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An Unusual Synthesis of Nickel(II) Coordinated Perchlorate Complexes

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The paramagnetic, six-coordinate complexes $[Ni(amine)_2(ClO_4)_2]$ are produced when the corresponding $[Ni(amine)_2](ClO_4)^2$ or $[Ni(amine)_2(H_2O)_2](ClO_4)_2$ compounds are heated to 110–130° under vacuum (where amine = N-methylen, N,N′-dimethylen, and N,N,N′-trimethylen).[1] Both N-methylen and N,N′-dimethylen form complexes in which the perchlorato group is bonded through one oxygen atom, whereas the complex $[Ni(N,N,N'\text{-trimethylen})_2(ClO_4)_2]$ contains a bidentate perchlorato group. Isolation of the stable perchlorato complexes was accomplished only when a total of two or more of the coordinated amino groups contained monomethyl substituents. The critical size of the N-substituent for coordination of a perchlorate ion is discussed.

Introduction

Generally chemists use perchlorate salts to minimize the possibility of anionic association both in physical-chemical studies and synthetic efforts. The perchlorate ion has been considered a very weak ligand because only a few examples of coordinated perchlorate complexes are known.

Harris, *et al.*,[2] postulated on the basis of conductance measurements that $[Ni(phen)_2(ClO_4)_2]$ and $[Cu(dipy)_2ClO_4]PF_6$ were formed. Very recently, McWhinnie[3] and Quagliano, *et al.*,[4] reported the isolation and infrared characterization of the compounds $[Cu(en)_2(ClO_4)_2]$ and $[Ni(3,5\text{-dimethylpyridine})_2(ClO_4)_2]$, respectively. The 3-bromo-, 3,5-dimethyl-, and 4-isopropylpyridine ligands have been reported to form complexes of the type $[Ni(x\text{-py})_4(ClO_4)_2]$ in another study.[5] In each of the last three cases above, the infrared data indicate that the perchlorate ion is coordinated as a monodentate ligand. Two examples of a bidentate perchlorate group have been postulated in anhydrous $Cu(ClO_4)_2$[6] and $(CH_3)_3SnClO_4$.[7] Very recently, the first anionic complexes, containing only the perchlorate ion as a ligand, have been prepared.[8]

Transition metal amine perchlorate complexes are hazardous and some have been reported to explode under rather mild temperature and shock conditions. By way of contrast,[9] this paper describes the complexes which result from heating N-alkylethylenediaminenickel(II) perchlorates to elevated temperatures for several hours. In some cases, the heating procedure converted four-coordinate, square-planar Ni(II) complexes into stable six-coordinate, pseudo-octahedral complexes which contain coordinated perchlorate ions.

Experimental

Materials.—Reagent grade methanol and ethanol were purified further by fractionation from a magnesium alkoxide mixture. The diamines were distilled either from sodium metal or anhydrous barium oxide until their boiling points agreed with literature values.

Nickel(II) perchlorate hexahydrate, $Ni(ClO_4)_2 \cdot 6H_2O$, was obtained from G. F. Smith Chemical Co. and used without further treatment. Dehydration of the nickel perchlorate was accomplished by reaction with 2,2-dimethoxypropane, and the resulting solution was filtered before mixing with the appropriate amine.

Preparation of the Complexes. $[Ni(N\text{-methylen})_2(H_2O)_2](ClO_4)_2$.—The intermediate complex, $[Ni(N\text{-methylen})_3](ClO_4)_2$, was prepared as previously described.[10]

A violet solution was obtained by dissolving 4.11 g. (8.5×10^{-3} mole) of $[Ni(N\text{-methylen})_3](ClO_4)_2$ in 20 ml. of methanol and 4 ml. of water, and then a 30% aqueous solution containing 1.70×10^{-2} mole of perchloric acid was added slowly to this solution. The blue hydrolyzed solution was evaporated at room tempera-

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[1] The suffix -en used in all ligand abbreviations represents ethylenediamine; *i.e.*, the abbreviation N-methylen = N-methylethylenediamine.

[2] N. T. Barker, C. M. Harris, and E. D. McKenzie, *Proc. Chem. Soc.*, 335 (1961); C. M. Harris and E. D. McKenzie, *J. Inorg. Nucl. Chem.*, **19**, 372 (1961).

[3] W. R. McWhinnie, *ibid.*, **26**, 21 (1964).

[4] S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 671 (1964).

[5] L. E. Moore, R. B. Gayhart, and W. E. Bull, *J. Inorg. Nucl. Chem.*, **26**, 896 (1964).

[6] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

[7] H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 740 (1963).

[8] D. K. Straub and Y. Yung, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 7-O; *Chem. Eng. News*, **42**, 53 (Sept. 21, 1964).

[9] Although we have never had an explosion in this study, it must be emphasized that perchlorate compounds and this procedure are *potentially very dangerous*. Extensive shields and safety precautions must be used *always*.

[10] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 20 (1965).

ture to a sirup and then further evaporated at 100° for 2 hr. Blue crystals formed when 8 ml. of ethanol was added to the cooled sirup. The crystals were collected on a filter, washed with a mixture of 1:1 ethanol–ether, and dried in a dry air stream; yield 2.06 g. Distinct and intense infrared absorption peaks at 3550, 3480, and 1632 cm.$^{-1}$ indicated the presence of coordinated water molecules and the analytical data correspond to $[Ni(N\text{-methylen})_2(H_2O)_2](ClO_4)_2$.

Anal. Calcd. for $C_6H_{24}N_4Cl_2NiO_{10}$: C, 16.30; H, 5.47; N, 12.66. Found: C, 16.56; H, 5.23; N, 12.97.

