is supported by all of the physical and chemical evidence.

Stepwise replacement of a fluorine atom on the pyrosulfuryl structure by a trifluoromethyl group increases the boiling point in a roughly linear manner: $S_2O_5F_2$, 51°;[27] $CF_3S_2O_5F$, 68.4°; $(CF_3)_2S_2O_5$, 84, 80.5°.[7,8]

Comparison of the infrared spectrum of $CF_3SO_2OSO_2F$ with that of similar compounds allows tentative assignments of group frequencies to be made. The strong bands at 1497 and 1473 cm^{-1} are assigned to the S═O asymmetric stretching modes of the fluorosulfuryl and trifluoromethylsulfuryl groups, respectively. These vibrational modes occur at 1513 cm^{-1} in $S_2O_5F_2$[27] and 1471 and 1460 cm^{-1} (doublet) in $(CF_3)_2S_2O_5$.[7] The band at 1242 cm^{-1} is assigned to the S═O symmetric stretching mode on the basis of arguments advanced by Robinson.[28] This band occurs at 1248 cm^{-1} in $S_2O_5F_2$[27] and 1239 cm^{-1} in $(CF_3)_2S_2O_5$.[7] The strong absorption at 1138 cm^{-1} is ascribed to the C–F stretching mode which occurs at 1131 cm^{-1} in $(CF_3)_2S_2O_5$[7] and 1150 cm^{-1} in CF_3SO_2F.[29]

Resonances appearing in the ^{19}F nmr spectrum of $CF_3SO_2OSO_2F$ are assigned to CF_3SO_2– (+68.3 ppm) and –OSO_2F (−49.3 ppm) on the basis of chemical shift data,[16] fine structure, and relative areas. The chemical shift for the CF_3 group in $(CF_3)_2S_2O_5$ occurs at +74.02 ppm.[24] The relatively small coupling constant of 2.1 Hz (that for CF_3OSO_2F is 6.8 Hz) is consistent with that observed for coupling of nonequivalent fluorine atoms over a somewhat related four-atom bond and space system in the compound FC(O)N(OCF_3)SO_2F for which $J_{CF_3-SO_2F} = 1.8$ Hz.[30]

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Nickel(II) Complexes with the Two Isomers of 1,3,5-Triaminocyclohexane

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The recent reports[1-3] describing the coordination complexes of 1,3,5-triaminocyclohexane prompt us to communicate our results with this ligand system. Wentworth[2,3] has described the metal ion complexes of *cis,cis*-triaminocyclohexane (*cis,cis*-tach) in which the three amino groups rotate into axial ring positions in order to occupy the trigonal face of an octahedral coordination geometry. In addition, evidence was presented for the existence of a second ligand isomer, *cis,trans*-1,3,5-triaminocyclohexane (*cis,trans*-tach), but no coordination compounds of this isomer were reported. We have investigated the coordinating ability of 1,3,5-triaminocyclohexane with nickel(II) ions and have isolated two isomeric bis(triaminocyclohexane)-nickel(II) complexes. This note describes the synthesis and characterization of these isomeric complexes.

Experimental Section

Preparation of the Complexes.—A methanol solution (25 ml) containing 0.9 g (3.8 mmol) of nickel(II) chloride hexahydrate was added dropwise to 1.0 g (7.7 mmol) of 1,3,5-triaminocyclohexane[4] in 10 ml of anhydrous methanol. Pink crystals separated almost immediately and continued to form until approximately half of the nickel chloride solution had been added. These crystals were removed, recrystallized (anhydrous methanol), and dried *in vacuo* at 79° for 12 hr. *Anal.* Calcd for $C_{12}H_{30}N_6Cl_2Ni$: C, 37.14; H, 7.79; N, 21.66; Cl, 18.27. Found: C, 37.34; H, 7.80; N, 21.23; Cl, 18.50; magnetic moment, μ_{eff} = 3.1 BM.

