Table III. Details of Ion-Pairing Constants (K_{IP}) and Rate Constants (k_{an}) for Replacement of H_2O in $Cr(NH_3)_5H_2O^{3+}$ (after Ion-Pair Formation) at 50 °C, $I = 1.00$ M ($LiClO_4$)

Reactant	$10^4k_{\mathrm{an}}K_{\mathrm{IP}}$, $M^{-1}\ s^{-1}$	K_{IP}, M^{-1}	10^4k_{an}, s^{-1}	Ref
$^+NH_3CH_2CO_2^-$	7.82	0.55[a]	14.2[a]	This work
$HC_2O_4^-$	6.45	1.16	5.86	5
$C_2O_4^{2-}$	29.1	4.5	6.46	5
H_2O			13.7[b]	2

[a] From data at 40, 47.5, and 55 °C. [b] Extrapolated from data at other temperatures.

$$\mathrm{Cr(NH_3)_5H_2O^{3+} + {}^+NH_3CH_2CO_2^-} \overset{K_{\mathrm{IP}}}{\rightleftharpoons} \mathrm{Cr(NH_3)_5H_2O^{3+},{}^-O_2CCH_2NH_3^+} \tag{5}$$

$$\mathrm{Cr(NH_3)_5H_2O^{3+},{}^-O_2CCH_2NH_3^+} \xrightarrow{k_{\mathrm{an}}} \mathrm{Cr(NH_3)_5(O_2CCH_2NH_3)^{3+} + H_2O} \tag{6}$$

species is nonreactive. Accordingly (7) can be derived and

$$k_{\mathrm{obsd}} = \frac{k_{\mathrm{an}}K_{\mathrm{IP}}K_{\mathrm{a}}[\mathrm{Gly}]_{\mathrm{T}}}{[\mathrm{H}^+] + K_{\mathrm{a}} + K_{\mathrm{IP}}K_{\mathrm{a}}[\mathrm{Gly}]_{\mathrm{T}}} \tag{7}$$

can be rearranged to give (8). Plots of k_{obsd}^{-1} against $[\mathrm{Gly}]_{\mathrm{T}}^{-1}$

$$\frac{1}{k_{\mathrm{obsd}}} = \frac{[\mathrm{H}^+] + K_{\mathrm{a}}}{k_{\mathrm{an}}K_{\mathrm{a}}K_{\mathrm{IP}}}\,\frac{1}{[\mathrm{Gly}]_{\mathrm{T}}} + \frac{1}{k_{\mathrm{an}}} \tag{8}$$

at constant $[H^+]$ should therefore be linear with a common intercept for all $[H^+]$. This is the case as illustrated in Figure 2. The slopes give a first-order dependence on $[H^+]$ as required by (8). From a least-squares fit[9] of rate constants k_{obsd} to (7) at 40, 47.5, and 55 °C, respectively, $k_{\mathrm{an}}K_{\mathrm{IP}}$ and K_{IP} were obtained, Table II. The K_{a} term was allowed to float yielding the values shown in Table II, which are in good agreement with those determined potentiometrically, e.g., 3.42×10^{-3} M at 47.5 °C. Activation parameters for the composite term $k_{\mathrm{an}}K_{\mathrm{IP}}$ for formation of the glycinato complex are $\Delta H^{\ddagger} = 25.3 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = 5.6 \pm 2.9$ cal K^{-1} mol^{-1}. Thermodynamic parameters for K_{IP} are less precise, $\Delta H = 5.1 \pm 4.7$ kcal mol^{-1} and $\Delta S = 14.5 \pm 14.6$ cal K^{-1} mol^{-1}.

