positions among which they can be distributed. The C_5H_5N groups are restricted one to each Nb and not permitted in the bridging positions. This means that one C_5H_5N must be in position a, b, c, or d and the other in g, h, i, or j. There are then only 16 different arrangements possible for the C_5H_5N groups. For each such arrangement there remain eight positions in which the two Cl and six OC_2H_5 groups are to be distributed. They can be placed in these positions in $8!/(6! \times 2!)$ or 28 ways. The total number of possibilities to be considered is then 16×28, or 448. It is possible to eliminate several of these blocks of 28 by considering only the 16 arrangements for the C_5H_5N groups. Only six of the blocks are unique, leaving 6×28, or 168, possibilities for detailed examination. These then reduce to 120 by consideration of rotations that have no net effect on the location of the C_5H_5N groups. These 120 forms include 50 enantiomorphic pairs, six species with centers of symmetry, six *meso* forms, and eight other inactive species, or the total of 70 geometrical isomers calculated by Kennedy, *et al.*[6]

For more symmetrical cases there is a greater number of symmetry elements to consider. An octahedron, point group O_h, for example, has three C_4 axes, four C_3 axes, and six C_2 axes. Therefore, 23 other configurations can be generated from the original octahedral arrangement (nine *via* the C_4 axes, eight *via* the C_3, and six *via* the C_2). It is interesting to note that this relationship leads directly to the calculation of 30 stereoisomers for Mabcdef, *i.e.*, $6!/24$.

Isomer counts for polynuclear species containing chelating ligands are quite rare. (See Table I.) Bailar has devised a scheme for determining the number of isomers for mononuclear octahedral complexes which includes chelated species.[8] However, general analytical methods, even for mononuclear chelated species, have not yet been developed although limited success with mononuclear systems has been claimed by Krivoshei.[9] We have not been able to include chelated species in our procedure, but its mechanics have helped us to examine the rather complicated case of the dimer $(AB)_2M(C)_2M(AB)_2$ in a straightforward manner, with some assurance that all possibilities were considered. There are eight ways the two unsymmetrical chelating groups can be bonded to the four nonbridging positions of the dimer, so that there are 64 possibilities to consider. Again the rotational permutations consist of three C_2 axes. Visual examination leads to the conclusion that there are 24 stereoisomers comprising 10 pairs of enantiomorphs, one *meso* form, one form with a center of symmetry, and two *meso* forms with centers of symmetry.

Table I summarizes the isomer counts we have made along with those already in the literature. More details and tabulations of individual configurations are available.[10]

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TABLE I

CLASSIFICATION OF ISOMERS FOR DOUBLE-BRIDGED DIMERS WITH OCTAHEDRAL CENTERS

					Total Isomers	
	Enantio-morphic	Inactive				
Formula[a]	pairs	*Meso*	Center	Other	Geo-metrical	Stereo
$M2Ma_6b_2$	2	2	2	2	8^c	10
$M2Ma_4b_2c_2$	46	4	4	14	68^c	114
$M2M[a_3b]^1[a_3b]^2$	1^d	2^d	2^d	...	5^d	6^d
$M2M[a_2bc]^1[a_2bc]^2$	17	4	4	...	25	42
$M2M(AA)_4$	1^e	1^e	...	...	2^e	3^e
$M2M(AB)_4$	10	3^b	3^b	...	14^b	24^b
$M2{*}Ma_5b_2c$	37	...	...	10	47^c	84
$M2{*}M(AA)_4$	1^e	1^e	...	...	2^e	3^c
$M2'M(AA)_4$	2^f	...	...	...	2^f	4^f
$M(2)M[a]^1[a]^2b_6c_2$	50	6	6	8	70^c	120

[a] M2M represents a pair of metal atoms joined by two identical symmetrical bridges. M2*M indicates that there are two different symmetrical bridges, M2′M that one bridge is symmetrical and the other not. M(2)M indicates that the groups being permuted can occupy the bridge as well as nonbridge positions. Symbols enclosed in $[\ ]^1$ are substituents only on the first M, those in $[\ ]^2$ only on the second. [b] Two of the inactive forms possess centers of symmetry and are also *meso* forms. [c] See ref 6. [d] F. Basolo in "Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, p 290. [e] W. C. Fernelius in "Chemical Architecture," R. E. Burk and O. Grummitt, Ed., Interscience Publishers, Inc., New York, N. Y., 1948, p 93. [f] C. E. Wilkes and R. A. Jacobson, *Inorg. Chem.*, **4**, 99 (1965).