Continued addition of the nickel chloride solution to the filtrate led to an orange solution which deposited a yellow microcrystalline precipitate upon cooling. This hygroscopic precipitate could not be recrystallized and gave nonreproducible analytical results. Substitution of 95% ethanol as the solvent after the removal of the pink isomer was found to yield a highly crystalline yellow complex upon standing after the further addition of nickel(II) chloride. The complex was recrystallized from 95% ethanol and dried *in vacuo* at 100° for 12 hr. The dried crystals were extremely hygroscopic. *Anal.* Calcd for $C_{12}H_{30}N_6Cl_2Ni$: C, 37.14; H, 7.79; N, 21.66; Cl, 18.27. Found: C, 36.90; H, 7.93; N, 21.36; Cl, 17.82; magnetic moment, μ_{eff} = 0.5–0.6 BM.

Physical Measurements.—Solution absorption spectra and solid-state diffuse transmittance spectra of Nujol mulls supported on filter paper were obtained with a Cary Model 14 recording spectrophotometer. Magnetic susceptibilities were measured by the Faraday method. The infrared spectra were obtained with Nujol mulls using a Beckman IR-8 spectrophotometer. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Results and Discussion

Characterization of the pink and yellow isomers indicates that they are the nickel(II) complexes of *cis,cis*-tach and *cis,trans*-tach, respectively. The physical properties of each of the isomers which lead to this conclusion will be discussed separately.

Pink Isomer, [Ni(*cis,cis*-tach)$_2$]Cl$_2$.—Our results for this isomer are in agreement with those reported previously[3] and it is concluded that this isomer is the bis-nickel(II) complex of *cis,cis*-tach with both ligands functioning as tridentate chelates. The solution electronic spectrum of this complex ion is presented in Table I. The low values of the molar absorptivities for the

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TABLE I

ELECTRONIC SPECTRA OF [Ni(tach)$_2$]Cl$_2$ COMPLEXES

	Electronic spectrum		
	ν_{max}, cm^{-1}	ϵ_{max}	Assignment
	[Ni(*cis,cis*-tach)$_2$]Cl$_2$[a]		
H_2O solution	11,550	5.2	${}^3A_{2g} \rightarrow {}^3T_{2g}$
	18,850	6.5	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
	29,600	9.4	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Diffuse transmittance	11,600	...	${}^3A_{2g} \rightarrow {}^3T_{2g}$
	18,900	...	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
	29,300	...	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$
	[Ni(*cis,trans*-tach)$_2$]Cl$_2$[b]		
Ethanol solution	21,500	34	${}^1A_{1g} \rightarrow {}^1B_{1g}$
Diffuse transmittance	21,800	...	${}^1A_{1g} \rightarrow {}^1B_{1g}$

[a] Transition assignment based on O_h symmetry. [b] Transition assignment based on D_{4h} symmetry.

TABLE II

INFRARED SPECTRA OF [Ni(tach)$_2$]Cl$_2$ COMPLEXES[a]

		[Ni(*cis,cis*-tach)$_2$]Cl$_2$		
3293 s	2700 w	1400 w	1225 w	909 m
3227 s	1618 m	1364 m	1161 s	893 s
3150 s	1577 s	1352 m	1063 w	662 s
2806 w	1449 m	1268 w	971 w	
		[Ni(*cis,trans*-tach)$_2$]Cl$_2$		
3225 s	1623 s	1288 w	1056 m	837 w
3359 s	1559 s	1233 s	995 m	788 m
3295 m	1403 m	1202 m	962 m	757 m
3240 s	1393 m	1132 m	944 s	652 w
3187 s	1361 m	1111 m	926 s	
3120 s	1352 m	1107 m	904 w	
1655 w	1314 w	1070 m	875 w	

[a] All values in wave numbers: s, strong; m, medium; w, weak.