$[Ni(N\text{-methylen})_2(ClO_4)_2]$.—A yellow compound was formed when less than 1 g. of the above diaquo complex was heated under vacuum at 50° for 18 hr. The infrared spectrum of the yellow product indicated the presence of ionic perchlorates. Subsequent heating under vacuum to 100° for 20 hr. and 115° for 40 hr. produced an orchid product which contained coordinated perchlorate ions as confirmed by the infrared spectrum.

Anal. Calcd. for $C_6H_{20}N_4Cl_2NiO_8$: C, 17.76; H, 4.97; N, 13.81. Found: C, 17.66; H, 4.97; N, 13.71.

$[Ni(N,N'\text{-dimethylen})_2(ClO_4)_2]$.—Approximately 1 g. of an analyzed sample of the yellow, square-planar $[Ni(N,N'\text{-dimethylen})_2](ClO_4)_2$ was heated under vacuum to 120–125° for 60 hr. The infrared spectrum of the resulting violet compound demonstrates that the perchlorate ion is coordinated.

Anal. Calcd. for $C_8H_{24}N_4Cl_2NiO_8$: C, 22.14; H, 5.58; N, 12.91. Found: C, 21.93; H, 5.69; N, 12.78.

$[Ni(N,N,N'\text{-trimethylen})_2(ClO_4)_2]$.—Mixing the dehydrated solution of nickel(II) perchlorate with an ethanol solution of N,N,N′-trimethylen produced a mixture of coral and blue crystals that was assumed to consist of the compounds $[Ni(\text{amine})_2](ClO_4)_2$ and $[Ni(\text{amine})_2(H_2O)_2](ClO_4)_2$, respectively. However, on heating 1 g. of this mixture under vacuum to 110° for 48 hr. a homogeneous green compound resulted, and no water peaks were present in its infrared spectrum.

Anal. Calcd. for $C_{10}H_{28}N_4Cl_2NiO_8$: C, 25.98; H, 6.11; N, 12.13. Found: C, 25.59; H, 6.20; N, 11.83.

Measurements. Electronic Spectra.—Spectra of finely ground solid samples were obtained with a Beckman DU spectrophotometer equipped with a standard Beckman reflectance attachment using U.S.P. $MgCO_3$ as a blank. The use of plastic cover plates permitted unrestricted examination over the range from 1100 to 300 mμ. Readings were taken at 10-mμ intervals except in the regions of absorption maxima where readings were taken every 5 mμ.

Nujol mull spectra of the complexes were obtained with a Cary Model 14 recording spectrophotometer, as were solution spectra using sets of matched 1- and 5-cm. quartz cells.

Infrared Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 337 grating spectrophotometer and a Beckman IR-9 high-resolution spectrophotometer. The samples were prepared as Nujol mulls between crystalline KBr disks and as solutions in dichloromethane. The polystyrene spectrum was used for calibration.

Samples used in the spectral measurements were manipulated and prepared in a nitrogen-filled drybox. The samples were never in contact with moist air.

Magnetic Measurements.—Magnetic moments were determined by the Gouy method at room temperature using $Hg[Co(NCS)_4]$ as the standard. The susceptibility of $[Ni(N\text{-methylen})_2(ClO_4)_2]$ was determined by the Faraday technique. The molar susceptibility in each case was corrected for the diamagnetism of the ligands.[11]

Heating Procedure.—The compounds were heated in an oil bath during evacuation only after extensive safety precautions had been taken. The reaction vessel was shielded on all sides and never disturbed while hot. Less than 1 g. of compound was used in each preparative attempt. The temperature was increased very slowly, and frequent inspections were made to determine the appearance of the compound.

Discussion

The magnetic moments, electronic absorption data, and the perchlorate infrared peaks of the complexes are given in Table I.

When $[Ni(N\text{-methylen})_2(H_2O)_2](ClO_4)_2$ is heated under vacuum, marked changes occur (Table II). The reflectance spectra of both the starting compound, $[Ni(N\text{-methylen})_2(H_2O)_2](ClO_4)_2$, and the compound obtained after heating to 115°, $[Ni(N\text{-methylen})_2(ClO_4)_2]$, are almost identical (Table I), but the intermediate yellow species contains an additional intense absorption band at 20,800 cm.$^{-1}$, characteristic of square-planar Ni(II) complexes. The decrease of the magnetic moment from 3.25 to 1.15 B.M. also indicates the presence of the square-planar intermediate, since tetrahedral Ni(II) complexes exhibit magnetic moments in the range of 3.7–4.1 B.M. When the temperature is raised to 115°, the magnetic moment rises to 3.27 B.M., indicating that the nickel again forms a six-coordinate complex. During the heating process it is apparent that water molecules are removed and perchlorate ions become coordinated. This transformation is substantiated by the disappearance of three infrared peaks at 3550, 3480, and 1632 cm.$^{-1}$, which are due to coordinated water molecules, and the subsequent splitting of the perchlorate absorption bands in the infrared spectrum.

Hathaway and Underhill[6] have shown that as the perchlorate ion becomes involved in covalent bonding, its symmetry is lowered from Td to C_{3v} or C_{2v} depending on whether one or two of its oxygen atoms are involved in bonding. Each of the two infrared active bands in Td symmetry, which occur at ~1100 cm.$^{-1}$ (antisymmetric stretch) and ~625 cm.$^{-1}$ (antisymmetric bend), are split into two components in C_{3v} symmetry and into three components in C_{2v} symmetry. Thus, one should be able to distinguish between the types of perchlorate group present.

Portions of the infrared spectra of the N-methylen and N,N′-dimethylen complexes are given in Figures 1 and 2. In the anhydrous compounds both major perchlorate bands are split into two components; thus, the perchlorate groups are bonded through one oxygen atom. As a result, the complexes contain four nitrogen atoms and two oxygen atoms in a pseudo-octahedral structure around the Ni(II) ion, where the two oxygen atoms are assumed to be in the *trans* position. The perchlorate antisymmetric stretching frequency is split approximately 100 cm.$^{-1}$, indicating strong perchlorato coordination. The antisymmetric bending mode is split about 15 cm.$^{-1}$ on coordination.

