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COORDINATION COMPOUNDS OF ETHYLHYDRAZINE AND 2,2,2-TRIFLUOROETHYLHYDRAZINE; CRYSTAL AND MOLECULAR STRUCTURE OF DICHLOROTETRAKIS(2,2,2-TRIFLUOROETHYLHYDRAZINE) NICKEL(II)

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Abstract—Ethylhydrazine (EH) forms the complexes $MX_2(EH)_2$ (M = Co, Ni; X = Cl; M = Co, X = Br), $NiBr_2(EH)_2(H_2O)$ and $MX_2(EH)$ (M = Zn, Cd; X = Cl; M = Zn, X = Br). Spectroscopic evidence suggests that these all contain bridging hydrazine ligands, the cobalt and nickel complexes containing six coordinated metal atoms while the zinc and cadmium complexes are tetrahedral. 2,2,2-Trifluoroethylhydrazine (TFEH) in contrast, forms six coordinate complexes of the type $MX_2(TFEH)_4$ (M = Co, Zn, X = Br; M = Co, Ni, X = NCS; M = Ni, X = Cl) for which spectroscopic evidence points to unidentate coordination by the hydrazine. An X-ray crystal structure determination on $NiCl_2(TFEH)_4$ confirms that the hydrazine bonds to nickel through the NH_2 nitrogen only, in a tetragonal structure with axial chlorine atoms. One bis(TFEH) complex $ZnBr_2(TFEH)_2$ and one hexakis (TFEH) complex, $NiBr_2(TFEH)_6$, have also been isolated.

Hydrazine complexes of metal(II) ions are of two principal types. By far the more common are compounds of the type $MX_2(N_2H_4)_2$ in which the hydrazine is acting as a bidentate bridging ligand in a six coordinate structure around the metal.[1] Complexes containing unidentate hydrazine are less common; they can sometimes be prepared by crystallization from anhydrous hydrazine e.g. $[Co(N_2H_4)_6]Cl_2$.[2] The complexes $M(N_2H_4)_2(N_2H_3CO_2)_2$ (M = Zn, Mn, Co, Ni) also contain unidentate hydrazines along with bidentate hydrazine carboxylate ligands.[3,4] With mono-substituted hydrazine ligands, e.g. methylhydrazines[5] and phenylethylhydrazine,[6] the bridging mode of bonding again predominates, but one remarkable complex of phenylhydrazine,[7] $[(\eta^5\text{-}C_5H_5)Mo(NO)I(NH_2NHPh)]_2[BF_4]_2$ represents the only established example of a hydrazine acting as a chelating ligand. With disubstituted hydrazines such as N,N-dimethylhydrazine, $Me_2N^1N^2H_2$, steric and electronic effects become important; the ligand is known to act as unidentate through N^1 in $CoCl_2(Me_2NNH_2)_2$,[2] unidentate through N^2 in $[RuH(cod)(NH_2NMe_2)]_3[PF_6]$[8] and bridging in $[RuCl(H)(cod)]_2(NH_2NMe_2)$[9] (cod = cyclo-octa-1,5-diene).

In this paper we report on attempts to prepare complexes of the monosubstituted hydrazines, ethylhydrazine (EH) and 2,2,2-trifluoroethylhydrazine (TFEH). These monosubstituted hydrazines $RNHNH_2$ differ in the relative electron withdrawing effect of the two R groups CH_3CH_2 and CF_3CH_2; this is likely to affect their relative basicities and tendencies to bond in a bridging fashion. In order to confirm the spectroscopic evidence for the mode of bonding of TFEH, a crystal structure determination has been carried out on $[Ni(TFEH)_4Cl_2]$.

EXPERIMENTAL

Experimental techniques were as described previously[10] except that reflectance spectra were re-

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Table 1. Complexes of ethylhydrazine (EH) and 2,2,2-trifluoroethylhydrazine (TFEH): colours and analytical data

