atomic site is only partially occupied, but the partial occupancy is not recognized, and refinement is carried out in the usual way in both R_1 and R_2 with unit weights in each case. The temperature parameters found were too large to be reasonable for the halogen atom in question, and larger for R_2 than for R_1. As pointed out by another referee, this suggests that deliberately carrying out two refinements with different weighting schemes might reveal the presence of significant but unsuspected defects in the model or systematic errors in the measurements.

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The Crystal and Molecular Structure of Bis-(2,4-dithiobiureto)nickel(II) Diperchlorate–Ethanol, Ni(HDTB)₂(ClO₄)₂ . EtOH

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The crystal structure was determined by Patterson and Fourier methods and refined by least-squares calculations using counter data (1363 reflexions), with anisotropic temperature factors for non-hydrogen atoms and positional parameters for hydrogen atoms, to a final $R = 0.075$. The crystals are monoclinic, space group $P2_1/c$, $a = 4.990$ (6), $b = 20.026$ (11), $c = 19.713$ (9) Å, $\beta = 93.70$ (5)°, $Z = 4$. The structure consists of four equivalent layers per unit cell, parallel to the xz plane, each containing the four constituents Ni(HDTB)₂.2ClO₄.EtOH of the asymmetric and stoichiometric unit. The nickel atom is planar-coordinated to four sulphur atoms. In the cationic complex Ni(HDTB)$_2^{2+}$ the interatomic distances and angles are very similar to those of the neutral complex Ni(DTB)₂, except that the S–C and C–N bond distances are respectively shorter and longer, and the bond angles S–C–N (terminal) and N(terminal)–C–N(central) are respectively higher and lower than in the neutral complex. Average bond distances: Ni–S = 2.162, S–C = 1.645, C–N(central) = 1.38, C–N(terminal) = 1.37 Å. The perchlorate ions (average Cl–O = 1.40 Å) and the ethanol molecule (C–C = 1.53, C–O = 1.41 Å) are linked to each other and to the complex molecules by several intermolecular hydrogen bonds. Each central NH group of the complex is linked to an oxygen atom of the perchlorate ions by the shortest observed hydrogen bonds (O···H distances = 1.86 and 1.88 Å). Another eleven intermolecular hydrogen bonds have O···H distances of 2.09–2.48 Å, and seven intramolecular hydrogen bonds have N···H distances of 2.23–2.51 Å.

Introduction

The ligand 2,4-dithiobiuret (HDTB) could possibly chelate *via* two sulphur or two nitrogen atoms or *via* a sulphur and a nitrogen atom, in each case to form a six-membered ring. It generally acts as a uninegative donor in neutral solution or as a neutral donor in acidic solution. The crystal and molecular structure of its square planar neutral complexes Pd(DTB)₂ (Girling & Amma, 1968) and Ni(DTB)₂ (Luth, Hall, Spofford & Amma, 1969) showed an S, S coordination of the ligand to the metal. The crystal structure of the addition compound Ni(DTB)₂.glycol (Pignedoli, Peyronel & Antolini, 1972) showed several hydrogen bonds between the

glycol and the complex molecules having a definite influence on their molecular structures.

The crystal and molecular structure of the cationic complex Ni(HDTB)₂(ClO₄)₂.EtOH has now been determined in order to investigate (*a*) the class of the metal–ligand bonds, (*b*) the structural differences between the coordinated neutral ligand in this complex and the uninegative ligand in the neutral complex, (*c*) the hydrogen-bond system in this ionic structure.

Experimental

The compound was prepared by cooling very slowly a warm ethanolic solution of the reagents containing

about 10% of a concentrated aqueous solution of perchloric acid. It crystallized directly in very thin, long prismatic needles, mostly bifurcated and twinned. The crystals are unstable in air, very rapidly releasing their ethanol molecule; they had to be sealed in Lindemann glass capillaries in an atmosphere of ethanol so as to enable X-ray investigation to be carried out. Even with this protection their surface became opaque after several weeks.

The measurements were performed on a six-faced, almost isodiametric (diameter = 0·15 mm) prismatic crystal elongated along the a axis. The b and c cell parameters were determined by measuring, to within 0·02°, the ω and 2θ positions of the $0k0$ and $00l$ reflexions with a Weissenberg–Stoe counter diffractometer and Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å). Plots of the $d(010)$ and $d(001)$ values versus the function $(\cos^2 \theta / \sin \theta + \cos^2 \theta/\theta)/2$ gave straight lines which were calculated and extrapolated at 90° by the least-squares method (Pignedoli & Peyronel, 1972). The a and β cell parameters were very carefully determined with a precision precession camera and with Mo $K\alpha$ radia-

tion. The systematic absences of reflexions were observed on Weissenberg and precession photographs by using both Cu $K\alpha$ and Mo $K\alpha$ radiation.

Crystal data

Bis(dithiobiureto)nickel(II)   diperchlorate–ethanol, $(NH_2 . CS . NH . CS . NH_2)_2 Ni(ClO_4)_2 . CH_3CH_2OH$ $[NiS_4N_6C_6Cl_2O_9H_{16}]$. Monoclinic prismatic. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences, $a = 4·990$ (6), $b = 20·026$ (11), $c = 19·713$ (9) Å, $\beta = 93·70$ (5)° at $t = 24°C$. $V = 1965·8$ Å^3, F.W. 574·13, $Z = 4$, $F(000) = 1168$, $D_c = 1·93$ g cm^{-3}, $\mu(Mo) = 17·18$ cm^{-1}.