Reactions of $Cr(NH_3)_5H_2O^{3+}$ in which K_{IP} has been obtained, thus allowing k_{an} for anation within the ion pair to be evaluated, are listed in Table III. Values of k_{an} are seen to lie within a narrow range (5–14) $\times 10^{-4}$ s^{-1} at 50 °C and are comparable to the rate constant for H_2O exchange on $Cr(NH_3)_5H_2O^{3+}$.[2] This observation that rate constants k_{an} for 1−, 2−, and zero charged reactants as well as the glycine zwitterion are comparable is indicative of $Cr-OH_2$ bond breaking being the dominant factor. It has previously been demonstrated that substitution reactions of $Co(NH_3)_5H_2O^{3+}$ occur by a dissociative mechanism.[10] For $Cr(H_2O)_6^{3+}$ however there is a strong case for an associative process.[3,11] The effect of different ligand environments on the mechanism of substitution and other results are discussed elsewhere.[12]

There are two additional points which emerge from this study with regard to the behavior of the glycine zwitterion, $^+NH_3CH_2CO_2^-$. First of all, the zwitterion behaves as a 1:1 electrolyte as far as ionic strength calculations are concerned. Second, values of the ion-pairing constant K_{IP} are as expected for a 3+,1− interaction.[13]

There is no evidence for chelation of glycine in the present study. For reaction times corresponding to >50% completion, product analyses indicate that there is entry of a second glycine and formation of diamine and triamine complexes. It is known that the reaction of glycine with some Cr(III) complexes at pH ~7 yields the chelated tris(glycinato) complex $Cr(Gly)_3$ along with the now well-characterized binuclear complex $Cr_2(Gly)_4(\mu OH)_2$.[14-17] By reacting excess glycine with $Cr(NH_3)_5H_2O^{3+}$ at pH ~5.0 (20 °C) we find that $Cr(Gly)_3$ is obtained.

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Registry No. $[Cr(NH_3)_5H_2O](ClO_4)_3$, 32700-25-7; glycine, 56-40-6; $Cr(NH_3)_5(O_2CCH_2NH_3)^{3+}$, 59765-77-4.

References and Notes

(1) N. V. Duffy and J. E. Earley, *J. Am. Chem. Soc.*, **89**, 272 (1967).
(2) T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc.*, **94**, 8357 (1972).
(3) T. W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974).
(4) Discussion as to the mechanism of substitution of chromium(III)–amine complexes is to be found in D. A. House, *Inorg. Nucl. Chem. Lett.*, **12**, 259 (1976), and references therein.
(5) O. Nor and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1232 (1973).
(6) T. Ramasami, R. K. Wharton, and A. G. Sykes, *Inorg. Chem.*, **14**, 359 (1975).
(7) M. Mori, *Inorg. Synth.*, **5**, 131 (1957).
(8) R. P. Martin and R. A. Paris, *Bull. Soc. Chim. Fr.*, 570 (1963). The second acid dissociation constant has also been determined and is 1.6×10^{-10} M under the same conditions.
(9) R. H. Moore and R. K. Zeigler, Los Alamos Report LA 2367 (1959) and Addenda.
(10) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965); A. Haim, *ibid.*, **9**, 426 (1970).
(11) J. H. Espenson, *Inorg. Chem.*, **8**, 1554 (1969); D. Thusius, *ibid.*, **10**, 1106 (1971).
(12) T. Ramsami and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 378 (1976); *Inorg. Chem.*, in press.
(13) See, e.g., values at 45–50 °C of D. F. C. Morris and S. D. Hammond, *Electrochim. Acta*, **13**, 545 (1968), and H. S. Gates and E. L. King, *J. Am. Chem. Soc.*, **80**, 5011 (1958), and values at 25 °C listed by H. Diebler, *Z. Phys. Chem. (Frankfurt am Main)*, **68**, 64 (1969).
(14) H. Ley and K. Ficken, *Ber. Dtsch. Chem. Ges.*, **45**, 377 (1912).
(15) B. J. Trzebiatowska, L. Pajdowski, and T. Starosta, *Roczn. Chem.*, **35**, 433, 445 (1961).
(16) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).
(17) J. T. Veal, W. E. Hatfield, D. Y. Jeter, J. C. Hempel, and D. J. Hodgson, *Inorg. Chem.*, **12**, 342 (1973).