Complex	Colour	Elemental analysis[a] (%) C	H	N	M
$CoCl_2(EH)_2$	Pink	19.1 (19.2)	6.3 (6.4)	21.3 (22.4)	23.5 (23.6)
$CoBr_2(EH)_2$	Pink	14.5 (14.2)	4.7 (4.7)	16.5 (16.5)	17.1 (17.4)
$NiCl_2(EH)_2$	Blue	19.2 (19.2)	6.4 (6.4)	22.2 (22.4)	23.2 (23.5)
$NiBr_2(EH)_2(H_2O)$	Blue–green	13.2 (13.5)	4.6 (5.0)	15.9 (15.7)	16.6 (16.5)
$ZnCl_2(EH)$	White	12.1 (12.2)	3.9 (4.1)	13.5 (14.3)	33.9 (33.3)
$ZnBr_2(EH)$	White	8.6 (8.4)	2.8 (2.8)	9.5 (9.8)	23.3 (22.9)
$CdCl_2(EH)$	White	9.7 (9.9)	3.3 (3.3)	11.0 (11.5)	46.6 (46.2)
$CoBr_2(TFEH)_4$	Orange	18.2[b] (14.2)	2.8 (3.0)	16.6 (16.6)	8.7 (8.7)
$Co(NCS)_2(TFEH)_4$	Pink	18.3 (19.0)	3.2 (3.2)	22.2 (22.2)	—
$NiCl_2(TFEH)_4$	Blue	16.5 (16.4)	3.3 (3.4)	18.8 (19.1)	9.9 (10.0)
$Ni(NCS)_2(TFEH)_4$	Violet	19.0 (19.0)	3.3 (3.2)	21.7 (22.2)	9.3 (9.3)
$NiBr_2(TFEH)_6$	Blue	16.6 (16.0)	3.1 (3.3)	17.6 (18.6)	—
$ZnBr_2(TFEH)_2$	White	10.3 (10.6)	2.2 (2.2)	11.9 (12.4)	—
$ZnBr_2(TFEH)_4$	White	14.3 (14.1)	3.1 (2.9)	15.5 (16.4)	—

[a] Theoretical percentages in parentheses.

[b] Because of the poor C figure, F was estimated; found, 33.7 (33.8).

corded on a Perkin–Elmer 330 spectrophotometer over the range 40,000–6,600 cm^{-1}.

Anhydrous cobalt(II) halides were prepared by dehydration of the hydrated salts at 100°C *in vacuo*. Ethylhydrazine was prepared via Fischer's synthesis as modified by Condon and Thakker,[11] it was dried by distillation from barium oxide. 2,2,2-Trifluoroethylhydrazine was obtained as a 70% aqueous solution (ex Aldrich) and was used as such.

The complexes (Table 1) were prepared from the metal salts and appropriate ligand in a variety of solvents. No single solvent was found satisfactory for the preparation of all the complexes so that their isolation proved more difficult than that of complexes of hydrazine and methylhydrazine.[5]

Ethanol was the most commonly used preparative solvent for complexes of EH but ether or water usually proved better for the precipitation of pure complexes of TFEH. Thus the EH complexes of cobalt and nickel halides were prepared by heating, under reflux, ethanolic solutions of the metal halide (anhydrous cobalt halides were necessary but hydrated nickel halides gave satisfactory results) with an excess of the ligand under an atmosphere of nitrogen [to prevent oxidation of cobalt(II)]. The complexes either precipitated immediately or upon cooling the mixtures to 0°C. They were filtered off, washed with ethanol and ether and dried *in vacuo*. An ethanol–ether mixture (1 : 1) was found to be the best medium from which to precipitate the zinc complexes of EH. The preparation of $[Ni(TFEH)_4Cl_2]$ is fully described below because of its importance in this paper. The other TFEH complexes were prepared, however, using concentrated solutions of the metal salts in ether, ($CoBr_2(TFEH)_4$ and $ZnBr_2(TFEH)_2$), or water, ($Co(NCS)_2(TFEH)_4$, $Ni(NCS)_2(FTEH)_4$, $NiBr_2(TFEH)_6$) as the crystallization medium. The zinc complex $ZnBr_2(TFEH)_4$ was obtained by precipitation from an ethereal solution using ethanol. In all cases an excess of the ligand was used (i.e. $>6:1$ ligand : metal); when the metal salts were in excess, only impure compounds or mixtures were isolated.

Preparation of $[Ni(TFEH)_4Cl_2]$

Nickel(II) chloride hexahydrate (0.48 g) was dissolved in hot ethanol (15 cm^3) and TFEH (2 cm^3) was slowly added until a dark blue solution was obtained. This was heated to boiling and then allowed to cool in a refrigerator for several days. The bright blue crystals which had grown were filtered off washed with ethanol and ether and dried *in vacuo*.

