(measured in a sealed off Teflon FEP tube) varied for different preparations from 35 to 88°. This variation could possibly be due to changes in the composition of the adduct.

X-Ray and Nmr Data.—Debye-Scherrer powder patterns were obtained for $ClF_5 \cdot SbF_5$. However, the pattern was too complex to allow determination of the crystal system and lattice parameters. Attempts to record the F^{19} nmr spectrum of the complex in HF solution failed owing to rapid exchange.

Vibrational Spectra.—The infrared spectra of solid ClF_5, $ClF_5 \cdot AsF_5$, and $ClF_5 \cdot SbF_5$ and the Raman spectrum of $ClF_5 \cdot SbF_5$ have been recorded. The spectra of the adducts are best interpreted in terms of ionic structures containing the ClF_4^+ cation. The latter most likely has symmetry C_{2v}. Detailed results on the vibrational spectra of ClF_4^+, BrF_4^+, and IF_4^+ will be published in a separate paper.[24]

Discussion

The synthesis of a well-defined 1:1 adduct between ClF_5 and AsF_5 presents no difficulties. In the case of SbF_5 the reaction conditions must be controlled more carefully owing to the absence of a common liquid range between ClF_5[20] (bp −14° (760 mm)) and SbF_5 (mp 7°) at ambient pressure. Hence, either a common solvent, such as HF, or increased pressure should be used in the synthesis of $ClF_5 \cdot SbF_5$. The formation of polymeric anions of the type $SbF_6^- \cdot xSbF_5$ is not unexpected and has been observed in similar systems.[25,26] It can be essentially avoided by adding the SbF_5-containing solution slowly to excess ClF_5 or by carrying out the synthesis under elevated pressure using again a large excess of ClF_5. Boron trifluoride appears to be too weak a Lewis acid for forming a complex with ClF_5. The vapor pressure of 590 mm measured above the liquid BF_3–ClF_5 system at −95.1° is only slightly lower than that of 594 mm calculated[27] for two ideal liquids according to Raoult's law. Since ClF_5 had been used in excess (55 mol %) and has a negligible vapor pressure[20] at −95°, it can be concluded that there is practically no positive interaction between BF_3 and ClF_5 at temperatures as low as −95°. The tendency to form adducts with ClF_5 decreases in the order $SbF_5 > AsF_5 > BF_3$ and is the same as that observed for other halogen fluorides such as ClF_3,[10] ClF,[1] or IF_5.[28,29] The heat of dissociation,[21] 25.23 kcal mol^{-1}, obtained for $ClF_5 \cdot AsF_5$ is of the same order of magnitude as the values obtained for similar ionic complexes such as $ClF_2^+BF_4^-$ [9] (23.6 kcal mol^{-1}) and $NO^+ClF_4^-$ [16] (15.8 kcal mol^{-1}).

The failure to observe complex formation between ClF_5 and Lewis bases is not surprising since the preparation of ClF_5 by fluorination of $Cs^+ClF_4^-$ [20] had indicated no interaction between CsF and ClF_5. Vapor pressure measurements on the liquid ClF_5–NOF system (in a 1:1 mole ratio) at −78.8° showed only a small negative deviation from the value (116 mm) calculated[20,30] for an ideal mixture according to Raoult's law. An infrared spectrum of the mixture after being kept at −78° for 24 hr showed that no chemical reaction, such as oxidation of NOF, had occurred.

The fact that ClF_5 (having one free localized electron pair) is capable of forming adducts with strong Lewis acids but not with Lewis bases suggests that in chlorine fluorides the highest possible coordination number of pentavalent chlorine toward fluorine (or localized free electron pairs) is 6. The conclusion that ClF_5 is saturated with respect to coordination number and hence also little associated in the liquid phase is further supported by spectroscopic evidence[31] and the low boiling point and Trouton constant[20] reported for ClF_5. Based on these data, the preparation of a stable, mainly covalent chlorine heptafluoride would be quite surprising.

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Transition Metal Dithiolene Complexes. V.[1] Ligand-Exchange Reactions in Nitrosyl Iron Bis-1,2-dithiolenes

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The assumption that transition metal dithiolene complexes do not undergo ligand-exchange reactions has been shown to be incorrect.[3] Using polarography, it has been possible to show that ligand exchange does occur between planar nickel bisdithiolenes in solution. We have subsequently found that similar exchange reactions occur between nitrosyliron bisdithiolene complexes.