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Fluoro-Containing Complexes of Chromium(III). 7. Isolation and Some Reactions of the *cis*-Fluoroaquobis(ethylenediamine)chromium(III) Cation[1]

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The *cis*-fluoroaquobis(ethylenediamine)chromium(III) cation was first detected in solution by Fehrmann and Garner[3] during an investigation of the perchloric acid hydrolysis of the *cis*-difluorobis(ethylenediamine)chromium(III) ion. In 1968 Vaughn, Stvan, and Magnuson[4] prepared the ion in solution by utilizing the Ag^+-induced aquation of *cis*-chlorofluorobis(ethylenediamine)chromium(III). More recently the ion was again detected and characterized in solution by Wirth and Linck.[5]

Since this particular cation would appear to be a good starting material for the rapid preparation of a number of cis FX complexes, this investigation was undertaken to develop a reliable method for the synthesis of solid salts of this cation in quantity. In addition some reactions of the *cis*-fluoroaquo complex were to be studied.

Experimental Section

Caution! Perchlorate salts of metal complexes with reducing ligands such as amines are potentially explosive and care should be exercised when handling these materials.

Preparation of Starting Material. *cis*-Difluorobis(ethylenediamine)chromium(III) tetrafluoro(ethylenediamine)chromate(III)-1-water was prepared by the reaction of 42.0 g (0.24 mol) of technical grade chromium(III) fluoride–3.5-water with 42.0 g (0.70 mol) of dry ethylenediamine in an open polyethylene beaker. The beaker and its contents were heated on a steam bath in a hood for 1 h. At the end of this time the pasty purple mass was placed in a large evaporating dish and heated on the steam bath until all of the excess amine evaporated (ca. 2 h). The lumpy solid was crushed to a fine powder and used without further purification. A yield of 52 g [96% based on chromium(III) fluoride–3.5-water] was obtained.

Isolation of *cis*-Difluorobis(ethylenediamine)chromium(III) Iodide. The *cis*-difluoro complex was isolated from the starting material by the method of Vaughn and Krainc[6] and used without further purification.

Synthesis of *cis*-Fluoroaquobis(ethylenediamine)chromium(III) Iodide–1-Water. A 10-g (30-mmol) sample of crude *cis*-difluorobis(ethylenediamine)chromium(III) iodide was dissolved in 24 ml of 48% hydriodic acid at room temperature. The reaction mixture was stirred until everything dissolved and filtered, and the filtrate was allowed to stand in the dark for 1 h at room temperature. At the end of this time the filtrate was cooled in an ice bath for 1 h, and the orange solid which precipitated was collected by filtration, washed with acetone, and air-dried. This reaction produced 6.5 g (46%) of crude *cis*-fluoroaquobis(ethylenediamine)chromium(III) iodide–1-water. A 1.0-g (2-mmol) sample of this material was dissolved in about 0.75 ml of water at room temperature, the solution was filtered, and the filtrate was cooled in ice. The precipitate was collected, washed with acetone, and air-dried; yield 0.30 g, 30%. Anal. Calcd for *cis*-$[Cr(en)_2F(OH_2)]I_2 \cdot H_2O$: C, 9.99; H, 4.20; N, 11.65; F, 3.95; I, 52.8. Found: C, 10.10; H, 4.23; N, 11.48; F, 3.81; I, 52.7. The strongest absorptions in the 400–600-cm^{-1} region of the infrared spectrum were at 410, 435, 485, 535, and 560 cm^{-1}. A very weak band was noted at 475 cm^{-1}. The electronic absorption spectrum in aqueous solution was characterized by λ_{max} 503 nm, ϵ (cm^{-1} M^{-1}) 74.2; λ_{max} 373, ϵ 32.4; λ_{min} 426 nm, ϵ 16.1 (lit.[5] 503, 72.5; 373, 31.5). Resistance measurements on a 10^{-3} M aqueous solution of the complex at 25 °C indicated the complex to be a 2:1 electrolyte.