The X-ray intensities ($0kl \rightarrow 3kl$) were recorded on the same crystal as described above using a two-circle Weissenberg–Stoe automatic counter diffractometer, the equi-inclination ω–2θ method and monochromated Mo $K\alpha$ radiation. The CORIN (1959) program was used to correct the intensities for Lorentz and polarization factors and for absorption, taking into account the shape of the equatorial section of the crystal, according to the method described by Busing & Levy

Table 1. *Fractional coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^2$)

Thermal parameters are defined by $T = \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$ for non-hydrogen atoms. Refined fractional coordinates ($\times 10^3$) and assumed thermal parameters B as defined by $\exp[-B(\sin \theta/\lambda)^2]$ for hydrogen atoms. Standard deviations are given in brackets.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	−0104 (4)	1246 (1)	2421 (1)	465 (10)	157 (5)	222 (6)	15 (7)	25 (6)	−3 (6)
S(1)	−1564 (9)	0495 (2)	1710 (2)	656 (30)	184 (15)	370 (17)	8 (17)	−39 (17)	−36 (13)
S(2)	−1686 (9)	2095 (2)	1842 (2)	591 (29)	184 (15)	365 (17)	7 (16)	−56 (18)	0 (12)
S(3)	1368 (10)	2009 (2)	3135 (2)	715 (30)	196 (15)	344 (17)	44 (17)	−103 (18)	−37 (13)
S(4)	1504 (10)	0401 (2)	2990 (2)	742 (32)	168 (15)	367 (17)	−24 (17)	−99 (18)	19 (13)
C(1)	−4211 (37)	0710 (6)	1201 (6)	665 (103)	261 (64)	191 (53)	22 (63)	−37 (63)	−1 (46)
C(2)	−4225 (31)	1933 (6)	1301 (6)	678 (104)	157 (55)	237 (57)	34 (61)	189 (62)	38 (45)
C(3)	3919 (34)	1769 (6)	3654 (6)	773 (113)	152 (55)	212 (55)	−13 (63)	31 (64)	8 (43)
C(4)	3971 (42)	0571 (7)	3548 (7)	1328 (156)	135 (59)	273 (62)	114 (79)	172 (79)	−13 (49)
N(1)	−5449 (27)	0238 (5)	0819 (6)	443 (79)	281 (54)	410 (56)	6 (49)	−42 (52)	−44 (44)
N(2)	−5396 (24)	1340 (6)	1105 (5)	603 (79)	203 (51)	354 (52)	−29 (53)	84 (48)	8 (41)
N(3)	−5655 (29)	2460 (5)	1016 (6)	635 (88)	254 (55)	478 (63)	78 (54)	−187 (60)	67 (46)
N(4)	5192 (27)	2264 (5)	4049 (6)	572 (84)	196 (48)	402 (56)	−62 (50)	−21 (55)	−91 (43)
N(5)	5125 (27)	1174 (6)	3760 (5)	777 (83)	209 (51)	284 (48)	−38 (60)	108 (48)	62 (42)
N(6)	5399 (27)	0043 (6)	3837 (6)	741 (95)	256 (54)	403 (59)	99 (57)	−153 (60)	73 (45)
Cl(1)	−0636 (7)	3709 (2)	4615 (2)	486 (22)	229 (13)	303 (14)	−2 (18)	−6 (13)	−22 (13)
Cl(2)	0562 (8)	3806 (2)	0219 (2)	481 (22)	254 (14)	279 (14)	−32 (17)	2 (13)	0 (13)
O(11)	−3480 (24)	3759 (7)	4514 (6)	584 (69)	495 (54)	762 (66)	−27 (66)	24 (52)	−23 (63)
O(12)	−0088 (34)	3391 (7)	5242 (6)	1297 (121)	851 (86)	567 (67)	−67 (82)	−301 (81)	278 (61)
O(13)	0515 (35)	3325 (7)	4118 (7)	1466 (138)	814 (87)	754 (80)	97 (87)	425 (85)	−433 (69)
O(14)	0563 (31)	4351 (5)	4638 (6)	1061 (99)	209 (48)	945 (80)	−85 (56)	−199 (77)	52 (50)
O(21)	3311 (25)	3805 (7)	0229 (5)	746 (74)	747 (69)	462 (53)	−71 (71)	−24 (51)	33 (58)
O(22)	−0436 (32)	4129 (7)	−0376 (7)	1001 (107)	793 (84)	837 (82)	−142 (72)	−341 (81)	328 (66)
O(23)	0034 (37)	4178 (8)	0788 (8)	1124 (126)	1185 (112)	1085 (100)	−127 (89)	104 (91)	−742 (88)
O(24)	−0284 (30)	3145 (5)	0208 (7)	910 (94)	317 (58)	1227 (102)	−164 (63)	124 (83)	56 (61)
O(X)	6058 (25)	3705 (6)	1739 (5)	804 (73)	264 (43)	472 (49)	124 (60)	78 (47)	−25 (44)
C(X1)	6251 (59)	3712 (16)	2455 (12)	1619 (217)	838 (135)	829 (131)	−147 (223)	−256 (149)	188 (123)
C(X2)	3339 (60)	3726 (14)	2653 (13)	1644 (217)	575 (110)	1148 (158)	−106 (189)	574 (148)	1 (129)

	x	y	z	B		x	y	z	B
H(11)	−510 (36)	−017 (8)	093 (8)	3·10	H(61)	551 (37)	−030 (8)	378 (8)	2·93
H(12)	−743 (40)	029 (8)	053 (8)	3·10	H(62)	612 (38)	005 (8)	420 (8)	2·93
H(2)	−731 (35)	133 (9)	087 (8)	2·77	H(OX)	419 (36)	367 (9)	145 (8)	3·98
H(31)	−497 (38)	287 (8)	106 (8)	2·64	H(X11)	715 (56)	324 (12)	254 (11)	8·50
H(32)	−738 (41)	239 (7)	072 (8)	2·64	H(X12)	702 (61)	414 (11)	245 (10)	8·50
H(41)	417 (41)	266 (8)	408 (8)	2·76	H(X21)	400 (47)	372 (12)	310 (11)	8·33
H(42)	635 (40)	219 (8)	446 (8)	2·76	H(X22)	325 (62)	424 (11)	245 (10)	8·33
H(5)	645 (36)	120 (9)	417 (8)	2·93	H(X23)	278 (55)	327 (12)	244 (11)	8·33

(1957), and evaluating the $\sigma(F_o)$'s by a statistical method. Only the values of $F_o > 4\sigma(F_o)$ were used for the calculations.

The crystal structure was solved by Patterson and Fourier three-dimensional syntheses using the *FOUR3D* program of Immirzi (1967a), which gives the coordinates of the maxima and their distances immediately. The refinement of the structure was carried out by the least-squares method using the *MIQUAD* program of Immirzi (1967b) on a CDC 6600 computer. The atomic scattering factors (Hanson, Herman, Lea & Skillman, 1964) of the heavier atoms were corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1962).