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Equimolar amounts (*ca.* 10^{-3} *M*) of the two iron complexes $[(C_2H_5)_4N][Fe(NO)S_4C_4(CN)_4]$ and $[(C_2H_5)_4N][Fe(NO)S_4C_4(C_6H_5)_4]$, together with the base electrolyte necessary for voltammetric measurements, were allowed to react in dichloromethane, and the voltammograms were recorded at 0 and 20 hr. The results are summarized in Table I. At 0 hr, the voltammograms consisted only of those waves characteristic of the two starting materials.[4] After 20 hr, however, the voltammograms had altered and a new reversible wave was located with a corrected half-wave potential of −0.55 V ($E_{3/4} - E_{1/4}$ = 56 mV). As the $E_{1/2}$ value of this new wave is intermediate in value between the $E_{1/2}$ values for the reactions

TABLE I

VOLTAMMETRIC DATA FOR LIGAND-EXCHANGE REACTIONS BETWEEN IRON NITROSYL BIS-1,2-DITHIOLENES IN DICHLOROMETHANE

Time, hr	$E_{1/2}$,[a] V	i_d, μA	Assignment[b]
0	−1.58	9.5	$A^{2-} \rightleftharpoons A^{3-}$
	−1.02	9.0	$B^{-} \rightleftharpoons B^{2-}$
	−0.14	16.5	$A^{-} \rightleftharpoons A^{2-}$; $B^{-} \rightleftharpoons B$
	+0.70	9.0	$B \rightleftharpoons B^{+}$
20	−1.60	12.0	$A^{2-} \rightleftharpoons A^{3-}$
	−1.08	10.0	$B^{-} \rightleftharpoons B^{2-}$
	−0.70	9.0	$[\text{mixed}]^{-} \rightleftharpoons [\text{mixed}]^{2-}$
	−0.14	15.5	$A^{-} \rightleftharpoons A^{2-}$; $B^{-} \rightleftharpoons B$

[a] Recorded with fast scan; value approximate and not corrected for *iR* drop. Corrected $E_{1/2}$ value for $[\text{mixed}]^{-} \rightleftharpoons [\text{mixed}]^{2-}$ in text. [b] A = $[(C_2H_5)_4N][Fe(NO)S_4C_4(CN)_4]$; B = $[(C_2H_5)_4N][Fe(NO)S_4C_4(C_6H_5)_4]$; concentrations are equimolar and approximately 10^{-3} *M*.

$$Fe(NO)S_4C_4(CN)_4^- + e^- \rightleftharpoons Fe(NO)S_4C_4(CN)_4^{2-}$$

$$Fe(NO)S_4C_4(C_6H_5)_4^- + e^- \rightleftharpoons Fe(NO)S_4C_4(C_6H_5)_4^{2-}$$

we attribute it to the reduction

$$Fe(NO)S_4C_4(CN)_2(C_6H_5)_2^- + e^- \rightleftharpoons Fe(NO)S_4C_4(CN)_2(C_6H_5)_2^{2-}$$

We were unable to detect the oxidation step corresponding to the formation of $Fe(NO)S_4C_4(CN)_2(C_6H_5)_2$.

Some evidence for the course of these exchange reactions may be gleaned from esr and infrared spectral studies. Thus, when freshly prepared solutions containing $Fe(NO)S_4C_4(CN)_4^-$ and $Fe(NO)S_4C_4(C_6H_5)_4^-$ are mixed and the esr spectrum is recorded at room temperature, four lines are observed. Since the precursors are *diamagnetic*, the presence of the esr signals must be explained by the occurrence of a redox reaction

$$Fe(NO)S_4^- + Fe(NO)S'_4{}^- \rightleftharpoons Fe(NO)S_4 + Fe(NO)S'_4{}^{2-}$$

The species on the right-hand side of this equation are paramagnetic,[4] and from an analysis of the esr spectral data,[5] it is clear that one of the four lines arises from $Fe(NO)S_4C_4(C_6H_5)_4$ and the other three arise from $Fe(NO)S_4C_4(CN)_4^{2-}$ (nitrogen hyperfine splitting; N^{14}, $I = 1$). The signals which develop immediately on mixing the components of the reaction solution decay over about 2 days and eventually vanish indicating that the neutral and dianionic species have undergone a further electron-transfer reaction in addition to ligand exchange, thereby generating the *diamagnetic* $Fe(NO)S_4C_4(CN)_2(C_6H_5)_2^-$.