Synthesis of *cis*-Fluorothiocyanatobis(ethylenediamine)chromium(III) Iodide–0.5-Water. An 8.7-g (18-mmol) sample of crude *cis*-$[Cr(en)_2F(OH_2)]I_2 \cdot H_2O$ was dissolved in 15 ml of water at room temperature, the solution was filtered, and 1.86 g (24 mmol) of solid ammonium thiocyanate was added. The resulting solution was filtered and the filtrate was heated on a steam bath for 10 min. At the end of this time the reaction mixture was cooled in ice for 20 min, and the solid which had precipitated was collected, washed with acetone, and air-dried. This method produced 3.38 g (49%) of product. Anal. Calcd for *cis*-$[Cr(en)_2FNCS]I \cdot 0.5H_2O$: C, 15.59; H, 4.46; N, 18.18; F, 4.93; I, 32.94. Found: C, 17.04; H, 4.63; N, 18.10; F, 5.0; I, 32.99. The electronic spectrum in aqueous solution was characterized by λ_{max} 500 nm, ϵ 104; λ_{max} 373, ϵ 50. The strongest absorptions in the 400–600-cm^{-1} region of the infrared spectrum were at 405, 439, 490, 525, 550, and 560 cm^{-1}. The infrared spectrum also confirmed the presence of N-bound thiocyanate.

Exchange of Perchlorate for Iodide. A solution of 19.8 g (51.4 mmol) of *cis*-fluorothiocyanotobis(ethylenediamine)chromium(III) iodide–0.5-water in 500 ml of water at room temperature was filtered and treated with 250 g (2.04 mol) of finely powdered anhydrous sodium perchlorate. The solution was stirred until all of the sodium perchlorate dissolved. The product was collected by filtration, washed twice with 25-ml portions of ice-cold acetone, and air-dried; yield 10.2 g (57%). Anal. Calcd for *cis*-$[Cr(en)_2FNCS]ClO_4$: C, 17.22; H, 4.63; N, 20.09; Cr, 14.91; S, 9.19. Found: C, 17.51; H, 4.34; N, 20.04; Cr, 14.98; S, 9.35.

The electronic spectrum of an aqueous solution of the complex was in agreement with that found for the corresponding iodide. The infrared spectrum in the 400–600-cm^{-1} region was in agreement with that reported for the corresponding iodide except that a single broad band was found at 560 cm^{-1}. The molar conductance at 25 °C of a 10^{-3} M aqueous solution was 96 cm^2 Ω^{-1} M^{-1}.

Resolution of *cis*-Fluorothiocyanotobis(ethylenediamine)chromium(III) Perchlorate. A 7.4-g (21.2-mmol) sample of the racemic complex was dissolved in 235 ml of water at room temperature. The solution was filtered to remove any undissolved material and 7.09 g (19.7 mmol) of solid ammonium α-bromocamphor-π-sulfonate was added; the solution was stirred until everything dissolved, filtered, and finally allowed to stand for 4 h. At the end of this time, the product was collected, washed with acetone, and air-dried. This method produced 1.77 g (14.2%) of product. A 0.14% aqueous solution of the complex had a specific rotation of +192° at 546 nm. Anal. Calcd for *cis*-$[Cr(en)_2FNCS]C_{10}H_{14}O_4BrS \cdot 1.5H_2O$: C, 30.71; H, 5.68; N, 11.94; Cr, 8.87. Found: C, 31.17; H, 5.63; N, 11.92; Cr, 8.88.

A 1.16-g sample of the crude diastereomer(s) was slurried with 37 ml of water at room temperature for 10 min. The insoluble fraction was collected, washed with acetone, and air-dried; yield 0.47 g. The specific rotation of the insoluble fraction was determined exactly as described previously ($[\alpha]_{546}$ +204°).

To remove the resolving agent from the diastereoisomer a 0.41-g (0.70-mmol) sample of the water-extracted material was dissolved in 23 ml of water, the solution was filtered, and the filtrate was treated with solid anhydrous sodium perchlorate until precipitation ceased. The reaction mixture was allowed to stand at room temperature for 15 min; the product was collected, washed with cold acetone, and air-dried; yield 0.13 g (53%). Anal. Calcd for *cis*-$[Cr(en)_2FNCS]ClO_4$: C, 17.22; H, 4.63; N, 20.09; Cr, 14.91; F, 5.45. Found: C, 17.38; H, 4.60; N, 19.82; Cr, 15.03; F, 5.75.