When the perchlorate ion is coordinated as a bidentate ligand, its symmetry is reduced to C_{2v}, and all vibrational states become nondegenerate. Thus, complexes which contain bidentate perchlorato groups are expected to show three peaks near 625 cm.$^{-1}$ and three more near 1100 cm.$^{-1}$, in addition to the 930 cm.$^{-1}$ peak, which becomes infrared-active when the symmetry is reduced from Td. The complex [Ni(N,N,N′-

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[11] N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 403.

TABLE I

PHYSICAL AND SPECTRAL PROPERTIES OF THE NICKEL(II) PERCHLORATO COMPLEXES

Complex	Color	μ_{eff}, B.M.	Electronic spectra[a] $\lambda_{\max}$, cm.$^{-1}$		Infrared spectra of the perchlorate bands,[b] cm.$^{-1}$	Assignment[d,e]
[Ni(N-methylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$	Blue	3.25	12,700			
			13,700		1110–1090 vi, br	T$_2$, antisym. str. ClO$_4$
			17,900		930 w, m	A$_1$, sym. breathing str. ClO$_4$
			28,300		626 m, m	T$_2$, antisym. bend. ClO$_4$
[Ni(N-methylen)$_2$(ClO$_4$)$_2$]	Orchid	3.27	12,900		2060 vw, br	Combination of 1130 and 933 bands below
			14,000		1960 vw, br	Combination of 1025 and 933 bands below
			18,200		1130 vi, s	E, antisym. str. ClO$_3$ in C$_{3v}$[f]
			28,300		1025 vi, s	A$_1$, Cl–O* str.[f]
					933 i, s	A$_1$, sym. str. ClO$_3$[g]
					630 i, m	E, antisym. bend. ClO$_3$
					616 i, s	A$_1$, sym. bend. ClO$_3$
[Ni(N,N′-dimethylen)$_2$(ClO$_4$)$_2$]	Violet	3.31	12,700		2060 vw, br	Combination of 1122 and 940 bands below
			13,800		1970 vw, br	Combination of 1040 and 940 bands below
			18,200		1122 vi, s	E, antisym. str. ClO$_3$[f]
			27,900		1040 vi, s	A$_1$, Cl–O* str.[f]
					940 i, s	A$_1$, sym. str. ClO$_3$[g]
					632 i, m	E, antisym. bend. ClO$_3$
					616 i, m	A$_1$, sym. bend. ClO$_3$
[Ni(N,N,N′-trimethylen)$_2$(ClO$_4$)$_2$]	Green	3.35		7,100 (2.8)[c]	2090 vw, br	Combination of 1170 and 928 bands below
			11,800	11,600 (4.7)	2050 vw, br	Combination of 1125 and 928 bands below
			13,100	12,900 (sh)	1960 vw, br	Combination of 1038 and 928 bands below
			16,000	16,000 (6.7)	1170 vi, s	B$_2$, antisym. str. ClO$_2$*
			26,500	26,500 (30.3)	1125 vi, s	B$_1$, antisym. str. ClO$_2$
					1038 vi, s	A$_1$, sym. str. ClO$_2$*
					928 i, s	A$_1$, sym. str. ClO$_2$
					635 i, s	A$_1$, sym. bend. ClO$_2$
					623 i, s 617 i, s	B$_1$ and B$_2$, rocking frequency

[a] The energy values are from diffuse reflectance spectra of the solid complexes. [b] Only the infrared perchlorate peaks are tabulated. The first symbol listed refers to the intensity of the absorption: vi, very intense; i, intense; m, medium; w, weak; vw, very weak. The second symbol refers to the width of the peak: br, broad; m, medium; s, sharp. [c] The energy values are from a dichloromethane solution of the complex. The molar extinction coefficients are given in parentheses. [d] O* denotes vibrations which involve the oxygen atom(s) bonded to the Ni(II) ion. [e] The word descriptions of the vibrational frequencies differ in some cases from those given by Hathaway and Underhill,[6] but the present assignments are more consistent and descriptive of the vibrations. [f] *Cf.* T$_2$, antisymmetric stretch of ClO$_4^-$ (Td) above. [g] Analogous to A$_1$ symmetric breathing frequency of ionic ClO$_4^-$ (Td) above.

TABLE II

CHANGES IN THE PHYSICAL PROPERTIES ON HEATING [Ni(N-methylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$

Compound	Color	μ_{eff}, B.M.	Temp.,[a] °C.
[Ni(N-methylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$	Blue	3.25	25
Intermediate products	Yellow	1.22	50
	Yellow	1.15	100
[Ni(N-methylen)$_2$(ClO$_4$)$_2$]	Orchid	3.27	115

[a] Temperature to which the original compound was heated at each step.

trimethylen)$_2$(ClO$_4$)$_2$] displays just this type of infrared spectrum (Figure 3). Three well-defined perchlorate peaks are present in each of the stretching and bending frequency regions. The assignment is aided by the fact that the three peaks at 1170, 1125, and 1038 cm.$^{-1}$ form combination peaks with the 928 cm.$^{-1}$ peak and reproduce the same splitting pattern at 2090, 2050, and 1960 cm.$^{-1}$.

Several infrared peaks are present in the 950–1200 cm.$^{-1}$ region of all three perchlorato complexes, in addition to the absorptions which have been assigned to the perchlorate group. In order to definitely assign these peaks to the respective ethylenediamine ligands, we prepared the corresponding NiCl$_2$ complexes.