Firstly, the positional parameters, the isotropic and the anisotropic temperature factors of the non-hydrogen atoms were refined. After a number of cycles of

anisotropic refinement 49 reflexions with low indices and unrefinable $F_o \ll F_c$ were excluded; they may have been affected by extinction or some other experimental errors. Anisotropic refinement was stopped when the least-squares parameter variations and the differences of the atomic positions in the F_o and F_c three-dimensional syntheses were lower than their positional standard deviations. Then all hydrogen atoms were identified by difference Fourier syntheses (observed electron densities of the peaks in the range $0.7-0.9$ eÅ^{-3}) and their positional parameters were refined by the least-squares method assuming for them the last isotropic temperature factors of the nitrogen or carbon atoms to which they are bonded.

With the last positional and thermal parameters (Table 1) the 1363 reflexions used gave a final reliability index $R = 0.075$ (0.11 including the 49 excluded re-

Table 2. *Interatomic distances* (Å) *and their e.s.d'.s*

Parts (a) and (b) of the complex molecule are compared.

Bond lengths

Ni——S(1)	2·151 (5)	Ni——S(3)	2·174 (5)	Cl(1)—O(11)	1·42 (2)
Ni——S(2)	2·167 (4)	Ni——S(4)	2·157 (5)	Cl(1)—O(12)	1·40 (2)
S(1)——C(1)	1·66 (2)	S(3)——C(3)	1·65 (2)	Cl(1)—O(13)	1·40 (2)
S(2)——C(2)	1·64 (2)	S(4)——C(4)	1·63 (2)	Cl(1)—O(14)	1·42 (2)
C(1)—N(1)	1·33 (2)	C(3)—N(4)	1·39 (2)	Cl(2)—O(21)	1·37 (2)
C(1)—N(2)	1·40 (2)	C(3)—N(5)	1·35 (2)	Cl(2)—O(22)	1·40 (2)
C(2)—N(2)	1·37 (2)	C(4)—N(5)	1·39 (2)	Cl(2)—O(23)	1·39 (2)
C(2)—N(3)	1·37 (2)	C(4)—N(6)	1·38 (2)	Cl(2)—O(24)	1·39 (2)
N(1)—H(11)	0·87 (16)	N(4)—H(41)	0·96 (17)	O(X)—C(X1)	1·41 (3)
N(1)—H(12)	1·11 (19)	N(4)—H(42)	0·97 (18)	C(X1)-C(X2)	1·53 (4)
N(2)—H(2)	1·04 (18)	N(5)—H(5)	1·01 (17)	O(X)—H(0X)	1·06 (18)
N(3)--H(31)	0·89 (17)	N(6)—H(61)	0·70 (17)	C(X1)-H(X11)	1·05 (25)
N(3)—H(32)	1·02 (20)	N(6)—H(62)	0·79 (17)	C(X1)-H(X12)	0·93 (23)
C(X2)-H(X21)	0·93 (22)	C(X2)-H(X22)	1·11 (21)	C(X2)-H(X23)	1·03 (24)

Intramolecular distances

S(1)–S(4)	2·873 (6)
S(2)–S(3)	2·889 (6)
S(1)–S(2)	3·216 (5)
S(3)–S(4)	3·235 (5)
S(1)–H(11)	2·64
S(2)–H(31)	2·66
S(3)–H(41)	2·61
S(4)–H(61)	2·83
N(1)–H(2)	2·37
N(2)–H(12)	2·56
N(2)–H(32)	2·43
N(3)–H(2)	2·43
N(4)–H(5)	2·23
N(5)–H(42)	2·51
N(5)–H(62)	2·46
N(6)–H(5)	2·46

Intermolecular distances

N(3)--O(X)	[−1]	2·97	N(3)—H(0X) [−1]		2·57
O(11)-N(1)	[−3]	3·07	O(11)-H(11) [−3]		2·40
O(11)-N(4)	[−1]	3·19	O(11)-H(41) [−1]		2·61
O(12)-N(2)	[+4]	2·85	O(12)-H(2) [+4]		1·88
O(12)-N(3)	[+4]	3·11	O(12)-H(32) [+4]		2·23
O(13)-N(4)		3·17	O(13)-H(41)		2·26
O(14)-N(1)	[3]	3·19	O(14)-H(11) [3]		2·76
O(14)-N(1)	[−3]	3·19	O(14)-H(12) [−3]		2·46
O(14)-N(1)	[+4]	3·08	O(14)-H(12) [+4]		2·09
O(21)-N(3)	[+1]	3·13	O(21)-H(31) [+1]		2·61
O(21)-N(5)	[2]	3·09	O(21)-H(5) [2]		2·69
O(21)-N(6)	[+3]	3·13	O(21)-H(61) [+3]		2·68
			O(21)-H(62) [+3]		2·74
O(21)-O(X)		3·20	O(21)-H(0X)		2·44
O(22)-N(5)	[−2]	2·77	O(22)-H(5) [−2]		1·86
O(22)-N(6)	[−2]	3·01	O(22)-H(62) [−2]		2·48
O(23)-N(6)	[+3]	2·92	O(23)-H(61) [+3]		2·55
			O(23)-H(62) [+3]		2·59
			O(23)-H(0X)		2·59
O(24)-N(3)	[+1]	3·05	O(24)-H(32) [+1]		2·28
O(24)-N(4)	[−2]	3·21	O(24)-H(42) [−2]		2·26
O(X)-N(3)	[+1]	2·97	O(X)-H(31) [+1]		2·18
O(X)-N(6)	[+3]	2·98	O(X)-H(61) [+3]		2·36

Asymmetric units

[1] x,y,z (not indicated); [−1] $x−1,y,z$; [+1] $x+1,y,z$;
[2] $x,\frac{1}{2}−y,−\frac{1}{2}+z$; [−2] $x−1,\frac{1}{2}−y,−\frac{1}{2}+z$;
[3] $−x,\frac{1}{2}+y,\frac{1}{2}−z$; [−3] $−x−1,\frac{1}{2}+y,\frac{1}{2}−z$; [+3] $1−x,\frac{1}{2}+y,\frac{1}{2}−z$;
[+4] $x+1,\frac{1}{2}−y,\frac{1}{2}+z$.

flexions). Residual $(\varrho_o-\varrho_c)$ densities of about 1 e Å^{-3} were observed in the vicinity of the heavier atoms. Interatomic distances and angles with their e.s.d.'s (Tables 2 and 3; Figs. 2 and 3) were calculated with the *MIQUAD* and *IMPACC* programs of Immirzi (1967*b*). The more relevant least-squares planes and the atomic distances from them (Table 4) were calculated with the *PIAMED* program of Immirzi (1967*b*). The thermal ellipsoids (Fig. 4) were plotted with the *ORTEP* program of Johnson (1965).*

Results and discussion

The structure of Ni(HDTB)$_2$.(ClO$_4$)$_2$.EtOH, represented in the projection of the unit cell on the *yz* plane in Fig. 1, consists of four layers parallel to the *xz* plane, each containing the four constituents of the stoichiometric and asymmetric unit. Because of this equivalence of the four layers the 0*k*0 reflexions could be observed only with $k=4n$. The Ni(HDTB)$_2^{2+}$ complex has its longitudinal axis almost parallel to the *z* axis, while its mean plane is at about 40° to the *yz* plane [Fig. 4(*b*)]. The perchlorate ions have one of their Cl–O bonds oriented in the direction of the *x* axis; the mean plane of the EtOH molecule is almost exactly parallel to the *xz* plane.