Crystal and molecular structure of $[Ni(TFEH)_4Cl_2]$

The material as prepared above contained suitable crystals for X-ray structure determination. Preliminary oscillation and Weissenberg photographs indicated a triclinic crystal; the intensities of 1540 unique reflections, to $\theta_{max} = 60°$, were recorded on a Stoe Siemens AED2 diffractometer at Edinburgh University, for a crystal of dimensions $0.4 \times 0.4 \times 0.2$ mm^3.

Table 2. Magnetic moments, molar conductivities and electronic spectra of ethylhydrazine (EH) and 2,2,2-trifluoroethylhydrazine (TFEH) complexes

Complex	Magnetic moments μ_{eff}(BM) at 20°C	Molar conductivities λ (Ω^{-1} mol^{-1} cm^3)	Electronic spectra ($cm^{-1} \times 10^3$) solid state (reflectance)	Solution spectra [ε ($lmol^{-1}$ cm^{-1}) in parentheses]
$CoCl_2(EH)_2$	4.97	[a]	35.7, 27.8sh, 20.2, 19.4sh, 17.0sh, 8.4	[a]
$CoBr_2(EH)_2$	5.03	[a]	35.3, 20.9, 19.6, 18.7sh, 16.3sh, 8.7	[a]
$NiCl_2(EH)_2$	3.12	[a]	34.5, 26.0, 15.5, 9.0	[a]
$NiBr_2(H_2O)(EH)_2$	3.41	[a]	34.1, 25.3, 17.1sh, 15.5, 8.4	[a]
$ZnCl_2(EH)$	Diamagnetic	[b] 7.9	36.6	
$CdCl_2(EH)$	Diamagnetic	[b] 12.8	38.6	
$COBr_2(TFEH)_4$	3.81		31.0, 22.2, 19.8sh, 11.6, 7.9	
$Co(NCS)_2(TFEH)_4$	5.39	[a]	34.1, 21.6sh, 20.6, 9.8	
$NiCl_2(TFEH)_4$	3.30	[c] 17.8 [d] 1.2	27.4, 17.4, 12.9sh, 10.6, 8.7	[c] 26.7(13), 16.4(7.5) 8.8(4.7)
$Ni(NCS)_2(TFEH)_4$	3.09	[d] 10.8	27.8sh, 18.0, 10.8	[d] 17.5(16), 10.6(13)
$NiBr_2(TFEH)_6$	3.49	[d] 6.3	obsc., 17.4, 10.5	
$ZnBr_2(TFEH)_2$	Diamagnetic	[a]	35.1	
$ZnBr_2(TFEH)_4$	Diamagnetic	[a]	36.1	

[a] Insoluble in suitable solvents.
[b] ~ 10^{-3} M in DMSO.
[c] ~ 10^{-3} M in acetonitrile.
[d] ~ 10^{-3} M in nitromethane.
sh = shoulder.
obs = obscured under charge transfer band.

The structure was solved from a nickel phased electron density map and then refined using SHELX76;[12] the assumption of space group $P\bar{1}$ proved satisfactory. Hydrogen atoms were placed at stereochemically expected positions and their coordinates refined with N—H and C—H distances restrained. All non-hydrogen atoms were treated as anisotropic. Unit weights were used. Refinement converged to $R = 0.063$, for 1505 reflections with $|I| > 3\sigma(I)$. The largest peaks in the final electron density difference map are *ca* 0.4 e A^{-3}, but appear to have no chemical significance.

*Crystal data**

Crystals of $C_8H_{20}Cl_2F_{12}N_8Ni$, MW 585.75 are triclinic, with $a = 5.864(1)$, $b = 8.923(1)$, $c = 11.016(2)$ Å, $\alpha = 101.23(1)$, $\beta = 94.38(1)$, $\gamma = 100.68(1)°$, $U = 551.78$ Å^3, $D_m = 1.78$ g cm^{-3}, $Z = 1$, $D_x = 1.763$ g cm^{-3}. Space group $P\bar{1}$, Cu-K_α radiation, $\lambda = 1.5418$ Å, $\mu = 46.52$ cm^{-1}.