Infrared spectral studies of mixtures of the nitrosyl bisdicyano- and bisdiphenyldithiolenes dissolved in dichloromethane are consistent with the esr results. The nitrosyl stretching frequencies in these compounds are dependent upon the nature of the sulfur ligands and on the over-all charge on the complexes thereby making ν_{NO} a particularly useful "fingerprint" in these experiments. Thus, on mixing equimolar amounts of the monoanionic precursors, NO stretching frequencies due to the precursors and to $Fe(NO)S_4C_4(CN)_4^{2-}$ and $Fe(NO)S_4C_4(C_6H_5)_4$ (Table II) were observed. The absorption arising from the dianionic and neutral species gradually decreased in intensity and a new absorption at *ca.* 1775 cm^{-1} grew until it was the strongest frequency in the spectra. Small amounts of $Fe(NO)S_4C_4(CN)_4^-$ were still present in the solution after several days since its characteristic NO stretching frequency remained; $Fe(NO)S_4C_4(C_6H_5)_4^-$ may also have been present but ν_{NO} for this complex occurs almost coincidentally with ν_{NO} for the mixed-ligand species. The continued presence of the precursors may indicate that an equilibrium is established between them and the mixed-ligand complex after several hours. In concluding that the frequency at 1775 cm^{-1} is probably due to the monoanionic mixed-ligand dithiolene, it must be recognized that the value of ν_{NO} is not exactly midway between those of its precursors as might have been expected. However, it is possible that the NO stretching frequency is influenced more by the ligand with the stronger electron-releasing power which pulls the frequency nearer to 1777 cm^{-1} (*i.e.*, that of $Fe(NO)S_4C_4(C_6H_5)_4^-$).

Unfortunately, it has not been possible to isolate any pure nitrosyl mixed-ligand dithiolene complex. On refluxing acetone–dichloromethane solutions containing equimolar amounts of the precursors (as $(C_2H_5)_4N^+$ salts), deep red solutions were obtained. These ex-

TABLE II

IR AND ESR SPECTRAL DATA OBTAINED FROM MIXED-LIGAND IRON NITROSYL BIS-1,2-DITHIOLENES AND THEIR PRECURSORS

Species[a]	Time	NO str freq,[b] cm^{-1}			
$Fe(NO)S_4C_4(CN)_4^-$ (A)					1840
$Fe(NO)S_4C_4(CN)_4^{2-}$		1650			
$Fe(NO)S_4C_4(C_6H_5)_4$				1802	
$Fe(NO)S_4C_4(C_6H_5)_4^-$ (B)			1777		
$Fe(NO)S_4C_4(C_6H_5)_4^{2-}$		1620			
A + B (1:1 mole ratio)	0 hr	1655 s		1805 vs	1836 sh, s
	1 hr	1656 w	1779 vs	1805 sh, w	1837 s
	2 hr	1655 w	1775 vs		1836 m
	1 day		1778 vs		1837 m
	6 days		1774 vs		1837 m

[a] As $(C_2H_5)_4N^+$ salts. [b] Recorded in CH_2Cl_2 solution.

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[5] Esr data from authentic samples in CH_2Cl_2: $Fe(NO)S_4C_4(C_6H_5)_4$, $\langle g \rangle$ = 2.009; $Fe(NO)S_4C_4(CN)_4^{2-}$, $\langle g \rangle$ = 2.028; $\langle A_N \rangle$ = 15.3 G. Esr data from mixed solutions: $\langle g \rangle$ = 2.026; $\langle g \rangle$ = 2.010; $\langle A_N \rangle$ = 15.0 G.

hibited strong NO stretching frequencies at *ca.* 1775 cm^{-1}, and borohydride reduction of these solutions afforded unstable yellow-green solutions. Neither of these solutions afforded solids when treated with a variety of countercations.

In conclusion, the voltammetric, esr, and infrared spectral results seem to indicate that the initial electron-transfer reaction is relatively fast whereas the subsequent reactions, either electron reexchange or ligand exchange, occurring simultaneously or sequentially, occur relatively slowly. The intermediate in these exchange reactions may be a dimeric species, as has been suggested for the nickel bisdithiolene exchange reactions.

