Marcus.[4] We find, however, that the exchange between ruthenate and perruthenate is too rapid to measure by the techniques available to us.

Experimental Section

Reagents.—Analytical and Reagent grade chemicals were used throughout. Sodium hydroxide solutions were prepared by diluting saturated solutions, after sodium carbonate was removed by decantation.

A stock solution of ruthenium(III) was prepared by fusing ruthenium metal with KOH and KNO_3 at 600° and dissolving the fused mass in aqueous sulfuric acid. The solution was evaporated until SO_3 fumes were observed. During the evaporation, several portions of aqueous HCl were added to destroy the excess nitrate. The final solution was then diluted with water and H_2SO_4 to make a stock of Ru(III) in 3 M H_2SO_4.

Perruthenate was prepared by oxidizing the Ru(III) with sodium bismuthate in the 3 M H_2SO_4. The RuO_4 vapor, thus produced, was carried in a stream of air into 1.0 M NaOH where it decomposed to give RuO_4^-. The conversion to RuO_4^- is taken to be complete when the ratio of the absorbancies at 465 and 385 mμ reaches 0.121.[5,6] A lower ratio indicates RuO_4 is still present; a higher ratio shows the presence of RuO_4^{2-}. The RuO_4^- solutions decompose slowly[5-7] to form RuO_4^{2-}; consequently, all of the RuO_4^- solutions, which we used, contained some RuO_4^{2-}.

Ruthenate solutions were prepared by passing the RuO_4 directly into 2.0 M NaOH and then heating at about 70° until the ratio of the absorbancies at 465 to 385 mμ reached 2.07, corresponding to pure ruthenate.[5] These stocks were then diluted and stored in an ice bath. They proved stable, as long as the hydroxide ion concentration exceeded 0.1 M.

Concentrations of the ruthenate and perruthenate in stocks and other solutions were determined spectrophotometrically. The following molar absorptivities were used: for RuO_4^-, 2150 at 385 mμ and 260 at 465 mμ; for RuO_4^{2-}, 840 at 385 mμ and 1740 at 465 mμ. The molar absorptivities are determined in this work and are in substantial agreement with those of Larsen and Ross.[5]

The ^{106}Ru tracer was obtained as ruthenium-106–rhodium-106, carrier free, from Oak Ridge National Laboratory as $RuCl_3$ in 6 N HCl. It was added to one sample of Ru(III) in 3 M H_2SO_4 before the BiO_3^- oxidation.

Procedures.—In experiments in which RuO_4^- was separated from the exchanging mixture, RuO_4^- solutions were added to RuO_4^{2-} (both in 0.1 M NaOH), at 0°, and the mixture was stirred mechanically. A quench solution consisting of 4.00 ml of 0.1 M tetraphenylarsonium chloride in 0.1 M NaOH and 5.00 ml of 0.01 M perrhenate (ReO_4^-, nonisotopic carrier) was added. The precipitate was filtered with suction, and the supernatant liquid was reserved for counting. When it had been learned that exchange was very rapid, several experiments were carried out with the quench solution added before the RuO_4^- and the solution was stirred vigorously during the addition.

In an effort to determine that the fast exchange was not due to separation-induced exchange, a second series of experiments was carried out, in which RuO_4^{2-} was precipitated. In these experiments RuO_4^{2-} was added to stirred RuO_4^- at 0° in 0.1 M NaOH. A quench solution was prepared with 4.00 ml of saturated $Ba(OH)_2$ plus 5.00 ml of 0.01 M Na_2SO_4 and was added rapidly to the exchange mixture. The $BaRuO_4$ was filtered off, and the filtrate was reserved for counting.

Samples of the various supernatant liquids (2.00 ml) were placed in 1-dram, screw-cap vials and were counted in an integral, well-type scintillation counter. The energetic γ rays (0.51–2.4 Mev) from the ^{106}Rh daughter were counted after the solutions reached radioactive equilibrium (a few minutes is required).

Results and Discussion

In all experiments conducted, even those with the quench added before the reagents were mixed, complete exchange was observed in the time of mixing and separating, which is estimated to be 5–15 sec for precipitation and another 10–40 sec for the filtration. Thus, the exchange must be complete in less than 5 sec, if there is no exchange between the precipitates and the supernatant liquids.

Table I gives the concentrations of reactants which were used.