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[10] A more detailed form of this paper, including tabulations of individual isomers for $M2Ma_6b_2$, $M2Ma_4b_2c_2$, $M2M[a_2bc]^1[a_2bc]^2$, $M2M(AB)_4$, $M2{*}Ma_5b_2c$, and $M(2)M[a]^1[a]^2b_6c_2$ has been deposited as Document No. 9535 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $3.75 for photoprints, or $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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Some Chemistry of Trichlorophosphazosulfuryl Chloride

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Although the chemistry of $PCl_3{=}NSO_2Cl$ has not been extensively investigated, one mode of reaction has been established. Treatment of $PCl_3{=}NSO_2Cl$ with either chlorosulfonic acid[1] or hydrogen fluoride[2] results in protonation of the nitrogen followed by P–N bond cleavage

$$HSO_3Cl + PCl_3{=}NSO_2Cl \longrightarrow HN(SO_2Cl)_2 + POCl_3$$

$$6HF + PCl_3{=}NSO_2Cl \xrightarrow{BF_3} 4HCl + PF_5 + H_2NSO_2F$$

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A halogen-exchange reaction has now been observed when $PCl_3{=}NSO_2Cl$ is treated with anhydrous arsenic(III) fluoride. However, exchange occurs only with the chlorine bound to sulfur. No evidence was found for any phosphorus–fluorine bond formation by F^{19} nmr and the isolated product $PCl_3{=}NSO_2F$ is identical with that obtained by the reaction of phosphorus pentachloride with H_2NSO_2F.[3] Attempts to prepare $PF_3{=}NSO_2F$ by halogen exchange utilizing other metal fluorides such as potassium fluoride or antimony(III) fluoride were unsuccessful.

The reactivity of $PCl_3{=}NSO_2F$ toward acids was found to be similar to the chloro derivative. Thus the interaction of fluorosulfonic acid with $PCl_3{=}NSO_2F$ in arsenic(III) fluoride solution produced imidodisulfuryl fluoride. However, it was not possible to isolate this product since it appears to form an azeotropic mixture with phosphorus oxychloride which has the composition $[HN(SO_2F)_2]_3 \cdot POCl_3$. Whether this is an actual compound or a normal azeotropic mixture is not known. However, some complexation probably occurs between the components since a relatively large downfield shift is observed in the H^1 nmr spectrum. The mixture can also be formed by mixing the pure components in arsenic(III) fluoride solution and it can be used to prepare salts of the $N(SO_2F)_2^-$ ion. For example, reaction of $[HN(SO_2F)_2]_3 \cdot POCl_3$ with cesium carbonate in aqueous solution produced the cesium salt in good yield. Pure imidodisulfuryl fluoride can be obtained by treatment of imidodisulfuryl chloride with arsenic(III) fluoride in the absence of phosphorus oxychloride. This is perhaps the most convenient preparative method for this material even though it requires the isolation of the chloride.

Hydrolysis of $PCl_3{=}NSO_2F$ produces H_2NSO_2F in moderate yield when the reaction is carried out in arsenic(III) fluoride solution. It is believed that water in this system behaves as fluorosulfuric acid. Unfortunately attempts to extend this reaction to other acids were not successful. For example, no reaction was observed when trifluoroacetic acid was employed and only the starting materials could be isolated.

Another mode of reaction that $PCl_3{=}NSO_2Cl$ is known to undergo is oxygen transfer from sulfur to phosphorus which occurs during its thermal decomposition.[4] This type of exchange has now been found to occur between sulfur dioxide and $PCl_3{=}NSO_2Cl$ at 150°. The product could be isolated in low yield by

$$PCl_3{=}NSO_2Cl + SO_2 \longrightarrow POCl_3 + OSNSO_2Cl$$

distillation. Formulation of the product as N-sulfinylsulfuryl chloride is based upon its infrared spectrum and its hydrolysis. The infrared spectrum of $OSNSO_2Cl$ contains bands due to the SO_2Cl group at 1381 and 1168 cm^{-1} and bands due to the OSN group at 1239 and 1099 cm^{-1}. These assignments were made by comparison with the infrared spectra of N-sulfinylsulfonamides which contain bands due to the SO_2R group and the OSN group at 1375 and 1175 cm^{-1} and at 1250 and 1090 cm^{-1}, respectively.[5] The infrared spectrum of $OSNSO_2Cl$ contains bands at 731 and 673 cm^{-1} in addition to those listed above. The hydrolysis of $OSNSO_2Cl$ was also found to be analogous to that observed for N-sulfinylsulfonamides.[5] When it was carried out in arsenic(III) fluoride solution, good yields of H_2NSO_2F could be isolated.