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* The table of observed and calculated structure factors has been deposited with the National Lending Library as Supplementary Publication No. SUP 30086. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ.

The nickel atom, out of a centre of symmetry, is planar-coordinated to four sulphur atoms: the S–Ni–S angles formed by the two opposite sulphur atoms are very close to 180° (Table 3) and the NiS$_4$ group is coplanar (Table 4) (r.m.s. deviation = 0·007 Å) within the experimental errors. The Ni–S bond distances, the intrachelate and interchelate S–Ni–S angles and S–S distances (Tables 2, 3, 5) are very close to those observed in the neutral complex in both the Ni(DTB)$_2$ and Ni(DTB)$_2$.glycol structures. The interchelate S–S distance of about 2·9 Å in both the neutral and the cationic complexes is well within the range of 3·04–3·17 Å postulated by Steifel, Dori & Gray (1967) as indicative of some residual S–S bonding; this shorter distance was considered by Luth, Hall, Spofford & Amma (1969) as significant and led them to conclude that in Ni(DTB)$_2$ there is some residual S–S interchelate bonding. This residual bonding could be at least partially responsible for the almost identical structure of the NiS$_4$ group in both the neutral and the cationic Ni(dithiobiureto)$_2$ complexes.

All the four S–C(N)–N groups are coplanar (maximum r.m.s. deviation = 0·037 Å) and the C–N(central) and C–N(terminal) bond distances are almost equivalent, as in the neutral Ni(DTB)$_2$ complex. The intrachelate Ni–S–C, S–C–N(*c*) and C–N(*c*)–C angles (Tables 3, 5) are also very close in the neutral and cationic complexes. The greatest differences between the two types of complexes may be observed in the S–C and C–N bond lengths, which are respectively shorter and longer in the cationic complex, and in the extrachelate

Table 3. *Interatomic angles* (°) *and their e.s.d's*

Parts (*a*) and (*b*) of the complex molecule are compared.

(*a*)		(*b*)	
S(1)——Ni——S(2)	96·3 (1)	S(3)—Ni——S(4)	96·6 (1)
S(2)——Ni——S(3)	83·4 (1)	S(1)—Ni——S(4)	83·6 (1)
S(1)——Ni——S(3)	179·7	S(2)—Ni——S(4)	179·4
Ni——S(1)—C(1)	115·8 (5)	Ni——S(3)—C(3)	114·3 (5)
Ni——S(2)—C(2)	115·4 (5)	Ni——S(4)—C(4)	115·2 (6)
S(1)——C(1)—N(1)	118·6 (7)	S(3)——C(3)–N(4)	116·5 (6)
S(2)——C(2)—N(3)	118·4 (6)	S(4)——C(4)–N(6)	117·7 (7)
S(1)——C(1)—N(2)	128·8 (7)	S(3)——C(3)–N(5)	132·3 (8)
S(2)——C(2)—N(2)	130·9 (7)	S(4)——C(4)–N(5)	131·6 (7)
N(1)——C(1)—N(2)	112·7 (6)	N(4)——C(3)–N(5)	111·2 (6)
N(3)——C(2)—N(2)	110·5 (5)	N(6)——C(4)–N(5)	110·4 (6)
C(1)——N(2)—C(2)	125·1 (6)	C(3)——N(5)–C(4)	123·4 (6)
O(11)—Cl(1)—O(12)	106·9 (5)	O(21)—Cl(2)–O(22)	108·4 (5)
O(11)—Cl(1)—O(13)	113·0 (5)	O(21)—Cl(2)–O(23)	103·4 (5)
O(11)—Cl(1)—O(14)	110·8 (5)	O(21)—Cl(2)–O(24)	107·5 (4)
O(12)—Cl(1)—O(13)	107·6 (5)	O(22)—Cl(2)–O(23)	110·7 (5)
O(12)—Cl(1)—O(14)	109·0 (4)	O(22)—Cl(2)–O(24)	109·6 (4)
O(13)—Cl(1)—O(14)	109·3 (4)	O(23)—Cl(2)–O(24)	116·8 (5)
O(*X*)—C(*X*1)–C(*X*2)	104·5 (8)		
H(11)—N(1)—H(12)	112 (7)	H(41)–N(4)–H(42)	112 (8)
H(11)—N(1)—C(1)	117 (2)	H(41)–N(4)–C(3)	114 (3)
H(12)—N(1)—C(1)	126 (2)	H(42)–N(4)–C(3)	126 (2)
H(2)——N(2)—C(1)	114 (2)	H(5)—N(5)–C(3)	110 (3)
H(2)——N(2)—C(2)	121 (2)	H(5)—N(5)–C(4)	122 (2)
H(31)—N(3)—H(32)	120 (9)	H(61)–N(6)–H(62)	97 (8)
H(31)—N(3)—C(2)	118 (2)	H(61)–N(6)–C(4)	138 (2)
H(32)—N(3)—C(2)	122 (2)	H(62)–N(6)–C(4)	124 (2)
H(O*X*)–O(*X*)—C(*X*1)	122 (2)		

Table 4. *Least-squares planes*

Equation in the form $Ax + By + Cz - D = 0$ referred to the crystallographic axes a, b and c; plane coefficients A, B, C, D ($\times 10^4$). Parts a and b of the complex molecule, as defined by the identification numbers of the atoms listed in the first two columns after the symbols, are compared in neighbouring columns. Deviations of the atoms from the planes and their r.m.s. deviation in Å ($\times 10^3$); the deviations of the atoms not included in the mean plane are indicated with an asterisk.