A discussion of the intense absorption at 660 cm.$^{-1}$ in the spectrum of [Ni(N-methylen)$_2$(ClO$_4$)$_2$] (Figure 1B) is necessary. If this band is assigned as a perchlorate frequency, than it would appear that the complex contains ClO$_4$ bonded through two oxygen atoms. Conversely, if this band is characteristic of the ethylenediamine, it is possible that the sharp 635 cm.$^{-1}$ peak in the [Ni(N,N,N′-trimethylen)$_2$(ClO$_4$)$_2$] complex (Figure 3) may arise from a similar vibration. Then its use as evidence for the presence of bidentate perchlorate groups in the N,N,N′-trimethylen complex could be questioned.

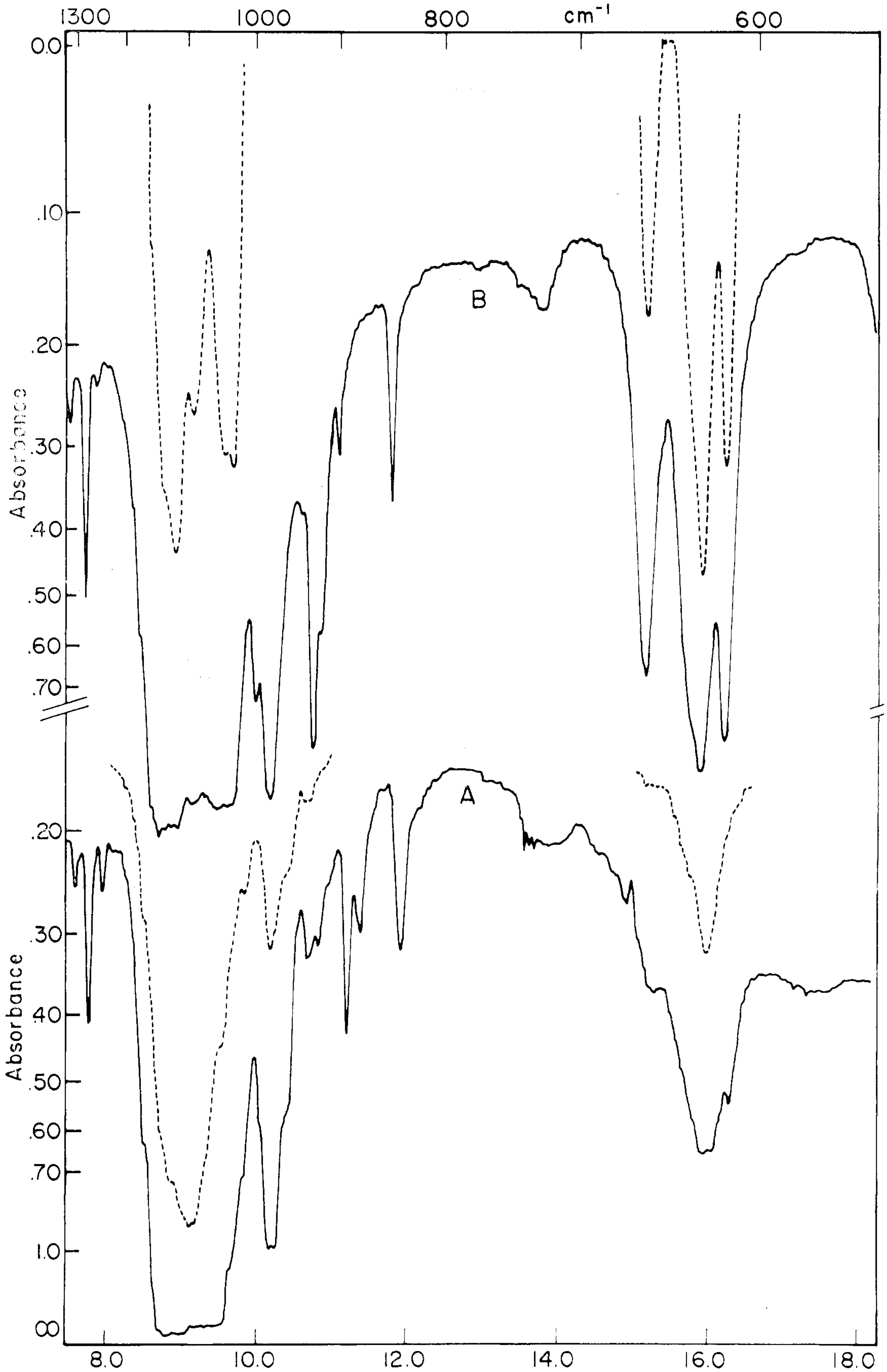

Figure 1.—A, the 1300–600 cm.$^{-1}$ region of the infrared spectrum of $[Ni(N\text{-methylen})_2(H_2O)_2](ClO_4)_2$ in Nujol; B, the same portion of the infrared spectrum of the compound after the heat treatment. The superposed broken line portions of each spectrum correspond to the original spectral sample diluted substantially with Nujol.

