, an approximate value of 2.0×10^2 M^{-1} for the dimerization constant was computed from the molecular weight data with the aid of eq 2.

$$K_D = \frac{M_x(M_x - M_A)}{A(2M_A - M_x)^2} \qquad (2)$$

where K_D = dimerization constant (M^{-1}) for the equilibrium 2(monomer) = dimer, A = concentration of $(C_6H_5)_5(OH)P_3N_3$ (M) assuming all of the solute is in the form of the monomer, M_x = apparent molecular weight obtained from molecular weight measurements, and M_A = molecular weight of monomer = 537. The tendency for phosphorus(V) acids to form polymers in solution is well known.[10,11]

Hydroxypentaphenylcyclotriphosphazatriene, serving as a nucleophilic reagent, reacts with I to give compound IV. Compound IV was isolated in the form of white needles, mp 238–239°. The infrared spectrum



IV

of IV contains a strong band at 948 cm^{-1}, attributed to the P–O–P asymmetric stretching vibration, and a weak band at 707 cm^{-1} which may be due to the P–O–P group.[1] Bands assigned to the phenyl group are found at 1592 (w), 1481 (w), 1438 (s), 743 (s), and 690 (s) cm^{-1}. A band at 1124 (m) cm^{-1} is due to a phenyl vibration coupled with P–C stretching. Strong bands at 1200 and 1167 cm^{-1} are assigned to the P=N—P stretching vibration.

Although it is reasonable to suppose that $(C_6H_5)_5(OH)P_3N_3$ would undergo simple condensation polymerization to form compound IV plus water, experimental evidence indicates that there is little tendency for such reaction. When $(C_6H_5)_5(OH)P_3N_3$ was refluxed in pyridine–benzene for 3 hr, the starting material was recovered quantitatively.

Experimental Section

Physical Measurements.—All melting points were taken in open capillary tubes and are uncorrected. The infrared spectra were of Nujol mulls and hexachlorobutadiene mulls taken on a Beckman IR-8 spectrophotometer. Molecular weight determinations were made on a Mechrolab vapor pressure osmometer, Model 301A. The chloroform used in the molecular weight studies was thoroughly dried.

Elemental Analyses.—All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Reagents.—Reagent grade benzene was purified by shaking with concentrated sulfuric acid, washing with water, and drying with calcium chloride. The benzene was then fractionally distilled. Reagent grade pyridine was purified by fractionally distilling from potassium hydroxide. The middle fraction was retained. Reagent grade carbon tetrachloride was used without further purification.

Preparation of $(C_6H_5)_5ClP_3N_3$.[12]—The compound $(C_6H_5)_4P_2N_3H_4Cl$ was synthesized according to the procedure described by Bezman and Smalley.[13] Phenyltetrachlorophosphorane was prepared by passing chlorine gas (Matheson) into a carbon tetrachloride solution of phenyldichlorophosphine (Victor Chemical) at −5°. The crystalline phenyltetrachlorophosphorane that separated was filtered and dried. This material melts at 75–77° (closed tube), mp 73° reported.[14]

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To 5.64 g (0.0125 mole) of $(C_6H_5)_4P_2N_3H_4Cl$ in 700 ml of refluxing anhydrous benzene was added with stirring 9.37 g (0.0375 mole) of $C_6H_5PCl_4$ in 100 ml of benzene. The reaction mixture was kept under an atmosphere of dry nitrogen and refluxed for a period of 24 hr. The reaction mixture separated into two layers. The lower layer was removed and found to contain a large quantity of unreacted phenyltetrachlorophosphorane. The upper benzene layer was washed with eight 100-ml portions of water to remove unreacted phosphorane and dried with anhydrous sodium sulfate. Removal of the benzene by vacuum distillation gave 6.02 g of impure product. Recrystallization from acetonitrile gave 4.48 g (64% yield) of white needles, mp 150–151°.

Anal. Calcd for $C_{30}H_{25}ClP_3N_3$: C, 64.81; H, 4.53; Cl, 6.38; P, 16.72; N, 7.56; mol wt, 556. Found: C, 64.78; H, 4.41; Cl, 6.20; P, 16.52; N, 7.28; mol wt, 567 (cryoscopic in benzene).

Chloropentaphenylcyclotriphosphazatriene is readily soluble in benzene, acetonitrile, methylene chloride, and *sym*-tetrachloroethane and insoluble in ether and hydrocarbon solvents.

Preparation of $(C_6H_5)_5(OH)P_3N_3$.—A solution of 2.1 g (3.8 mmoles) of $(C_6H_5)_5ClP_3N_3$ and 0.10 g (5.6 mmoles) of water in 10 ml of pyridine was allowed to react for 30 min at room temperature. The removal of pyridine left 2.0 g of a white crystalline material, equivalent to a 97% yield. Recrystallization from ethanol gave white, prismatic crystals, mp 275–276°.

Anal. Calcd for $C_{30}H_{26}P_3N_3O$: C, 67.04; H, 4.88; N, 7.82; P, 17.29. Found: C, 66.83; H, 5.08; N, 7.77; P, 17.18.