The optical rotatory dispersion spectrum was characterized by a maximum negative rotation at 449 nm (specific rotation −317°), zero rotation at 487 nm, and a maximum positive rotation at 524 nm (specific rotation +397°). At 589 and 546 nm the specific rotations were +6.0 and +234°, respectively, for a 0.17% aqueous solution.

Isolation of Iodoaquobis(ethylenediamine)chromium(III) Iodide–1-Water. The filtrate from which *cis*-$[Cr(en)_2F(OH_2)]I_2 \cdot H_2O$ had been isolated was allowed to evaporate overnight in a hood. The dark purple crystals were collected, washed with absolute alcohol and acetone, and air-dried. Extraction of aqueous solutions of the complex with carbon tetrachloride indicated the absence of free iodine. Anal. Calcd for $[Cr(en)_2I(OH_2)]I_2 \cdot H_2O$: C, 8.16; H, 3.43; N, 9.51; I, 64.64; H_2O, 6.12. Found: C, 8.01; H, 3.23; N, 9.65; I, 64.30; H_2O, 6.10. The strongest absorptions in the 400–600-cm^{-1} region of the infrared spectrum were at 406, 428, 485, 545 (sh), and 555 cm^{-1}.

A weighed sample of the complex was heated at 115–120 °C for 24 h. The sample turned from a purple to a dark green and lost 6.1% of its weight. Anal. Calcd for $[Cr(en)_2I_2]I$: C, 8.69; H, 2.92; N, 10.14. Found: C, 8.63; H, 2.84; N, 10.25.

Isolation of *cis*-Difluorobis(ethylenediamine)chromium(III) Perchlorate. A 32-g (77-mmol) sample of *cis*-$[Cr(en)_2F_2][Cr(en)F_4] \cdot H_2O$ was dissolved in 130 ml of water at room temperature, the solution was filtered, and 42.5 ml of 6 M perchloric acid was added. The stirred solution was diluted by the slow addition of 640 ml of absolute alcohol followed by 215 ml of ether. The red-purple solid was collected, washed with acetone, and air-dried. This method produced 11.5 g (48%) of crude product. Purification was by extracting a 5.5-g sample of the crude product with 15 ml of water. The insoluble material was collected, washed with acetone, and air-dried; yield 2.8 g. Anal. Calcd for *cis*-$[Cr(en)_2F_2]ClO_4$: C, 15.51; H, 5.22; N, 18.10; F, 12.27; Cr, 16.79. Found: C, 15.60; H, 5.45; N, 17.85; F, 12.50; Cr, 16.86. The molar conductance of a 10^{-3} M aqueous solution of the complex at 25 °C was 101 cm^2 Ω^{-1} M^{-1}. The electronic spectrum was in agreement with that reported previously for the corresponding iodide.

Analytical Methods and Instrumentation. The analytical methods and instrumentation were the same as those described previously.[1,7]

Discussion

Aquation of *cis*-difluorobis(ethylenediamine)chromium(III) iodide in a concentrated hydriodic acid solution proceeds with retention of geometric configuration to produce fluoroaquobis(ethylenediamine)chromium(III) iodide as the less soluble product. If the monofluoro product is removed and the aquation allowed to continue, the second fluoro ligand is lost from the starting material.

Under the experimental conditions utilized in this study the aquation is accompanied by iodide ion coordination. The coordination of the iodide by the chromium(III) ion probably occurs in the later stages of the reaction after the second fluoro ligand has been removed. This supposition is supported by the observation that compounds of the type *cis*-$[Cr(en)_2FX]I$ (X = Cl, Br) have relatively low solubilities in water,[8] and *cis*-$[Cr(en)_2FI]I$ was never detected in the early stages of the aquation. However, it is not possible at present to state definitely that iodide coordination occurs after the second fluoro ligand is lost. This point is still under investigation.