RESULTS AND DISCUSSION

Ethylhydrazine complexes of cobalt(II), nickel (II), zinc(II) and cadmium(II) (Table 1) have been isolated. When iron(III) chloride or bromide in ethanolic solution were treated with the ligand, only black oils were obtained and copper(II) chloride, when similarly treated, gave only a white precipitate of copper(I) chloride. The pink cobalt(II) complexes $CoX_2(EH)_2$ have magnetic moments and electronic spectra (Table 2) typical of pseudo-octahedral complexes; the bands around 8,500 cm^{-1} being assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}$ transition, the bands at 17,000 (chloride) and 16,300 cm^{-1} (bromide) to the $^4T_{1g} \rightarrow {}^4A_{2g}$ transition and those at 20,200 (chloride) and 19,600 cm^{-1} (bromide) to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition. These complexes were not indefinitely stable in dry air; they slowly changed colour first to violet and then to blue. The reflectance spectra recorded during these changes showed the slow disappearance of the bands in the 19–20,000 cm^{-1} region and the growth of a band

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* Atomic coordinates, tables of thermal parameters, and observed and calculated structure factors have been deposited with the Editor as supplementary data; atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

at 15,200 (chloride) or 14,400 cm^{-1} (bromide) (assignable to the $^4A_2 \rightarrow {}^4T_1(P)$ transition in a tetrahedral complex) and the formulae of the complexes approached $CoX_2(EH)$. A similar effect was observed when $CoBr(EH)_2$ was heated *in vacuo* to 100°C for 24 h; the blue residue had an empirical formula close to $CoBr_2(EH)$ and gave the same spectrum as the blue material obtained at room temperature. Thus the bis(ethylhydrazine) complexes appear to evolve 1 mol of ligand and the cobalt to change from an octahedral to a tetrahedral environment. A similar transformation was noted for cobalt(II) complexes of phenelzine.[6] Curiously it was not possible to isolate pure mono (ethylhydrazine) complexes from solutions containing an excess of cobalt(II). The spectral and magnetic data on the bis(ethylhydrazine)nickel(II) complexes again clearly show pseudo-octahedral coordination around the nickel, the three peaks being assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$ ($\sim$ 9000 cm^{-1}), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ($\sim$ 15,500 cm^{-1}) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ($\sim$ 26,000 cm^{-1}). There is evidence of splitting of the $^3T_{1g}(F)$ band in the bromide complex arising from tetragonality ($^3B_{1g} \rightarrow {}^3E_g$ and $^3B_{1g} \rightarrow {}^3A_{2g}$ transitions). The positions of these transitions are as expected for a NiN_4X_2 chromophore, i.e. very close to those found in $Ni(py)_4Cl_2$,[13] so that our complexes must contain bridging ethylhydrazine. The IR spectrum of $NiBr_2(EH)_2(H_2O)$ confirms that the water molecule is present as lattice water.

The IR spectra of the bis(ethylhydrazine) complexes of cobalt(II) and nickel(II) are similar. The shift in the N—N stretching band (Table 3) from 1110 cm^{-1}, observed for the free ligand, to around 1170 cm^{-1} in the complexes indicates a bridging mode for the hydrazine. A similar shift in ν(N—N) is observed when hydrazine becomes a bridging ligand.[14] The M—Cl stretches in these complexes are in the region usually found[15] for terminal metal–chlorine bonds in six coordinate complexes. The non-appearance of ν(M—Br) above 200 cm^{-1} is also expected in such a structure. It is almost certain, therefore, that these complexes possess a polymeric structure with bridging ethylhydrazines and terminal halides as found in $Co(N_2H_4)_2Cl_2$[1] and $Co(MeNHNH_2)_2Cl_2$.[2]

A less likely, but possible structure for these bis (ethylhydrazine) complexes is one containing bidentate ethylhydrazine(2−) ligands. Such a bonding mode has been found recently[16] in $[VCl_2(H_2NNMePh)_2(NNMePh)]Cl$ and the scarcity of bis(trifluoroethylhydrazine) complexes (see later) may be attributable to the lesser tendency to form hydrazide(2−) complexes arising from the presence of the electron withdrawing CF_3 groups on the ligand. In nickel and cobalt chemistry however, the occurrence of η^{2-}-NNHEt ligands in six coordinate complexes containing terminal metal–halogens would require unusually high oxidation states for the metals. The general insolubility of the complexes also supports the preferred polymeric structure.