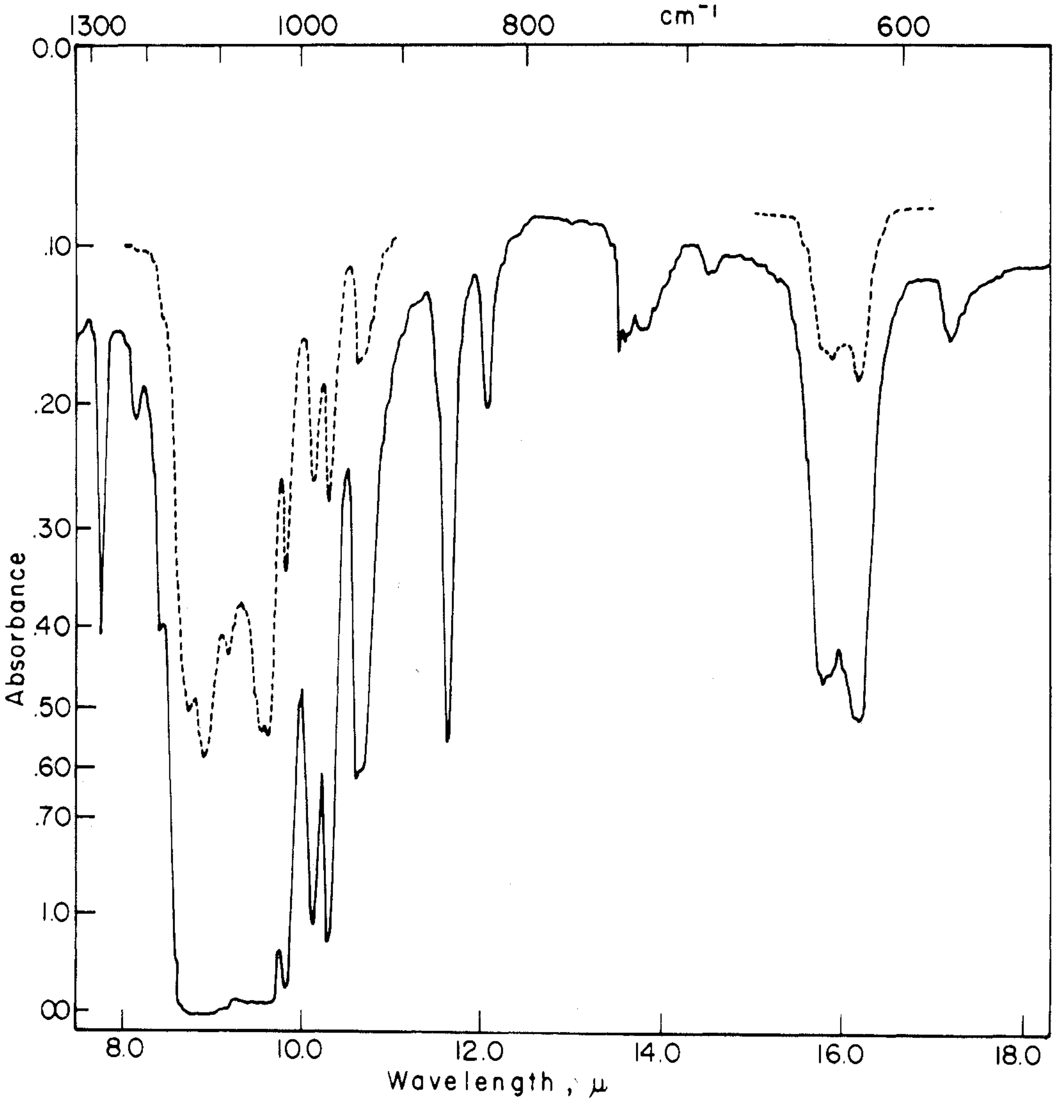

Figure 2.—The 1300–600 cm.$^{-1}$ region of the infrared spectrum of [Ni(N,N′-dimethylen)$_2$](ClO$_4$)$_2$ in Nujol after the heat treatment, *i.e.*, the spectrum of [Ni(N,N′-dimethylen)$_2$(ClO$_4$)$_2$]. The superposed broken lines correspond to the original spectral sample diluted with Nujol.

Table III lists all the infrared peaks observed in the 400–850 cm.$^{-1}$ range for the NiCl$_2$ and Ni(ClO$_4$)$_2$ complexes of N-methylen, N,N′-dimethylen, and N,N,N′-trimethylen, exclusive of the peaks assigned to the perchlorate group in Table I. The data in Table III show that the 660 cm.$^{-1}$ peak is characteristic of the N-methylen ligand and that no N,N,N′-trimethylen absorption occurs near the sharp peak at 635 cm.$^{-1}$ in the [Ni(N,N,N′-trimethylen)$_2$(ClO$_4$)$_2$] complex. The intensity of the 660 cm.$^{-1}$ peak in the N-methylen complex increased markedly on coordination of the perchlorate group. This may indicate that the vibration is strongly coupled with the perchlorate frequencies.

TABLE III

INFRARED ABSORPTION MAXIMA NOT ASSIGNED TO PERCHLORATE IN THE 400–850 CM.$^{-1}$ RANGE

Compound type	Ligand		
	N-methylen	N,N′-dimethylen	N,N,N′-trimethylen
NiLCl$_2$	824 w, 680 w, 545 w[a]	844 m, 574 w	792 i, 588 w, 490 m
NiL$_2$Cl$_2$	833 w, 680 w, 545 w	828 m, 578 w	786 i, 590 w, 475 m
[NiL$_2$(H$_2$O)$_2$]-(ClO$_4$)$_2$	840 w, 658 w, 540 i	825 m, 580 w	
[NiL$_2$(ClO$_4$)$_2$]	850 m, 660 i, 540 i	830 m, 582 w	788 i, 590 w, 490 m

[a] The symbol refers to the intensity of the absorption: i, intense; m, medium; w, weak.

Various investigators have observed weak splittings of the perchlorate peaks due to strong crystalline lattice effects which distort the Td symmetry of the ClO$_4$ group. However, because of the strong intensities, the sharpness of the peaks, and the clean resolution into the components of the perchlorate bands, this possibility can be discounted in explaining the splitting of the perchlorate peaks in this series of complexes.