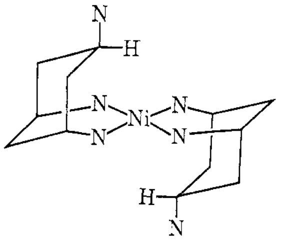
ligand field transitions are consistent with the high symmetry of the proposed complex ion, D_{3d}, which maintains a center of inversion. No effect of the trigonal symmetry is observed in the room-temperature solution spectrum, indicating that the amine donors can occupy octahedral coordination positions without strain. This lack of trigonal splitting has been noted previously for the bis-nickel(II) complexes of the similar facial tridentate ligands 1,3-diamino-2-aminomethylpropane[5] and 1,3-bis(methylamino)-2-(methylaminomethyl)-2-methylpropane.[6]

The value of 10*Dq* for *cis,cis*-tach, taken as the energy of the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition, is 11,550 cm^{-1}. This value is significantly higher than 10*Dq* for tris(ethylenediamine)nickel(II), which has been reported[7] to be 11,200 cm^{-1}. The higher value of the ligand field splitting parameter for *cis,cis*-tach may be a reflection of the constrained nature of this ligand forcing the amine donors rigidly in octahedral positions and presenting a stronger ligand field to the metal ion.

Further evidence for the structure of the pink isomer is obtained from the infrared spectrum of the complex (Table II). In general the simplicity of the infrared spectrum indicates a highly symmetrical structure. Specifically the spectral region attributed to coordinated N–H stretching modes consists of three bands (3293, 3227, 3150 cm^{-1}), similar to that reported[8] for tris(ethylenediamine)nickel(II) and consistent with the proposed structure which possesses only one type of amine group. In addition, there is only one strong band in the region assigned to the $-NH_2$ deformation mode[9] (1577 cm^{-1}) in agreement with one type of amine group.

Yellow Isomer, [Ni(*cis,trans*-tach)$_2$]Cl$_2$.—In contrast to the high-spin, six-coordinate structure proposed for the pink isomer, the physical properties of the yellow isomer are indicative of a spin-paired, square-planar nickel(II) complex. The electronic spectrum of the yellow isomer in the visible region consists of a single band at approximately 21,600 cm^{-1}, in agreement with several other nickel(II) complexes[10-13] containing four amine donors and proposed to be square-planar. This isomer was not found to be diamagnetic as is required for spin-paired square-planar nickel(II) complexes; however, a large portion of the observed magnetic moment may be rationalized by invoking a contribution from temperature-independent paramagnetism.[14]

In order to account for the observed data, it is proposed that the yellow isomer may be formulated as the bis-nickel(II) complex of *cis,trans*-tach with the ligand functioning as a bidentate chelate through the two amine groups which may rotate into axial ring positions. If the cyclohexane ring retains its chair conformation, the third amine group must then occupy an equatorial position and is unavailable for coordination. This idealized structure for the complex ion is shown below. From this model it may be seen that the portion of cyclohexane ring containing the uncoordinated



amine group effectively blocks the axial coordination positions of the metal ion. It is likely that this axial blocking determines the spin state of the nickel(II) ion since amine donors do not normally produce spin-paired nickel(II) complexes in the absence of a steric effect.[15]

The infrared spectrum (Table II) of the yellow isomer is consistent with the proposed structure. The NH

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stretching region (3120–3525 cm^{-1}) is complicated and shows bands which may be attributed to uncoordinated and coordinated amine groups. The NH_2 deformation mode also consists of two strong bands (1623, 1559 cm^{-1}) indicating two types of amine groups. In general, the spectrum of the yellow isomer is more complicated than that for the pink isomer indicative of a less symmetric structure for the yellow isomer.

The difficulty in obtaining analytically pure samples of the yellow isomer may be attributed to the presence of the uncoordinated amine group. This polar group would have a distinct tendency to hydrogen bond to hydroxylic solvent molecules and also to coprecipitate excess ligand. In the hydrated form of the yellow isomer the water does not coordinate to the metal ion as shown by the magnetic moment of the hygroscopic complex which does not change significantly as it absorbs water from the atmosphere. The uncoordinated amine group is probably also responsible for the fact that the yellow isomer is unstable in aqueous solution, precipitating nickel hydroxide immediately. This accounts for the failure to observe this isomer when the preparative reactions are carried out in water.