Mono(ethylhydrazine) complexes are formed by zinc chloride. These complexes show, (Table 3), ν(M—X) in the regions expected for terminal halogens in tetrahedral structures[15] while the ν(N—N) bands are in similar positions to those of the cobalt

Table 3. Some important IR bands in complexes of ethylhydrazine (EH) and 2,2,2-trifluoroethylhydrazine (TFEH)

Compound	ν(CN)	ν(NN)	ν(CS)	δ(NCS)	ν(MN)	ν(MX)
EH		1110				
$CoCl_2(EH)_2$		1175			295, 279	251, 249
$CoBr_2(EH)_2$		1175			288, 280	
$NiCl_2(EH)_2$		1179			302, 280	250
$NiBr_2(EH)_2(H_2O)$		1172				
$ZnCl_2(EH)$		1169			338	325, 278
$ZnBr_2(EH)$		1164			382	260, 255
$CdCl_2(EH)$		1162			375	340, 310
TFEH		1148				
$CoBr_2(TFEH)_4$		1145			261, 230	
$Co(NCS)_2(TFEH)_4$	2070	1150	790	470, 450	230	
$NiCl_2(TFEH)_4$		1153			275	238
$Ni(NCS)_2(TFEH)_4$	2090	1160	795, 781	471	258	
$NiBr_2(TFEH)_6$		1158			290, 275	
$ZnBr_2(TFEH)_2$		1152			360	230
$ZnBr_2(TFEH)_4$		1162			370	

and nickel complexes. These complexes thus probably contain tetrahedrally coordinated zinc and cadmium atoms in polymeric structures with bridging ethylhydrazine. The polymeric structure may be broken down in dimethylsulphoxide in which the compounds behave as non-electrolytes.

Trifluoroethylhydrazine formed complexes less readily then hydrazine,[2] methylhydrazines,[5] ethylhydrazine and phenylethylhydrazine,[6] the reactions generally requiring concentrated solutions of the metal salt and heat. Even then precipitation and crystal growth were slow. This is most likely to be due to the lower basicity of the hydrazine which results from the electron withdrawing effect of the trifluoromethyl group. As with ethylhydrazine, an excess of the ligand was necessary in order to isolate pure complexes. In contrast to the reactions of hydrazine however, trifluoroethylhydrazine yielded bis(ligand) complexes only rarely (Table 3); several tetrakis(TFEH) complexes have been isolated and one hexakis(TFEH) complex. Further, some of these complexes are soluble in nitromethane in which they behave as weak or non-electrolytes. It seems likely therefore that the TFEH complexes are not polymeric and that only unidentate TFEH is present. The electronic spectra of the cobalt(II) tetrakis(TFEH) complexes are clearly indicative of six coordination around the cobalt; the 9,800 cm^{-1} peak in Co(NCS)$_2$(TFEH)$_4$ assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}$ transition is in fact split in CoBr$_2$(TFEH)$_4$ into the two components at 11,560 (^4E_g) and 7,900 cm^{-1} ($^4B_{2g}$) expected in a tetragonal field. The magnetic moment of this complex is surprisingly low at room temperature; it may arise from an equilibrium between spin states as has been observed in similar tetragonal complexes such as CoBr$_2$(diacetyldihydrazone).[17] The similarity of the ligand field strengths of —NCS and TFEH again result in no tetragonal splitting being observed in Ni(NCS)$_2$(TFEH)$_4$. With the chloro complex NiCl$_2$(TFEH)$_4$ however the transitions to the ^3E_g (8,700 cm^{-1}), $^3B_{2g}$ (10,600 cm^{-1}), $^3A_{2g}$ (12,900 cm^{-1}) and ^3E_g (17,400 cm^{-1}) are all visible resulting from a tetragonal D_{4h} structure. The hexakis(TFEH) complex of nickel(II) bromide shows no splitting in its spectral bands which are in very similar positions to those in [Ni(MeCN)$_6$]$^{2+}$;[18] it may therefore contain the [Ni(TFEH)$_6$]$^{2+}$ cation. Because of its surprisingly low conductivity in nitromethane we carried out conductivity studies over the concentration range 10^{-3}–10^{-6} M and found that the Onsager plot of Λ_M against C (C = concentration in gram moles per litre) has the characteristic curve shape found for weak electrolytes. The complex is thus heavily ion-paired at the higher concentration.