During the course of the above work a reaction between imidodisulfuryl chloride and phosphorus pentachloride was observed. This proceeds according to the equation

$$PCl_5 + HN(SO_2Cl)_2 \longrightarrow HCl + PCl_4N(SO_2Cl)_2$$

When carried out in $POCl_3$ solution the product crystallizes out on cooling. It is easily hydrolyzed and should be handled in the absence of moisture. Several attempts were made to extend this reaction to include $HN(SO_2F)_2$. They were not successful owing to a chlorine–fluorine exchange between phosphorus and sulfur and only the above-mentioned chloride derivative could be isolated. In nitromethane solution, $PCl_4N(SO_2Cl)_2$ behaves as a 1:1 electrolyte and should probably be considered as the tetrachlorophosphonium salt of the $N(SO_2Cl)_2^{\ominus}$ ion. Since the nature of the ions formed in solution is not known, other possibilities such as $Cl_2P(NSO_2Cl)_2^{\oplus}PCl_6^{\ominus}$ cannot be eliminated.

Experimental Section

Materials.—Arsenic trifluoride was obtained from Ozark-Mahoning and dried by distillation from sodium fluoride. The compound $PCl_3{=}NSO_2Cl$ was prepared by the literature method.[5] Fluorosulfonic acid was used as obtained from commercial sources.

Preparation of $PCl_3{=}NSO_2F$.—A 25-g sample of $PCl_3{=}NSO_2Cl$ in 25 ml of arsenic(III) fluoride was placed in a polyethylene bottle fitted with a reflux condenser. The mixture was refluxed 2 hr. Then 25 ml of CH_2Cl_2 was added and the mixture was filtered. The solvent was again removed under vacuum and the residue distilled. The fraction boiling at 74–75° (1 mm) solidified in the receiver. It was recrystallized from pentane–carbon tetrachloride; yield, 15.2 g.

Anal. Calcd for PCl_3NSO_2F: Cl, 45.5; F, 8.1; N, 5.96; S, 13.6. Found: Cl, 44.9; F, 7.8; N, 5.97; S, 13.3.

The F^{19} nmr spectrum consisted of a doublet (J_{PF} = 4 cps) centered at ϕ −59.6.

Preparation of $HN(SO_2F)_2A$.—A 50-g sample of $PCl_3{=}NSO_2Cl$ and 100 ml of arsenic(III) fluoride were placed in a polyethylene bottle and brought to reflux. Then 20 g of HSO_3F in 25 ml of arsenic(III) fluoride was slowly added. The mixture was refluxed 1 additional hr and then worked up as described above. A 28.2-g sample, bp 78–80° (25 mm), was obtained.

Anal. Calcd for $[HN(SO_2F)_2]_3 \cdot POCl_3$: N, 6.03; F, 16.4; P, 5.0; Cl, 17.0, S, 27.6. Found: N, 5.89; F, 15.7; P, 5.2; Cl, 18.4; S, 26.9; F:N = 1.97; Cl:P = 3.08.

The F^{19} nmr spectrum of the mixture showed a single band at ϕ −57.8 while the proton spectrum had a band at −10.3 ppm (from TMS). Imidodisulfuryl fluoride has a single band in the H^1 nmr spectrum at −9.0 ppm (from TMS) and a single band in the F^{19} nmr spectrum at ϕ −56.9.[6] When 9.3 g of $HN(SO_2F)_2$ and 8.1 g of $POCl_3$ were mixed in 25 ml of AsF_3, stirred for 10 min, and then distilled, 12.4 g of a constant-boiling product (bp 78–80° (25 mm)) was obtained. It had H^1 and F^{19} nmr spectra that were identical with that obtained above.

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A 10-g sample of $[HN(SO_2F)_2]_3 \cdot POCl_3$ was slowly added to 50 ml of ice water. The resulting acid solution was neutralized with Cs_2CO_3. The mixture was filtered and the water removed under vacuum. The residue was recrystallized from ethanol to yield 13.5 g of $CsN(SO_2F)_2$ (mp 116–118°, lit.[7] 115–117°).

A 187-g sample of $HN(SO_2Cl)_2$[8] and 300 ml of arsenic(III) fluoride were placed in a polyethylene bottle and refluxed for 2 hr. The mixture was treated as described above appropriately scaled by a factor of 6. The residue was distilled to give 132 g of $HN(SO_2F)_2$ (bp 83–84° (25 mm)). Purification and identification of the product were achieved as described in the literature.[6]

Preparation of H_2NSO_2F.—To a 50-g sample of $PCl_3{=}NSO_2Cl$ in 50 ml of arsenic(III) fluoride contained in a polyethylene bottle, 4.0 g of H_2O was slowly added. The mixture was refluxed for 1 hr and then cooled. It was worked up as described above and the residue was distilled. A 12.3-g sample of H_2NSO_2F (bp 71–72° (3 mm), lit.[2] 70° (3 mm); mp 6°, lit.[2] 7–8°) was obtained. The F^{19} nmr spectrum contained a single peak at ϕ −57.3.