The assignment of a cis geometry to the initial reaction product is well supported by the following pieces of evidence: (1) the aqueous solution electronic absorption spectrum of the compound prepared in this study is in good agreement with that reported by Wirth and Linck,[5] who prepared solutions of the ion by photolysis of *trans*-$[Cr(en)_2FCl]ClO_4$; (2) the wavelengths of maximum absorption in the electronic spectrum are very close to those found for solutions of the ion produced by Ag^+-induced aquation of *cis*-$[Cr(en)_2FCl]Cl$;[4] (3) the infrared spectrum in the 400–600-cm^{-1} region is consistent with that previously reported for cis isomers of the type $[Cr(en)_2FX]^{n+}$.[9]

The anation of *cis*-$[Cr(en)_2F(OH_2)]^{2+}$ with thiocyanate ion proceeds with retention of geometric configuration to produce *cis*-$[Cr(en)_2FNCS]^+$. In this case the geometry of the F(NCS) product is unequivocally cis since the product was resolved into its optical antipodes. The optical rotatory dispersion studies indicate that $(+)_{5461}$-*cis*-$[Cr(en)_2FNCS]ClO_4$ and (+)-*cis*-$[Cr(en)_2F_2]I$ both have the same absolute configuration which is the same as $\Lambda(+)$-$[Co(en)_3]^{3+}$.

The *cis*-fluorothiocyanatobis(ethylenediamine)chromium(III) ion was prepared earlier by a longer, more tedious synthesis and the geometry was inferred from the electronic spectral data.[4] Resolution of the ion into its optical antipodes confirms the original assignment of the geometry.

The molar absorptivities of the *cis*-F(NCS) complex prepared in this study differ considerably from those reported earlier. This is due to the fact that the compound prepared earlier was impure.[4]

The purple product obtained in the latter stages of the aquation, $[Cr(en)_2I(OH_2)]I_2 \cdot H_2O$, appears to involve a cis arrangement of the iodo and aquo ligands. This geometry is consistent with the electronic absorption spectrum in aqueous solution, its infrared spectrum in the 400–600-cm^{-1} region, and the fact that aquation of the complex in dilute perchloric acid produces a solution whose electronic spectrum is identical with that of *cis*-$[Cr(en)_2(OH_2)_2]^{3+}$.[10]

The purple product on the basis of elemental analyses could be any one of three compounds. The complex $[Cr(en)_2(OH_2)_2]I_3$ can be eliminated at once since the electronic spectrum changes rapidly with time and $[Cr(en)_2(OH_2)_2]^{3+}$ is stable in aqueous solution. $[Cr(en)_2I_2]I \cdot 2H_2O$ was eliminated by rapid measurements of the resistance of aqueous solutions of the complex. The results always indicated three or more ions per complex ion. Thus the purple product was formulated as $[Cr(en)_2I(OH_2)]I_2 \cdot H_2O$.

Thermal dehydration of $[Cr(en)_2I(OH_2)]I_2 \cdot H_2O$ produced purple-green $[Cr(en)_2I_2]I$ as a final product.

Registry No. *cis*-$[Cr(en)_2F(OH_2)]I_2$, 59765-91-2; *cis*-$[Cr(en)_2FNCS]I$, 59765-92-3; *cis*-$[Cr(en)_2FNCS]ClO_4$, 59765-93-4; *cis*-$[Cr(en)_2FNCS]C_{10}H_{14}O_4BrS$, 59796-02-0; Λ-(+)-*cis*-$[Cr(en)_2FNCS]ClO_4$, 59796-03-1; $[Cr(en)_2IOH_2]I_2$, 59765-94-5; $[Cr(en)_2I_2]I$, 59765-95-6; *cis*-$[Cr(en)_2F_2]ClO_4$, 59765-96-7; *cis*-$[Cr(en)_2F_2][Cr(en)F_4]$, 13842-99-4; Λ-(+)-*cis*-$[Cr(en)_2F_2]I$, 14588-00-2.