Experimental Section

The nitrosyl complexes employed in this work were prepared as described previously.[4] Voltammetric measurements were made using a Heathkit Model EUW-401 instrument with a platinum electrode rotating at 620 rpm. All results were obtained in dried and redistilled dichloromethane at 25°, which contained the complexes at 10^{-3} *M* and the base electrolyte $[(C_2H_5)_4]ClO_4$ at 0.1 *M* concentrations. The results are quoted against a saturated calomel electrode containing 1 *M* aqueous LiCl solutions. The electron spin resonance spectra were obtained at room temperature using a Varian Model V-4500 spectrometer and the infrared spectra in dichloromethane solution were recorded using Unicam SP100 and Infracord 457 spectrophotometers.

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Water Exchange Rate of the Mono(2,2′,2′′-terpyridine)nickel(II) Ion by Oxygen-17 Nuclear Magnetic Resonance[1a]

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In two recent publications, Wilkins and coworkers[2,3] have reported the substitution kinetics of a number of first-row transition series bivalent metal ions with the ligands phenanthroline (including substituted phenanthrolines), bipyridine, and 2,2′,2′′-terpyridine (terpyridine). The substitution rates observed for formation of all 1:1 complexes and the higher bipyridine and phenanthroline complexes conformed to the general ligand–metal ion complex formation mechanism[4] with no significant effect of previously coordinated ligands on the substitution rate. However, in the case of formation of bis(terpyridine) complexes from the mono complexes for Fe(II), Co(II), and Ni(II) (the only metal ions for which the reaction could be conveniently studied) substitution rates were observed to be respectively 7×10^2, 6×10^2, and 2×10^2 times more rapid than the formation rates of the corresponding mono complexes.[5] Since these results strongly suggested that the coordinated terpyridine had labilized the water in the first coordination sphere of these ions, we considered it of interest to test this hypothesis by directly measuring the water-exchange rate by means of the oxygen-17 nuclear magnetic resonance line-broadening technique.[6,7] Since the mono(terpyridine)-nickel(II) complex is considerably more inert to disproportionation[8] than the corresponding complexes of Fe(II) and Co(II), it was selected for study.

In addition, measurements of the rate of water exchange for the aquonickel ion were made and are compared to those reported by Connick and coworkers.[6,9]

Experimental Section

Bis(terpyridine)nickel(II) bromide was prepared according to the procedure of Morgan and Burstall.[10] Mono(terpyridine)-nickel(II) bromide was prepared by thermal decomposition of the bis complex as described by Hogg and Wilkins.[8] *Anal.* Calcd for $NiC_{15}H_{11}N_3Br_2$: C, 39.6; H, 2.5; N, 9.1. Found: C, 39.8; H, 2.45; N, 9.3.

The terpyridine used in these preparations was obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio. It was purified by sublimation; the melting point (85.5–86.0°) was in good agreement with the literature value.[8] The water employed in the nmr experiments was obtained from Yeda Research and Development Co., Ltd., Rehovoth, Israel, and contained 2.14% O^{17} and 14.2% O^{18}.

The nuclear magnetic resonance line width measurements were carried out on two independently prepared solutions for both the aquonickel and mono(terpyridine)nickel(II) ions. The solutions were prepared by weight and molarities were calculated from densities which were measured by weighing solutions in a calibrated polyethylene pipet. Solution A of mono(terpyridine)-nickel(II) bromide was prepared from a sample of this salt generously provided by R. G. Wilkins. In all cases, solutions were sufficiently acidic to avoid any possibility of errors caused by the strong pH dependence of the line width of water in the vicinity of the neutral point.[11] Solutions were acidified with small portions of nitric acid which were added to the enriched water samples with a microliter syringe and the pH values were checked with a Beckman Model G pH meter. In order to detect any possible disproportionation of the mono(terpyridine)nickel(II) complex, the optical absorption spectra of solutions were recorded before and after the nmr line width measurements by means of a Cary 14 spectrophotometer. At 900 mμ, these measurements

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[1] (a) Part of a Ph.D. Thesis submitted by D. Rablen to the University of Maryland, Jan 1968. (b) Address enquiries to this author at the Department of Chemistry, University of Iowa, Iowa City, Iowa 52240.

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