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Complexes of the Group VI Metal Hexacarbonyls with the Difluorodithiophosphate and Difluorothiophosphate Anions

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The interaction of the group VI metal hexacarbonyls with electron donors has been widely explored. This reaction has generally required thermal activation although in a few cases (where neutral ligands were employed) photolytic activation was found to be applicable. We wish to report the photolytic preparation of some new anionic derivatives of chromium, molybdenum, and tungsten hexacarbonyls involving both the difluorodithiophosphate anion and the difluorothiophosphate anion as ligands. Although a few neutral carbonyl complexes of organic dithiophosphates are known[1,2] no anionic derivatives have been prepared. Furthermore, the use of organic thiophosphates as ligands has been little explored,[3] and no known carbonyl derivatives have been reported. Therefore, it was of interest to determine if the recently reported difluorodithiophosphate[4,5] and difluorothiophosphate[6] anions would function as ligands.

The reaction between the metal hexacarbonyl and the complexing anion was carried out in methylene chloride solution using a twofold excess of the carbonyl. An immediate difference in the behavior of the two anions was noted. Reasonable yields were obtained with the difluorodithiophosphate anion only when the irradiation was carried to the point where 2 equiv of carbon monoxide was evolved, whereas, with the difluorothiophosphate anion, the reaction could be stopped after 1 equiv of carbon monoxide had been evolved. In fact, the addition of the difluorodithiophosphate anion to a solution of $Cr(CO)_5 \cdot THF$ (THF = tetrahydrofuran) in the absence of light produced only trace amounts of the product. In both cases the yield was much lower for the molybdenum derivatives than for the others.

The chemical analyses (see Table I) and the spectroscopic properties of the products (see Table II) suggest that the difluorodithiophosphate anion acts as a bidentate ligand, while the difluorothiophosphate anion acts as a monodentate ligand

$$M(CO)_6 + PF_2S_2^- \longrightarrow M(CO)_4PF_2S_2^- + 2CO$$

$$M(CO)_6 + PF_2OS^- \longrightarrow M(CO)_5PF_2OS^- + CO$$

where M = Cr, Mo, or W.

All of the products are yellow solids which are fairly stable in air in the solid state, although solutions are oxidized by atmospheric oxygen. The stability increases from the chromium to tungsten derivatives. The complexes formed with the difluorodithiophosphate anion appear to be more stable than the complexes obtained by treatment of the hexacarbonyls with the difluorothiophosphate anion. The analytical data for the materials prepared are summarized in Table I. The proton nmr spectra of the complexes showed the absence of hydridic hydrogen or paramagnetic impurities. The F^{19} nmr spectra are given in Table III. The small change in the P–F coupling constants in the free and complexed anion indicates that only a small change in the amount of s character in the P–F bond has occurred upon complexation.[7]

The infrared spectra of the complexes in the carbonyl stretching region are quite similar for all the metals employed regardless of whether the difluorodithiophosphate or difluorothiophosphate anions are employed as ligands. In general, four bands are observed (see Table II). To a first approximation this number of bands is anticipated for a molecule of the type $M(CO)_4L$, where L acts as a bidentate ligand bonded to the metal in a *cis* position (C_{2v} symmetry), whereas for a monosubstituted metal hexacarbonyl derivative, $M(CO)_5L$, only three bands are expected (C_{4v} symmetry). Thus, it would appear that both the $PS_2F_2^-$ and $POSF_2^-$ anions are acting as bidentate ligands. However, the infrared spectra in the P—O and P—S regions (see Table II) of the complexes containing the difluorothiophosphate anion as a ligand all exhibit an

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