The electronic absorption spectra of the solid complexes [Ni(N-methylen)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$, [Ni(N-methylen)$_2$(ClO$_4$)$_2$], and [Ni(N,N′-dimethylen)$_2$(ClO$_4$)$_2$] are similar to each other (Table I and Figure 4). In addition, other [Ni(amine)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ complexes (amine = N-ethylen, N,N-dimethylen, N-methyl-N′-ethylen, and N,N′-diethylen) which have been prepared in this laboratory exhibit very similar

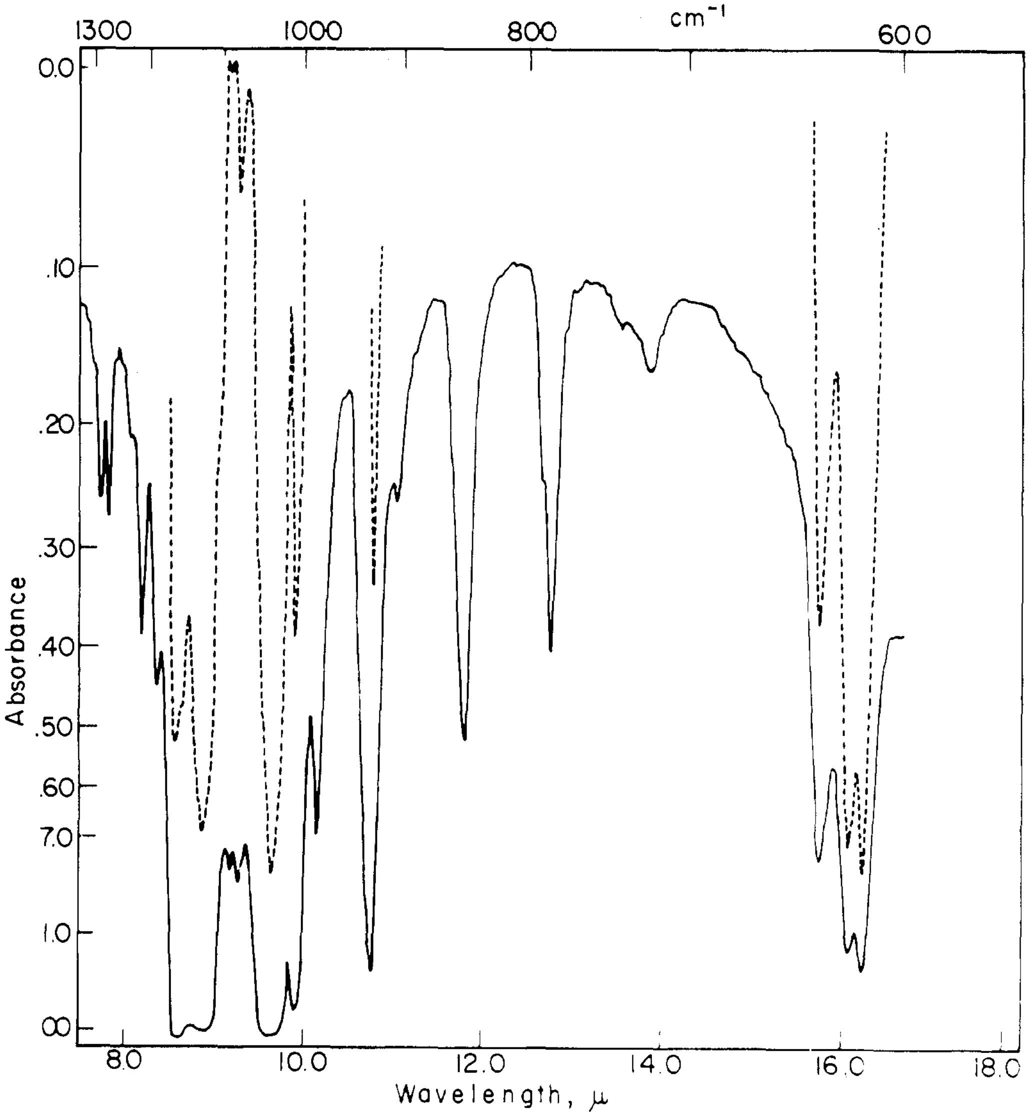

Figure 3.—The 1300–600 cm.$^{-1}$ region of the infrared spectrum of [Ni(N,N,N′-trimethylen)$_2$(ClO$_4$)$_2$] in Nujol. The superposed broken lines correspond to the original spectral sample diluted substantially with Nujol.

spectra. These spectral data are comparable with those in Jørgensen's tabulation of nickel(II) complexes which contain four nitrogen and two *trans* oxygen donor atoms in the first coordination sphere.[12] Such spectral correlations support formulation of the N-methylen and N,N′-dimethylen complex as containing coordinated monodentate perchlorato groups.

The electronic absorption spectrum of [Ni(N,N,N′-trimethylen)$_2$(ClO$_4$)$_2$] (Table I and Figure 4) also indicates an octahedral arrangement, with a significantly weaker ligand field. Intuitively, it is hard to believe that the N,N,N′-trimethylen ligands are functioning as monodentate ligands while the perchlorato groups are chelated (Figure 5a). A possible alternative structure is shown in Figure 5b, where the perchlorato groups occupy octahedral positions, but are so oriented that two of the oxygen atoms lie near the nickel ion, instead of one as in monodentate coordination. This arrangement may give a weaker ligand field, yet the resulting interaction could split the infrared peaks sufficiently to indicate bidentate coordination. An analogous structure has been given for the "bidentate" coordination of the nitrate group in [Co((CH$_3$)$_3$PO)$_2$(NO$_3$)$_2$][13,14] and in [Co(NO$_3$)$_4$]$^{-2}$.[15] Single crystals of [Ni(N,N,N′-trimethylen)$_2$(ClO$_4$)$_2$] have been isolated for an X-ray study; at present we feel that this compound is the best characterized example of bidentate perchlorato coordination.

If the perchlorate ions are situated in the crystalline lattice approximately in the *trans* positions to the planar four-coordinate nickel ion, one can rationalize the coordination of the perchlorate groups during the heat treatment of certain N-alkylethylenediamine-nickel(II) complexes. Initially the perchlorate groups are too distant from the Ni(II) ion for bonding to occur, but it may be possible for thermal vibrations to induce packing rearrangements and trap the perchlorate ion

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(12) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 182 (1955); **10**, 887 (1956).

(13) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 162 (1963).

(14) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).

(15) F. A. Cotton and J. G. Bergman, *ibid.*, **86**, 2941 (1964).