	Part a b	1 a	1 b	2 a	3 b	4 a	4 b	5 a	6 a	7 b	8 b	9 a	10 b	11 a	12 b
Ni		005		218	-200	-013						536*	-484*	473*	-433*
S	(1)(3)	003	003	-174	158	-297	270	-0002	010	-004	-010	-006	005	-012	009
S	(2)(4)	-006	-006	-180	163	-313	266	0007		014		006	-006	-018	015
C	(1)(3)			006	006	-001	027		-030		032	008	006	059	-045
C	(2)(4)			-028	030	-044	045	-0002		-004		-008	099*	026	-021
N	(1)(4)			-031	023	031	-004	-0002	011	-004	-012	-127*	-148*	-039	029
N	(2)(5)			197	-136	229	-202	-0002	009	-005	-010	145*	061*	209*	-199*
N	(3)(6)			-008	006	040	-034		034	016	037	-077*	011	-016	012
								0008				015		046	035
r.m.s.		007		174	160	190									
A		-8805		-7199	-7312	-7687		-6517	-6495	-6685	-6692	-6443	-6673	-6713	-6880
B		-0623		-0755	-0811	-0752		-1898	0246	-1875	0109	-0734	-0304	-0781	-0840
C		5258		7350	7231	6835		7748	8003	7613	7846	8012	7819	7789	7638
D		23950		31391	34862	31270		29332	35469	34993	41429	31378	40492	30845	39042

Type of plane
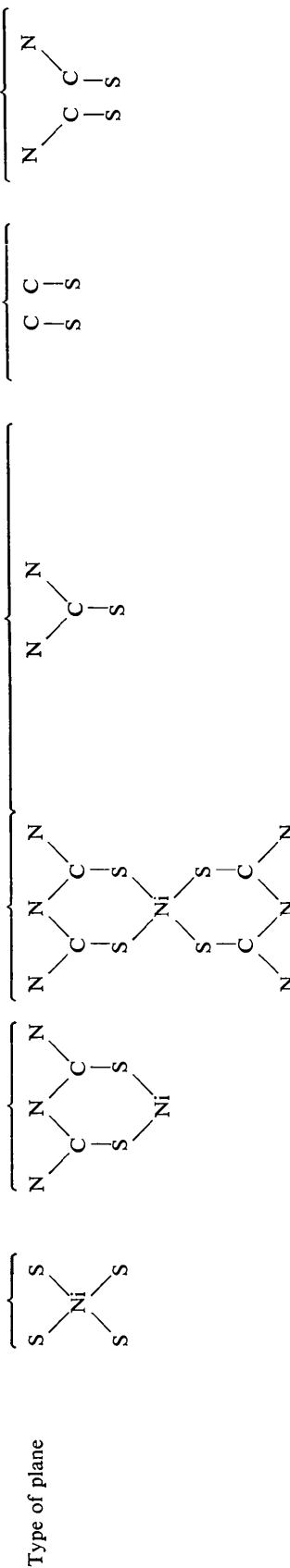
S–C–N(t) and N(t)–C–N(c) angles, which are respectively greater and smaller for the cationic complex (Table 5).

The complete molecules of both the neutral and the cationic complexes adopt a 'chair' configuration between the two opposite central nitrogen atoms. The dihedral angle between the planes S–Ni–S and S–N(c)–S was considered by Luth, Hall, Spofford & Amma (1969) as being characteristic for the chair form as defined above. However, the structure of the addition compound Ni(DTB)$_2$ glycol has shown that this angle is sensitive to the environment of the complex molecule and does not depend only on intrachelate forces, as do other characteristic angular values of both the neutral and cationic complexes.

Half of the complex molecule, from nickel to the central nitrogen atom, adopts a 'boat' configuration [Fig. 4(b)]. In the Ni(HDTB)$_2^{2+}$ complex both groups

of the four atoms S–C, S–C of the half molecule are coplanar within experimental error (maximum r.m.s. deviation = 0·015 Å) (Table 4). The least-squares planes S–C, S–C make angles of 21·9° and 19·6° with the S–Ni–S and of 13·1 and 13·2° with the C–N–C planes. The S–C, S–C atoms in the Ni(DTB)$_2$ glycol complex are considerably less coplanar (r.m.s. deviation = 0·187 Å): their least-squares plane is at 28·9° to the S–Ni–S and at 9·1° to the C–N–C planes. In the cationic complex the six atoms S–C–N(t), S–C–N(t) are also coplanar (mean r.m.s. deviation = 0·04 Å).