Preparation of $[(C_6H_5)_5P_3N_3]_2O$.—A solution of 0.98 g (1.8 mmoles) of $(C_6H_5)_5ClP_3N_3$ and 0.95 g (1.8 mmoles) of $(C_6H_5)_5(OH)P_3N_3$ in 25 ml of benzene and 25 ml of pyridine was refluxed for 1 hr. The solvents were then removed under reduced pressure. The solid which remained was treated with boiling acetonitrile and the undissolved, unreacted $(C_6H_5)_5(OH)P_3N_3$ was removed by filtration. Upon cooling, the filtrate yielded 0.20 g of white needlelike crystals of $[(C_6H_5)_5P_3N_3]_2O$, mp 238–239°.

Anal. Calcd for $C_{60}H_{50}P_6N_6O$: C, 68.18; H, 4.74; N, 7.95; P, 17.61; mol wt, 1057. Found: C, 68.80; H, 4.96; N, 7.96; P, 17.65; mol wt, 1070 (vapor pressure lowering in benzene).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY, KANPUR, INDIA

Crystal Field Spectra of Some Tris(salicylaldimine)cobalt(III) Chelates

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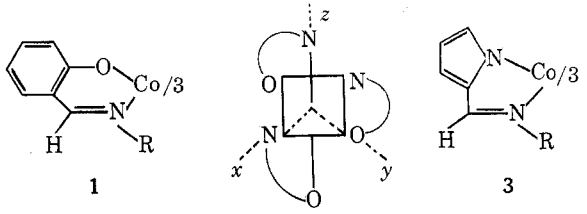
Hexacoordinated metal complexes containing three unsymmetrical bidentate ligands can exist in two geometrically isomeric forms: *cis* and *trans*. Considering coordinated atoms only, the two isomers belong to the point groups C_{3v} and C_{2v}, respectively. Tris(N-alkyl salicylaldimine)cobalt(III) (**1**) can be isolated only in the sterically less hindered *trans* form (**2**) as proved conclusively by nuclear resonance[1] and dipole moment[2] data in solution. The same is true of tris(N-alkylpyrrole-2-aldimine)cobalt(III)[1] (**3**). Diamagnetic Co(III) in crystal fields of O_h symmetry shows two spin-allowed transitions: $^1A_{1g} \rightarrow {}^1T_{1g}$ and $\rightarrow {}^1T_{2g}$, the latter being at higher energy and often masked by strong ultraviolet absorptions when the ligand contains conjugated organic fragments, as is true for the compounds under the present investigation.



1 2 3

In fields of appropriate lower symmetry the upper states are split as shown below

O_h	C_{3v}	C_{2v}
T_{1g}	$A_2 + E$	$A_2 + B_1 + B_2$
T_{2g}	$A_1 + E$	$A_1 + B_1 + B_2$

(From here on, the g designation of states in O_h will be left out as understood.) In the *cis* form (C_{3v}) E and A have the same energy,[3] and no splitting of bands is expected; for crystal field purposes the *cis* isomer is essentially cubic.[4] In the *trans* form (C_{2v}) all components have different energies,[3] and, in principle, multiple bands are predicted. Clear-cut splittings are, however, rarely observed experimentally. Thus, of the two isomers of tris(glycinato)cobalt, one shows a broader and more asymmetric $^1A_1 \rightarrow {}^1T_1$ band and was hence assigned the *trans* configuration.[5] Since **1** and **3** exist only in the *trans* form, the present investigation was undertaken to determine if the C_{2v} components of the crystal field in **1** and **3** are strong enough to show clear splitting of bands. Attempts will also be made to determine the strength of the rhombic component, if any.

Experimental Section

The chelates used in the present study have all been reported previously. The salicylaldimines were made by hydrogen peroxide oxidation of an aqueous alcoholic solution containing cobalt acetate, salicylaldehyde, and the appropriate amine.[1,6,7] They form greenish black, crystalline solids. A nonaqueous chelation reaction was used for preparation of the orange-red pyrrole-2-aldimines.[1]

Anal. Calcd for **1** (R = CH_3), $C_{24}H_{24}N_3O_3Co$: C, 62.46; H, 5.24; N, 9.11. Found: C, 62.50; H, 5.00; N, 9.10. Calcd for **1** (R = C_2H_5), $C_{27}H_{30}N_3O_3Co$: C, 64.39; H, 6.01; N, 8.34. Found: 64.19; H, 5.98; N, 8.45. Calcd for **1** (R = C_4H_9), $C_{33}H_{42}N_3O_3Co$: C, 67.45; H, 7.21; N, 7.15. Found: C, 67.40; H, 7.25; N, 7.23. Calcd for **3** (R = CH_3), $C_{18}H_{21}N_6Co$: C, 56.85; H, 5.57; N, 22.11. Found: C, 56.80; H, 5.30; N, 22.00. Calcd for **3** (R = C_3H_7), $C_{24}H_{33}N_6Co$: C, 62.04; H, 7.16; N, 18.09. Found: C, 62.10; H, 6.99; N, 18.15.

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