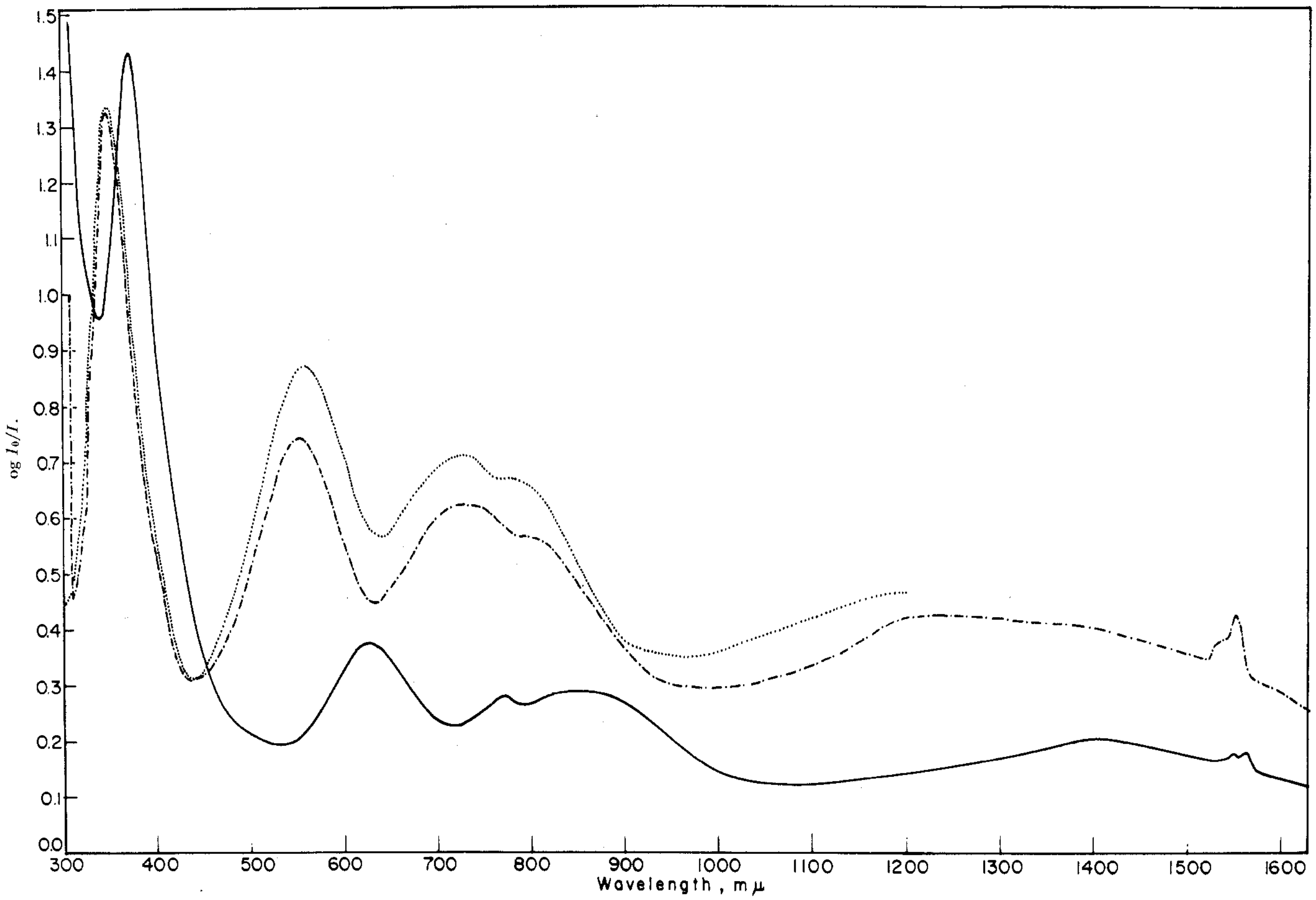

Figure 4.—Reflectance spectra of: ......, $[Ni(N\text{-methylen})_2(H_2O)_2](ClO_4)_2$; and —·—·—·—, $[Ni(N\text{-methylen})_2(ClO_4)_2]$; ———, spectrum of $[Ni(N,N,N'\text{-trimethylen})_2(ClO_4)_2]$ in CH_2Cl_2 solution. The peaks at 1550 mμ are overtones of the NH_2 stretching frequencies.

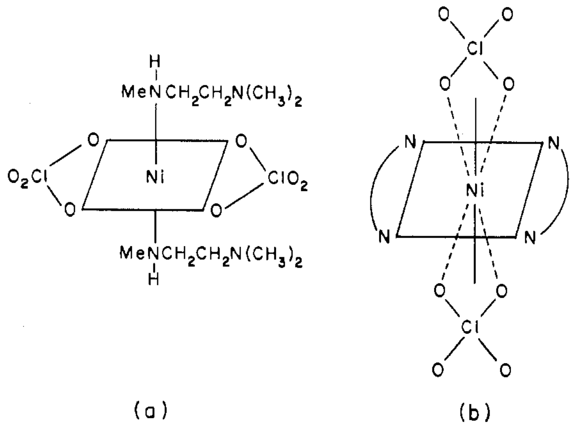

Figure 5.—Possible structures of the complex $[Ni(N,N,N'\text{-trimethylen})_2(ClO_4)_2]$.

in an environment where the Ni–O bond distance is favorable for coordination.

Isolation of stable coordinated perchlorate complexes with the specific N-methylethylenediamines implies that the structural requirements of the ligands must be very critical. For example, the bis-amine complex of an unsymmetrically substituted dimethylethylenediamine, *i.e.*, $[Ni(N,N\text{-dimethylen})_2](ClO_4)_2$, did not form a perchlorato complex. The compound was heated but its diamagnetic character and infrared spectrum remained unchanged until it decomposed at 130°. Neither could a stable $[Ni(N,N\text{-dimethylen})_2(H_2O)_2](ClO_4)_2$ complex by prepared. However, the bis-amine complex of the isomeric N,N′-dimethylen readily forms both the diperchlorato and diaquo complexes.