The EtOH molecule has a C–O bond distance of 1·41 (3) Å close to the literature value of 1·43 (2) Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1958) and to the glycol value of 1·43 (1) Å (Pignedoli, Peyronel & Antolini, 1972). The hydrogen H(OX), which is very well defined in its difference map, makes an H(OX)–O(X)–C(X1) angle of
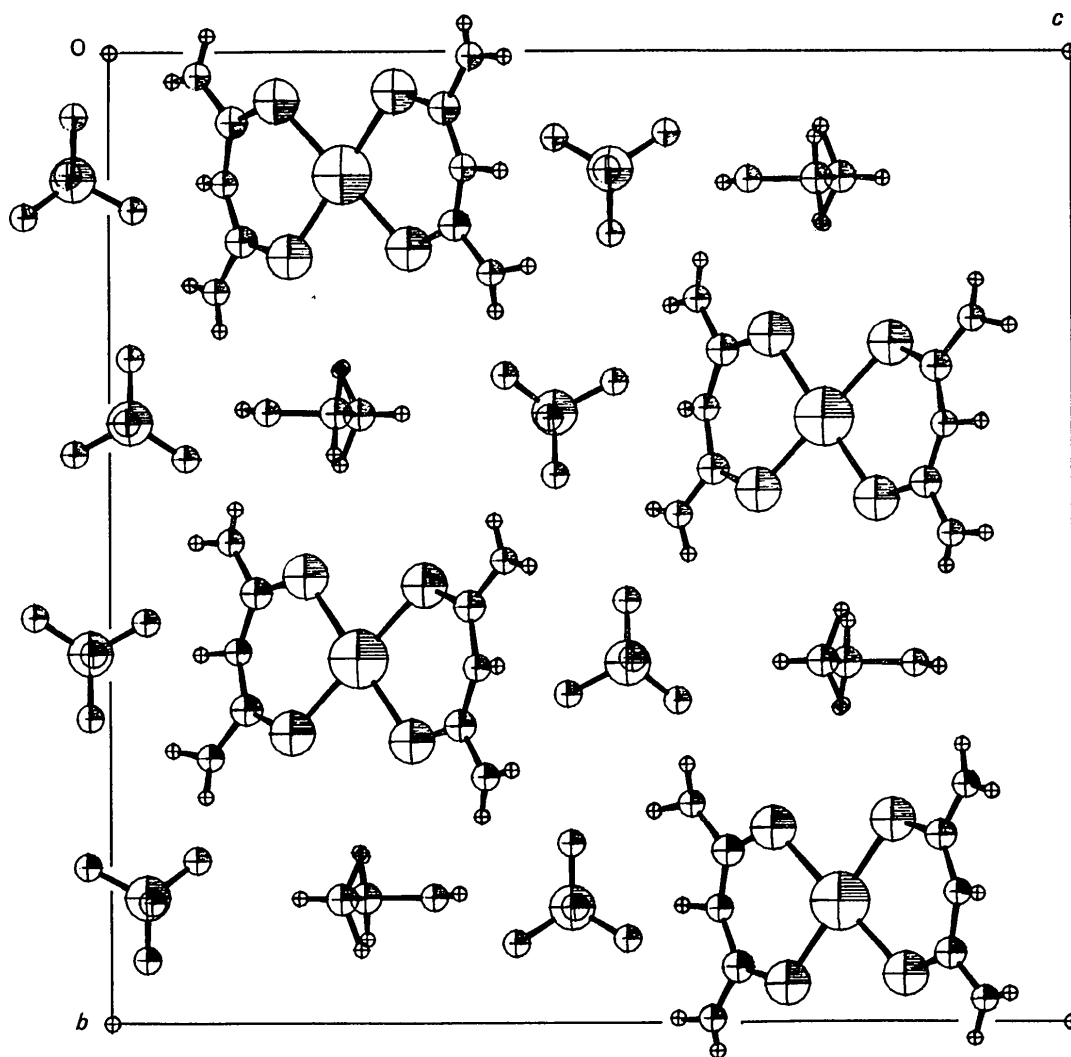

Fig. 1. Orthographic projection of the unit cell on the yz plane showing the four layers parallel to the xz plane, each containing the stoichiometric unit (HDTB)$_2$.2ClO$_4$.EtOH (*ORTEP* plot).

122 (2)°, comparable to the H(O)–O–C angle of 126 (5)° found in the glycol molecule in the Ni(DTB)$_2$.glycol structure (Pignedoli, Peyronel & Antolini, 1972). The CH$_2$ and CH$_3$ hydrogen atoms of the ethanol molecule are less well defined because of their higher thermal agitation. The perchlorate ions have an average Cl–O distance of 1·40 (2) Å and an average O–Cl–O angle of 109·3 (3·2)°.

In Table 2 are reported some intramolecular and intermolecular contacts. The non-hydrogen atom intermolecular contacts are given only for interatomic distances equal to or less than 3·2 Å. All these distances correspond to hydrogen contacts equal to or less than about 2·7 Å. In Fig. 3 are reported only the hydrogen contacts equal to or lower than the O···H van der Waals distance 2·60 Å (Pauling, 1960).

The two shortest intermolecular hydrogen bonds, having distances: O(12)···H(2) = 1·88 Å and O(22)··· H(5) = 1·86 Å, strongly bond each perchlorate ion (1) and (2) to one of the central NH groups on the opposite side of the complex molecule, indicated as [−2] and [+4] in Fig. 3. The ethanol molecule seems to be hydrogen-bonded to the O(21) atom of the perchlorate ion (2) (H···O distance = 2·44 Å) and to the NH$_2$ groups of two parallel complex molecules (N···H distances = 2·18 and 2·36 Å). Another eight O···H bonds between the perchlorate ions and the NH$_2$ groups of neighbouring complex molecules have O···H distances 2·09–2·48 Å, while another six hydrogen contacts (2·55–2·61 Å) are at the limit of the van der Waals distance.

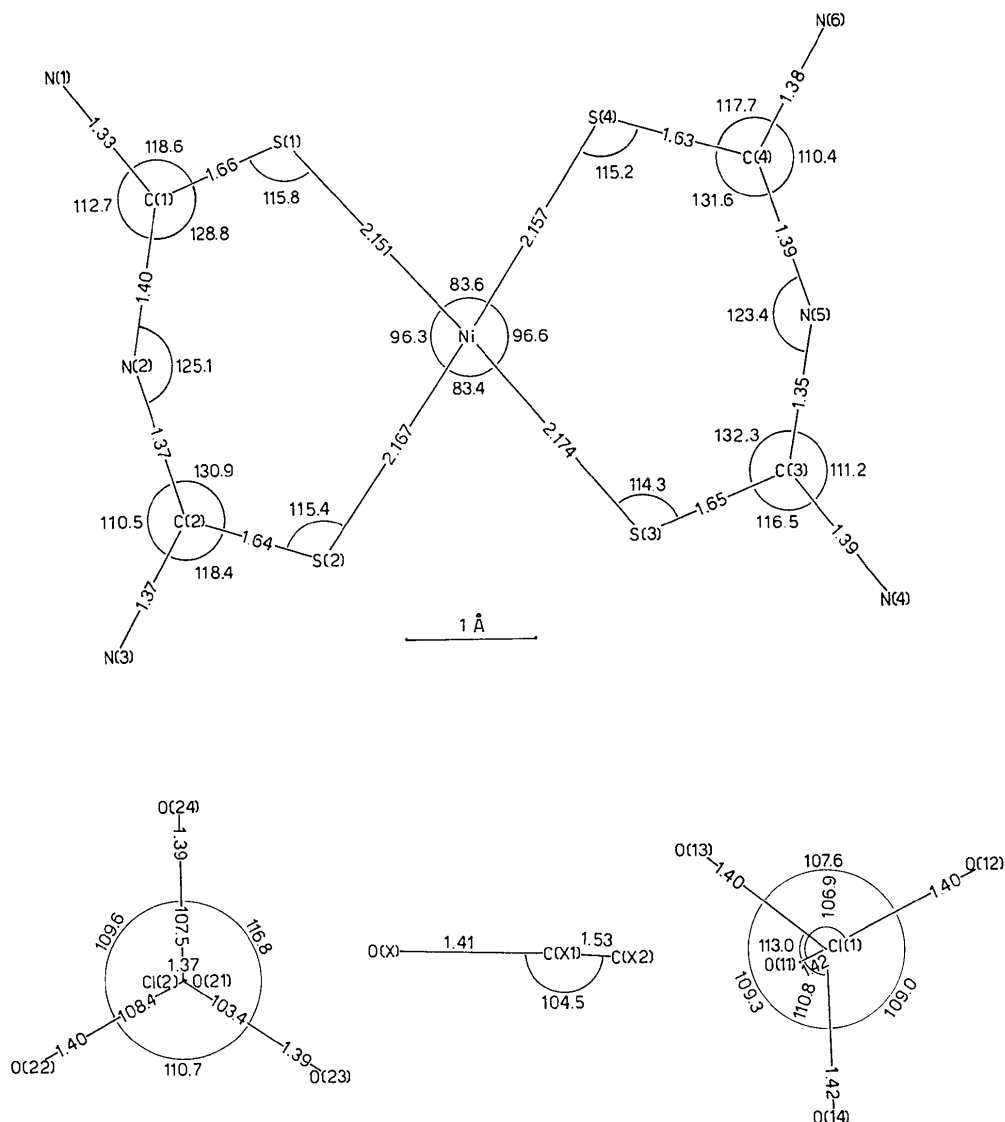The two shortest intramolecular N···H contacts,