TABLE I

CONCENTRATIONS OF RuO_4^-, RuO_4^{2-}, AND OH^- IN THE EXCHANGE STUDIES AT 0°. ALL SOLUTIONS SHOW COMPLETE EXCHANGE IN TIME OF MIXING AND SEPARATION

$10^5[RuO_4^{2-}]$, M	$10^5[RuO_4^-]$, M	$[OH^-]$, M
2.5	4.9	0.1[a]
2.8	2.95	0.1[b]

[a] $(C_6H_5)_4AsRuO_4$ separation. [b] $BaRuO_4$ separation.

Sheppard and Wahl[1] were able to measure half-lives as short as 0.25 sec in the MnO_4^-–MnO_2^{2-} exchange by similar experimental procedures. Thus, we may estimate a second-order rate constant $>3.3 \times 10^4$ M^{-1} sec^{-1} if we assume 0.25 sec as a lower limit, and 1.7×10^3 if we assume 5 sec as a lower limit.

Separation-induced exchange cannot be ruled out, but two methods of separation were tested and Sheppard and Wahl[1] found little induced exchange in the tetraphenylarsonium chloride method.

Electron spin resonance measurements were made on solutions of 2.0×10^{-2} M RuO_4^{2-} in 2.0 M NaOH and 1.0×10^{-2} M RuO_4^- in 1.0 M NaOH, in the hope that suitable signals could be detected for following the exchange by line broadening. A very weak signal, probably peroxide, was found in the perruthenate, and no other signal was detected.

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Ultraviolet Spectra of Some First Transition Series Pseudohalide Complexes

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The π–π* transitions of many conjugated ligands are very little modified by complex formation, but the spectra of thiocyanate complexes usually contain intense absorption bands at much lower energies than the free anion. In certain cases (*e.g.*, iron(III)) these are

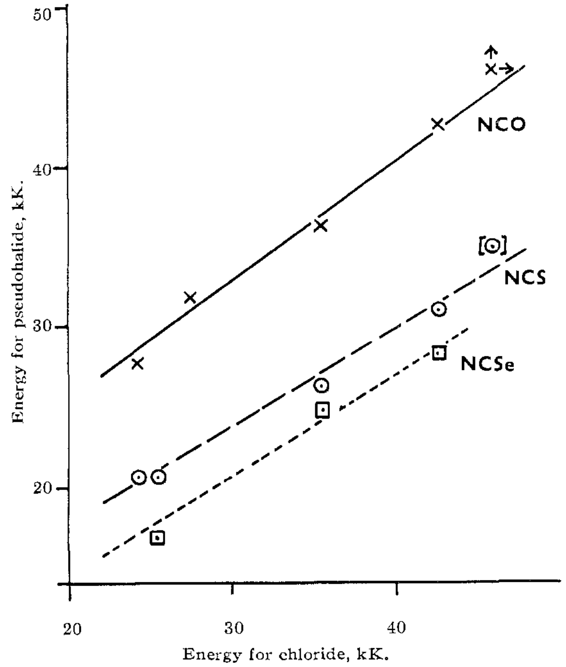

Figure 1.—The lowest energy allowed transitions in chloride and pseudohalide complexes.

clearly charge-transfer bands, though in others (*e.g.*, platinum(II) and -(IV)) the rather weak dependence of band energy on the oxidizing or reducing power of the metal suggests that they may be intraligand π–π^* transitions. In an earlier investigation,[1] the energies of the first intense bands in two series of thiocyanate complexes $M(NCS)(H_2O)_n{}^{m+}$ and $M(SCN)_p{}^{q-}$ were plotted against the energies of the first intense bands in the corresponding halide complexes $MX(H_2O)_n{}^{m+}$ and $MX_p{}^{q-}$ on the assumption that the halide bands resulted from ligand-to-metal charge transfer. In the former series, straight lines of almost unit slope were obtained, but in the latter the slopes were much less than unity. This suggested that, when the thiocyanate ion is bonded to the metal through nitrogen, the first intense band is due to ligand-to-metal charge transfer but that, when it is bonded through sulfur, the band is primarily intraligand π–π^* in origin.

Forster and Goodgame recently reported the preparations and ligand field and vibrational spectra of a number of first transition series pseudohalide complexes.[2] Though the solids in a number of cases had octahedral coordination, when dissolved in dipolar, weakly coordinating solvents, most of the divalent metals gave complexes $M(NCX)_4{}^{2-}$, and far-infrared spectra showed that coordination was always through nitrogen. Since the charge-transfer spectra of all of the tetrahalide complexes of manganese(II) to copper(II) have recently been reported,[3] a comparison of the type described above should help in assigning the pseudohalide spectra.