Preparation of $OSNSO_2Cl$.—A 25-g sample of $PCl_3{=}NSO_2Cl$ was loaded into a 100-ml stainless steel Hoke cylinder equipped with a needle valve. Then 50 ml of SO_2 was condensed into the bomb with liquid nitrogen. The bomb was heated for 2 hr at 145–150° before being cooled to ambient temperature. The excess SO_2 was allowed to escape and the residue was washed out of the bomb with CH_2Cl_2. The solvent was removed under vacuum and the residue was distilled. A 2.8-g sample of $OSNSO_2Cl$ (bp 41–42° (1 mm)) was obtained.

Anal. Calcd for $OSNSO_2Cl$: Cl, 22.0; N, 8.67; S, 39.6. Found: Cl, 21.4; N, 8.61; S, 38.9.

Preparation of $PCl_4N(SO_2Cl)_2$.—A 7.1-g sample of PCl_5 was added to a solution of 7.3 g of $HN(SO_2Cl)_2$ in 25 ml of $POCl_3$. The mixture was heated to 80° under nitrogen for 2.5 hr. Upon cooling, the product crystallized out. The crystals were removed by filtration in an inert atmosphere to give 8.6 g of $PCl_4N(SO_2Cl)_2$ (mp 176–188°).

Anal. Calcd for $PCl_4N(SO_2Cl)_2$: N, 3.66; Cl, 55.2; S, 16.6. Found: N, 3.70; Cl, 54.8; S, 16.2.

The conductivity of $PCl_4N(SO_2Cl)_2$ was determined in nitromethane using equipment previously described.[9] The concentration (M) and equivalent conductance (cm²/ohm equiv), respectively, are: 8.376×10^{-3}, 90; 4.188×10^{-3}, 97.3; 2.094×10^{-3}, 102.3; and 1.047×10^{-3}, 105.9. The equivalent conductance at infinite dilution was found to be 114.4. A plot of $\Omega_\infty - \Omega$ *vs.* $\sqrt{C}$ had a slope of 250 which is in the range for a 1:1 electrolyte.[10]

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Nuclear Magnetic Resonance Study of Cobalt and Nickel Tetrafluoroborates

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A number of recent studies have made use of nuclear magnetic resonance spectra to obtain solvation numbers, electronic–nuclear coupling constants, and solvent-exchange rates for various metal ions in solution. This type of information is vital to a better understanding of the molecular and electronic structure and of the chemical reactions of these ions in solution. The perchlorate salts of Co(II) and Ni(II) in particular have received considerable attention.[2-9] It was of interest to determine whether the tetrafluoroborate salts of Co(II) and Ni(II) in acetonitrile gave essentially the same results as the perchlorate salts.

Experimental Section

The nmr spectra were obtained with a Varian A-60 spectrometer equipped with a V-6040 nmr variable-temperature controller. Temperatures were measured to ±1° by means of an iron–constantan thermocouple.

The salts were prepared in anhydrous acetonitrile solution under a dry nitrogen atmosphere. The acetonitrile was purified by successive distillations from phosphorus pentoxide. The solutions were analyzed for cobalt by EDTA titration and for nickel by the gravimetric dimethylglyoximate method.

Results and Discussion

The $\Delta\nu_{\rm M}$ shifts were obtained using the fast-exchange form of eq 8 of Swift and Connick[10]

$$\Delta\nu_{\rm obsd} = P_{\rm M}\Delta\nu_{\rm M} \qquad (1)$$

where $\Delta\nu_{\rm obsd}$ is the observed shift of the solvent peak, $P_{\rm M}$ is the mole fraction of bound sites assuming a coordination number of six, and $\Delta\nu_{\rm M}$ is the shift for unit mole fraction of coordinated sites. The results are given in Table I. The values of $\Delta\nu_{\rm M}$ showed a linear dependence on $1/T$ with a nonzero intercept as also found by Matwiyoff and Hooker[6] and by Ravage, Stengle, and Langford.[7] A least-squares treatment of the Co(II) data gave a slope of $(5.88 \pm 0.32) \times 10^5$ cps deg and an intercept of -1440 ± 100 cps. Since $\mu_{\rm eff}$ was equal to 5.18 BM[11] at room temperature for $Co(CH_3CN)_6{}^{2+}$ and was assumed to be temperature independent,[6] the coupling constant, A, was calculated to be $-(1.85 \pm 0.10) \times 10^5$ cps from eq 8 of Matwiyoff and Hooker.[6] A similar least-squares treatment for the Ni(II) data gave a coupling constant of $-(5.21 \pm 0.41) \times 10^5$ cps and an intercept of -910 ± 170 cps. The value used for $\mu_{\rm eff}$ was 3.22 BM.[11] It too was assumed to be temperature independent.[7] The results obtained are listed in Table II, together with values previously reported.[6,7] The value of the Co(II) coupling constant is larger than that of Matwiyoff and Hooker;[6] the Ni(II) coupling constant is also larger than that obtained by Matwiyoff and Hooker,[6] but smaller than that of Ravage, Stengle, and Langford.[7]

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