Some important IR bands in complexes of TFEH are given in Table 3. In the free ligand we assign the band at 1148 cm^{-1} to ν(N—N) (bands at 1305 and 1268 cm^{-1} being assigned to C—F stretching bands). The complexes show only a slight shift to higher frequencies for this band indicating that the TFEH is bonded from one nitrogen atom only. The complexes Co(NCS)$_2$(TFEH)$_4$ and Ni(NCS)$_2$(TFEH)$_4$ exhibit bands assignable to ν(CN), ν(CS) and δ(NCS) in the regions characteristically found[19] with N-bonded thiocyanates. Zinc bromide curiously forms a bis- and a tetrakis (TFEH) complex; the IR spectra imply (through the presence and absence of ν(Zn—Br) that these complexes may be tetrahedral and octahedral, respectively.

In order to provide unambiguous proof of structure, an X-ray diffraction study has been carried out on NiCl$_2$(TFEH)$_4$. The compound is confirmed to be NiCl$_2$(H$_2$N·NH·CH$_2$·CF$_3$)$_4$ with molecular

Table 4. Selected interatomic distances (Å) and angles (°) in NiCl$_2$(H$_2$N·NH·CH$_2$·CF$_3$)$_4$

Ni(1)—Cl(1)	2.444(2)
Ni(1)—N(1)	2.091(6)
Ni(1)—N(11)	2.120(5)
N(2)—N(1)	1.427(8)
N(2)—C(3)	1.43(1)
C(3)—C(4)	1.46(1)
C(4)—F(5)	1.36(1)
C(4)—F(6)	1.30(1)
C(4)—F(7)	1.32(1)
N(11)—N(12)	1.44(1)
N(12)—C(13)	1.45(1)
C(13)—C(14)	1.47(1)
C(14)—F(15)	1.33(1)
C(14)—F(16)	1.34(1)
C(14)—F(17)	1.35(1)
Cl(1)—Ni(1)—N(1)	89.0(2)
Cl(1)—Ni(1)—N(11)	89.1(1)
N(1)—Ni(1)—N(11)	91.8(2)
N(1)—N(2)—C(3)	115.0(6)
Ni(1)—N(1)—N(2)	115.3(4)
N(2)—C(3)—C(4)	112.6(7)
Ni(1)—N(11)—N(12)	114.4(4)
N(11)—N(12)—C(13)	114.9(5)
N(12)—C(13)—C(14)	115.4(6)
Cl(1)—Ni(1)—N(1)—N(2)	−52.9(4)
N(11)—Ni(1)—N(1)—N(2)	36.2(4)
Cl(1)—Ni(1)—N(11)—N(12)	−142.8(4)
C(3)—N(2)—N(1)—Ni(1)	168.4(5)
N(1)—N(2)—C(3)—C(4)	84.8(8)
N(2)—C(3)—C(4)—F(5)	−60.6(10)
Ni(1)—N(11)—N(12)—C(13)	−161.8(4)
N(12)—C(13)—C(14)—F(15)	−61.4(9)

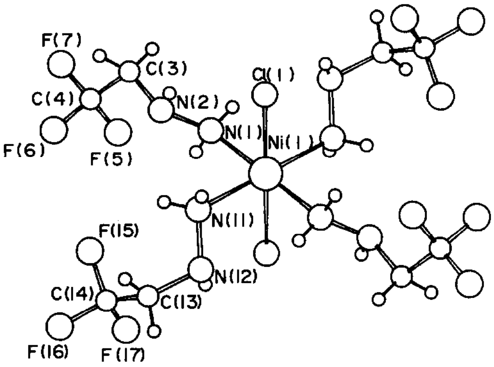

Fig. 1. A view of the $NiCl_2(TFEH)_4$ molecule (hydrogen atoms are shown unlabelled).

symmetry $\bar{1}(i)$ and octahedrally coordinated nickel; the molecule is illustrated in Fig. 1. The hydrazine is seen to be unidentate through the more basic NH_2 nitrogen atom. Selected bond lengths and angles are given in Table 4 and it is seen that the two chemically equivalent but crystallographically inequivalent ligands are not significantly different from each other or from expected values.

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