Fig. 2. Interatomic distances (Å) and angles (°). The four components af the assumed fundamental asymmetric unit are given in their projection on the *yz* plane with their mutual orientation but at reciprocal arbitrary distances.

Table 5. *Comparison of some characteristical structural mean values of the neutral complexes*
$Pd(DTB)_2$ *and* $Ni(DTB)_2$ *and the cationic complex* $Ni(HDTB)_2^{2+}$

Mean value of	$Pd(DTB)_2$*	$Ni(DTB)_2$†	$Ni(DTB)_2$‡ glycol	$Ni(HDTB)_2$ $(ClO_6)_2$ EtOH
M–S	2·295 Å	2·165 Å	2·170 Å	2·162 Å
S–C	1·745	1·724	1·731	1·645
C–N(c)	1·315	1·33	1·34	1·38
C–N(t)	1·335	1·33	1·33	1·37
S–S (intrachelate)	3·32	3·220	3·200	3·250
S–S (interchelate)	3·16	2·895	2·933	2·880
S–M–S (intrachelate)	92·8°	96·1°	95·0°	96·3°
S–M–S (interchelate)	87·2	83·9	85·0	83·4
M–S–C	109·5	115·8	112·9	115·2
S–C–N(c)	130	130·5	130·6	130·9
C–N(c)–C	128	125·0	124·4	124·3
S–C–N(t)	112·5	114·1	114·4	117·8
N(t)–C–N(c)	116	115·2	114·9	111·2
S–M–S ∧ S, N, S	38	11	30·8	24·5

* Girling & Amma (1963).
† Luth, Hall, Spofford & Amma (1969).
‡ Pignedoli, Peyronel & Antolini (1972).

Fig. 3. Hydrogen contacts (broken lines). Asymmetric units are given in square brackets with the numbers listed in Table 2. The distance is considered from the non-hydrogen atom of the fundamental asymmetric unit [1] to the hydrogen atom of the same or different asymmetric unit. The signs (−) or (+) in the direction of the hydrogen atom indicate that it belongs to the inferior or superior cell, respectively. The atoms, being easily recognizable, are characterized only by their identification numbers.

having distances $N(4)\cdots H(5)=2\cdot23$ and $N(1)\cdots H(2)=2\cdot37$ Å, involve the hydrogen atoms of the central NH groups of the complex molecule, already involved in the two $N-H\cdots O$ shortest bonds with two perchlorate ions. $H(2)$ and $H(5)$ atoms are further involved in two other short intramolecular $N\cdots H$ contacts: $N(3)\cdots H(2)=2\cdot43$ and $N(6)\cdots H(5)=2\cdot46$ Å.

The multiplicity of the $H(2)$ and $H(5)$ shortest oxygen and nitrogen contacts seems to indicate that these hydrogen atoms have the greatest positive charge. This is in agreement with the fact that these NH hydrogens are lost by the ligand molecule in forming the neutral complex $Ni(DTB)_2$. The large positive charge of these hydrogen atoms in the cationic complex can be related to the electron distribution in the coordinated ligand which is very uniform in the four $N-C-N-C-N$ bonds for both the cationic and the neutral complexes: this implies a greater electron contribution from the central nitrogen atom and a weakening of its $N-H$ bond.

The corresponding angles involving hydrogen atoms have comparable values in the two halves of the complex molecule (Table 3) except the two involving the $H(61)$ atom, which is probably less well located. The 'chair' form of the whole $Ni(HDTB)_2^{2+}$ complex, which is nearly centrosymmetric, and the 'boat' form of each half molecule are clearly recognizable in Fig. 4(b). As expected, the higher thermal vibration of the terminal nitrogen atoms of the complex and of the oxygen atoms of the perchlorate ions is almost perpendicular to the direction of their bonds (Fig. 4). In many cases this direction coincides with the shortest axis of the ellipsoid.