We attempted to prepare $[Ni(en)_2(ClO_4)_2]$ since ethylenediamine itself has the smallest steric requirements of all the amine ligands used in this study. A mixture of $[Ni(en)_2](ClO_4)_2$ and $[Ni(en)_2(H_2O)_2](ClO_4)_2$ gave no change in the perchlorate regions of the infrared spectrum when heated to 130° for 5 days. In this case, either there is not a sufficient "steric border" around the planar nickel ion to "trap" the perchlorate ions or the four primary amino groups create such a strong in-plane field that no axial ligand can be coordinated.

We have been successful in synthesis of perchlorato complexes by this heating procedure only when a total of two or more of the coordinated amino groups contained monomethyl substituents. Each of the bis-amine complexes of en, N-ethylen, N-propylen, N-isopropylen, N,N-dimethylen, and N-methyl-N′-diethylen changed color when heated to 120°, but the color reverted back to the original on cooling to room temperature. Also the infrared spectra of these cooled complexes showed no evidence for perchlorate coordination. The size of the alkyl substituent then must be very critical. These observations support the idea that the perchlorate ion is trapped into coordination by a tailor-made structural environment.[16]

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[16] NOTE ADDED IN PROOF.—Examples of both monodentate and bidentate perchlorato groups in acetonitrile complexes of nickel(II) were reported recently: A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

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Ionic Perfluoroalkyl Complexes of Cobalt[1]

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Complexes of the general formula $\pi\text{-}C_5H_5CoLL'R_F{}^+ClO_4{}^-$ (where L and L' are electron-pair donors such as carbon monoxide, triphenylphosphine, acetonitrile, or pyridine and R_F is C_2F_5 or $n\text{-}C_3F_7$) have been prepared by reaction of $C_5H_5Co(CO)R_FI$, the respective donor molecule, and $AgClO_4$ in benzene solution. These ionic complexes are soluble in acetone and other polar solvents. Ligand exchange reactions have been studied which lead to an order of stability among the complexes roughly paralleling the basicity of the ligand L. The infrared and ^{19}F n.m.r. spectra of these complexes are discussed.

A number of cationic carbonyl complexes of transition metals have been described in the scientific literature. Among these, the compounds $M(CO)_6{}^+AlCl_4{}^-$ (M = Mn, Re),[2] $C_5H_5Fe(CO)_3{}^+X^-$,[3] and $C_5H_5Mo(CO)_4{}^+AlCl_4{}^-$,[4] and some derivatives of these ionic complexes,[5] represent isostructural analogs of known neutral or anionic complexes. These compounds have been prepared by rather straightforward reactions involving a metal carbonyl halide, a halogen acceptor such as $AlCl_3$, and carbon monoxide or another electron-pair donor. It might be noted, however, that other cationic derivatives predate these; for example the complexes $C_6H_6Mn(CO)_3{}^+$,[6] and $C_7H_7Mo(CO)_3{}^+$,[7] were prepared several years earlier. A variety of cationic complexes of other delocalized π-systems such as the pentadienyl,[8] cyclohexadienyl,[6,9] and other more complex groups[10] have also been investigated. In general, these latter derivatives are formed by protonation or hydride abstraction from neutral complexes; these reactions are sometimes accompanied by rearrangement of the hydrocarbon group.

It seems reasonable to consider both the neutral and ionic coordination complexes of metal carbonyls as related species, in that they are both complexes formed by coordination of ligands with a metal atom in a low oxidation state. In general such derivatives would be expected to obey the inert gas formalism; thus a rather simple means of predicting possible compounds is available. However it is evident from chemical behavior and physical properties of these complexes that pronounced differences result from the presence of positive or negative charges. It is such differences that led us to initiate this study of cationic complexes containing a perfluoroalkyl group bonded to a metal. In this paper complexes of the formula $C_5H_5Co(CO)_2R_F{}^+ClO_4{}^-$ (R_F = C_2F_5, $n\text{-}C_3F_7$), the parent carbonyl, and substitution derivatives of this complex are discussed.

Experimental

Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and the Alfred Bernhardt Microanalytical Laboratory, Mulheim, Germany. Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137B spectrophotometer, generally using Nujol mulls. The ^{19}F n.m.r. spectra in acetone or acetonitrile were obtained using a Varian HR-60 spectrometer at 56.4 Mc. with trichlorofluoromethane as an internal standard.

The preparation of the starting complexes $\pi\text{-}C_5H_5Co(CO)R_FI$ (R_F = C_2F_5, $n\text{-}C_3F_7$) has been described in the literature.[11] Commercial $AgClO_4$ was used; this material was always somewhat wet due to its deliquescent nature, but the small amounts of water present did not appear to affect these preparations greatly.

Infrared spectral absorptions of the compounds discussed below are tabulated in Table I, and ^{19}F n.m.r. results in Table II.

Preparation of $\pi\text{-}C_5H_5Co[(C_6H_5)_3P]C_2F_5I$.—This compound, which is used in a subsequent reaction, was prepared from triphenylphosphine (0.30 g., 1.14 mmoles) and $\pi\text{-}C_5H_5Co(CO)(C_2F_5)I$ (0.30 g., 0.67 mmole) in 50 ml. of benzene. The reactants were heated in benzene for 2 hr. at 50°. After the solvent was removed *in vacuo* the black crystalline product was purified by recrystallization from a benzene–petroleum ether mixture (0.25 g., 60% yield).

Anal. Calcd. for $C_{25}H_{20}F_5IPCo$: C, 47.5; H, 3.2; F, 15.0. Found: C, 47.3; H, 3.2; F, 14.9.

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