Table I shows the energies and extinction coefficients of the available tetrahedral pseudohalide complexes. The manganese(II) and zinc(II) complexes have no intense absorption bands at appreciably lower energies than those of the uncomplexed pseudohalide ions. In contrast, Figure 1 shows the energies of the first intense bands in the other isocyanates and isothiocyanates plotted against those in the chlorides with corresponding formulas. An excellent correlation is seen, the slopes of the plots being approximately 0.7, compared with 1.0 for lanthanide and other thiocyanate ion pairs plotted against chloride ion pairs, and about 0.3 when sulfur-bonded thiocyanates are plotted against chlorides. Thus, the bands are clearly of predominantly charge-transfer character, though in a description of the complexes according to a self-consistent field (*e.g.*, Pariser–Parr–Pople) formalism, the classification of excited states as charge transfer, π–π^*, etc., might not be possible.

TABLE I

SPECTRA OF PSEUDOHALIDE COMPLEXES (kK) WITH EXTINCTION COEFFICIENTS IN PARENTHESES

Mn(II)	NCO	>46
	NCS	~35[a]
Fe(III)	NCO[c]	27.8 (5120); 31.8 (14,400); 34 (13,980); 40 (6220)
	NCS[b]	20.70 (>17,000); 32; 34.2 (5000); 40.5 (>20,000)
	NCSe[a,b]	~17
Co(II)	NCO	42.50 (9320)
	NCS	31.00 (12,170); 39.5 (2500); >44 (>30,000)
	NCSe	28.30 (6850); 43.2 (32,000)
Ni(II)	NCO	36.30 (5890); 39.5 (3500); >44
	NCS	26.30 (5000); ~34 (~800); ~39 (~1600)
	NCSe[a,b]	~25
Cu(II)	NCO	27.80 (4160); 32.30 (2503)
	NCS	20.65 (2490); 39 (3560); 42.75 (40,500)
Zn(II)	NCO	>46
	NCS	>44
	NCSe	41 (10,000)

[a] Powder reflectance. [b] Octahedral. [c] In acetonitrile solution.

Several other points of interest about the pseudohalide ultraviolet spectra are worth mentioning. First, the extinction coefficients are generally similar to those in the corresponding tetrahalides, but the half-widths are often much greater, *e.g.*, $Cu(NCS)_4{}^{2-}$, 4.1 kK, and $CuCl_4{}^{2-}$, 1.5 kK. Second, where the first intense band is at a low energy, there is frequently no further intense absorption over an energy range up to 20 kK. Thus, for example, after the bands at 31.00 kK in $Co(NCS)_4{}^{2-}$, 28.30 kK in $Co(NCSe)_4{}^{2-}$, and 20.65 kK in $Cu(NCS)_4{}^{2-}$, the next absorption maximum does not occur until well above 40 kK. Indeed, it is most likely that the very intense bands then occurring are related to the internal absorption bands of free pseudohalide anions rather than charge-transfer transitions. This is in marked contrast to the tetrahalides, where a complicated succession of closely spaced bands is frequently observed.[3] The higher energy transitions in tetrahalides may be due either to $t_2\sigma \rightarrow t_2\sigma^*$ or to $e\pi \rightarrow t_2\sigma^*$, though there is the further possibility that some of the fine structure results from intermediate

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[2] D. Forster and D. M. L. Goodgame, *ibid.*, 2790 (1964); 262, 268 (1965); *Inorg. Chem.*, **4**, 715, 823, 1712 (1965).

[3] P. Day and C. K. Jørgensen, *J. Chem. Soc.*, 6226 (1964).

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

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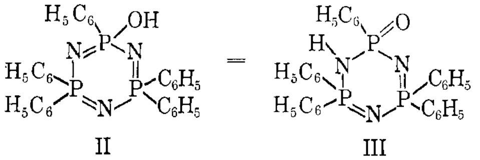
In the course of kinetic studies of base-catalyzed hydrolysis of chloropentaphenylcyclotriphosphazatriene (I), a stable white solid, hydroxypentaphenylcyclotriphosphazatriene (II), was isolated. The physical properties and chemical behavior of this compound proved sufficiently interesting to warrant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