References and Notes

(1) Part 6: J. W. Vaughn and G. J. Seiler, *Inorg. Chem.*, **13**, 598 (1974).
(2) Taken in part from a thesis submitted by A.M.Y. to the Graduate School of Northern Illinois University in partial fulfillment for the M.S. degree.
(3) K. R. A. Fehrmann and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 1276 (1961).
(4) J. W. Vaughn, O. J. Stvan, and V. E. Magnuson, *Inorg. Chem.*, **7**, 736 (1968).
(5) G. Wirth and R. G. Linck, *J. Am. Chem. Soc.*, **95**, 5913 (1973).
(6) J. W. Vaughn and B. J. Krainc, *Inorg. Chem.*, **4**, 1077 (1965).
(7) J. W. Vaughn, V. E. Magnuson, and G. J. Seiler, *Inorg. Chem.*, **8**, 1201 (1969).
(8) J. W. Vaughn and A. M. Yeoman, unpublished data.
(9) J. W. Vaughn, J. M. DeJovine, and G. J. Seiler, *Inorg. Chem.*, **9**, 684 (1970).
(10) H. L. Schläfer and O. Kling, *Z. Anorg. Allg. Chem.*, **287**, 296 (1956).

Correspondence

Phosphorus-31 Nuclear Magnetic Resonance Study of the Structure of Some "Triphosphites"

AIC60013V

Sir:

Condensation reactions between alkyl- or arylchlorophosphines and trialkyl phosphites have been shown to yield products which possess P–P bonds with the phosphorus atoms existing in different oxidation states, eq 1 and 2.[1,2] Conclusive

$$R_2PCl + P(OR')_3 \rightarrow R_2P\text{-}P(O)(OR')_2 + R'Cl \qquad (1)$$

$$RPCl_2 + 2P(OR')_3 \rightarrow RP[P(O)(OR')_2]_2 + 2R'Cl \qquad (2)$$

$$R = \text{alkyl or aryl group; } R' = CH_3 \text{ or } C_2H_5$$

evidence for the formation of these products in eq 1 and 2 was obtained from ^{31}P NMR spectroscopy. In the ^{31}P NMR spectra of these compounds the triply connected phosphorus atoms show positive chemical shifts from 85% H_3PO_4, whereas the quadruply connected phosphorus atoms exhibit negative chemical shifts from the same reference. Furthermore, these spectra exhibit the characteristic homonuclear P–P coupling constant values greater than 150 Hz.

In contrast to this observation, the products resulting from the treatment of alkylchlorophosphines with the sodium salt of dialkyl phosphites and those obtained from alkylchlorophosphines and dialkyl phosphites in the presence of triethylamine have been assigned[3] structures with P–O–P linkages, eq 3 and 4, based on triply connected phosphorus atoms.

$$RPCl_2 + 2NaOP(OC_2H_5)_2 \rightarrow RP[OP(OC_2H_5)_2]_2 + 2NaCl \qquad (3)$$

$$RPCl_2 + 2HOP(OC_2H_5)_2 \xrightarrow{2N(C_2H_5)_3} RP[OP(OC_2H_5)_2]_2 + 2N(C_2H_5)_3HCl \qquad (4)$$

$$R = \text{alkyl group}$$

Apparently, there has been no ^{31}P spectral study reported for the products of eq 3 and 4 and, therefore, these structural assignments are far from conclusive. Furthermore, in some reactions related to eq 3, Michalski and co-workers[4] obtained phosphorus products which contain P–P bonds, eq 5.

$$(RO)_2PONa + ClP(O)(OR)_2 \rightarrow (RO)_2(O)P\text{-}P(O)(OR)_2 + NaCl \qquad (5)$$

$$R = \text{alkyl group}$$

While spectroscopic evidence[5] on the dialkyl phosphites is overwhelmingly in favor of the structure $(RO)_2P(O)H$, based on quadruply connected phosphorus, spectral data on their sodium salt strongly indicate[5] the structure $(RO)_2PONa$ based on triply connected phosphorus. Since both of the reactions 3 and 4 gave identical products, it was not unreasonable nearly 20 years ago[3] to assign to these compounds a structure based on triply connected phosphorus atoms.

Because of our recent interest[2,6,7] in the catenation compounds of group 5 elements, we thought it desirable to reexamine the products of reactions 3 and 4 and establish their structures from ^{31}P NMR spectra.

Experimental Work. The ^{31}P NMR measurements were carried out on a Varian XL-100-15 spectrometer equipped with