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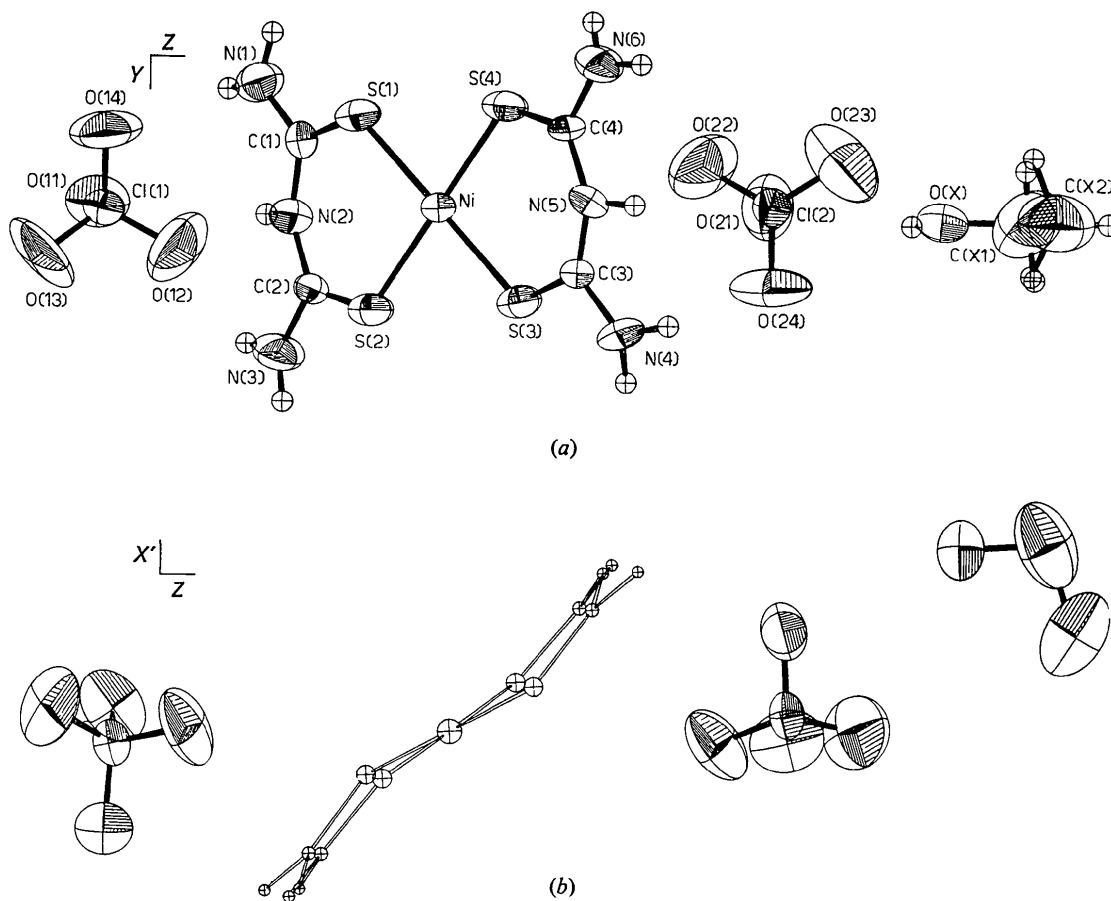

Fig. 4. (a) Orthographic *yz* projection of the first layer of the unit cell as shown in Fig. 1. *ORTEP* plot of thermal ellipsoids scaled to include 60 % probability for non-hydrogen atoms. The hydrogen atoms are represented by spheres of 0·1 Å radius. (b) Orthographic projection of the same layer of the unit cell on the *xz* plane; *X'* corresponds to the $a\sin\beta$ direction. *ORTEP* plot of thermal ellipsoids scaled to include 50 % probability for non-hydrogen atoms of the ethanol molecule and the perchlorate ions. For the complex molecule the atoms are represented by spheres of different radii: Ni = 0·13, S = 0·10, C = 0·07, N = 0·06 Å

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The Molecular Structure of C₂F₄Fe(CO)₄ by Gas-Phase Electron Diffraction

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The molecular structure of tetrafluoroethyleneirontetracarbonyl has been studied by gas-phase electron diffraction. Data reduced by standard techniques are consistent with a distorted octahedral complex of iron with C_{2v} symmetry; the carbon atoms of the non-planar C_2F_4 unit occupy two adjacent equatorial sites. Fe–C(C_2F_4) = 1.989 ± 0.010, Fe–C(O)eq. = 1.846 ± 0.010, Fe–C(O)ax. = 1.823 ± 0.010, C–C = 1.530 ± 0.015, C–F = 1.336 ± 0.005, C–O = 1.138 ± 0.003 Å. The F–C–F angle is $111.3 \pm 1.1°$, and the supplement to the angle C–C–(midpoint of vicinal F atoms) is $41.6 \pm 1.1°$. The angle between equatorial carbonyl groups is $104.2 \pm 1.4°$ and the axial carbonyl groups are essentially linear. The results suggest that the C_2F_4 unit resembles a fragment of perfluorocyclopropane rather than perfluoroethylene, and that the complexing with iron is σ, rather than π, in character.

Introduction

Structurally, olefin complexes of transition metals are of interest because of their unusual bonding, which appears to be neither entirely π nor entirely σ in character (see e.g. Cotton & Wilkinson, 1966). The direct determination of molecular structures by the method of gas-phase electron diffraction has helped to establish the nature of the bonding. Typical of π-complexes is ferrocene, where the ten equal, rather long 2·06 Å Fe–C distances (Bohn & Haaland, 1966; Haaland & Nilsson, 1968) involve only 18 available electrons, insufficient for ten normal σ-bonds. At the other extreme, σ-complexes are typified by CH₃Mn(CO)₅ (Seip & Seip, 1970), where the Mn–CH₃ bond may be considered as a normal two-electron σ-bond. The intermediate character of the bonding in olefin complexes is supported by the electron-diffraction study (Davis & Speed, 1970) of ethylene iron tetracarbonyl, C₂H₄Fe(CO)₄, which shows that the Fe–C ('olefin') distances are equivalent and again rather long (2·12 Å), as in ferrocene. However the carbon–carbon bond length of 1.46 ± 0.03 Å is considerably greater than that found in ethylene itself,

$r_g = 1.337 \pm 0.002$ Å (Bartell, Roth, Hollowell, Kuchitsu & Young Jr, 1965; Kuchitsu, 1966); in fact it is nearer that in cyclopropane, $r_g = 1.511 \pm 0.002$ Å (Bastiansen, Fritsch & Hedberg, 1964). Similar lengthenings of such carbon–carbon bonds have been observed in X-ray crystallographic studies, particularly of tetracyanoethylene (TCNE) complexes; Stalick & Ibers (1970) point out that the lengthening is accompanied by a bending back of the CX₂ planes of the olefin, C₂X₄, away from the metal atom; they also suggest that the lengthening and the bending back are quantitatively correlated. In TCNE complexes the deviation of the CX₂ plane from the original olefin plane is typically 30°; it is typically 40° for CCl₂ groups in chloro-olefin platinum complexes (McAdam, Francis & Ibers, 1971). It seems possible, from the discussion of Stalick & Ibers, that the extent of the distortion from olefinic geometry may be used as a measure of the degree of σ-complexing with the metal, and if the sparse data they report for C₂H₄ complexes are also considered, the results suggest that the distortion, and thus the degree of σ-complexing, may be greatest for electronegative substituents, X. The study of C₂F₄Fe(CO)₄, described here, extends these in-