Studies in Werner Clathrates.
Part 8. Secondary Bonding to Halogenated Guest Molecules

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Abstract

The crystal structures of $[Ni(NCS)_2(4\text{-}ViPy)_4]\cdot 2CCl_4$, $[Ni(NCS)_2(4\text{-}ViPy)_4]\cdot CHI_3$ and $[Ni(NCS)_2(4\text{-}ViPy)_4][Ni(NCS)_2(thf)(4\text{-}ViPy)_3]\cdot 2CHI_3$ (4-ViPy = 4-vinylpyridine; thf = tetrahydrofuran) have been elucidated.

The carbon tetrachloride clathrate has a similar packing to the chloroform analogue previously described.

There is significant secondary bonding between the sulphur (donor) and iodines (acceptors) in the iodoform-containing clathrates. The latter also show strong packing similarities.

Introduction

Werner clathrates are inclusion compounds with the host component having general formula MX_2B_4, where M is a divalent transition metal cation (e.g. Fe(II), Ni(II), Cu(II), Co(II) etc.), X is an ionic ligand (e.g. NCS^-, halide$^-$, etc.) and B is an electrically neutral substituted pyridine or α-arylalkylamine. We have studied several compounds of this kind having 4-vinylpyridine as the coordinated base. In particular, we have elucidated the structures of the non-porous α-phase and of its β-phase clathrates with *o*-, *m*- and *p*-xylenes [1] and chloroform [2]. We have also studied the thermal decomposition of these clathrates and measured the solubility of the $[Ni(NCS)_2(4\text{-}ViPy)_4]$ host in a number of organic liquids which were potential guests [2]. This host complex forms clathrates which are generally more stable than the corresponding compound formed with 4-Etpy as the coordinating base. The latter compound also forms a variety of clathrates with the xylenes, CCl_4 and CS_2, but the compounds thus formed are highly unstable and the crystals decompose with the loss of the guest molecules [3]. One of the possible reasons to explain the formation of clathrates by these kind of inorganic complexes is the rotational freedom about the Ni–N bonds. This supposedly allows adjustment of the substituted pyridines to accommodate the various guest molecules. However another aspect of host–guest interaction which has not received attention involves the thiocyanato moiety. Alcock has described the nature of secondary bonding to non-metallic elements [4] and this work investigates the interaction between the sulphur atoms of the host molecules and the halogens of the guests.

Experimental Procedure and Structure Solutions

The host complex was prepared by reacting an ethanolic solution of nickel isothiocyanate with a 10% excess of the stoichiometric amount of 4-vinylpyridine.

Compound I, $[Ni(NCS)_2(4\text{-}ViPy)_4]\cdot 2CCl_4$, was formed by dissolving the host compound in tetrahydrofuran and layering this solution over carbon tetrachloride. Crystals showing an octahedral habit grew within 5 h.

Compound II, $[Ni(NCS)_2(4\text{-}ViPy)_4]\cdot CHI_3$, was prepared by dissolving 0.60 g (1 mmol) of the host compound in 5 ml of warm ethanol and adding 0.79 g (2 mmol) of iodoform to this solution. Crystals of tabular habit grew within 24 h.

Compound III, $[Ni(NCS)_2(4\text{-}ViPy)_4][Ni(NCS)_2(thf)(4\text{-}ViPy)_3]\cdot 2CHI_3$ was prepared by dissolving 0.60 g (1 mmol) of the host complex in a warmed mixture of 3 ml ethanol and 2 ml tetrahydrofuran. The solution was boiled under reflux for 10 min and allowed to cool. Tabular crystals appeared within 24 h.

For all structural determinations, which were carried out at 293 K, small crystals were mounted in Lindemann tubes with mother liquor to prevent deterioration in air. Preliminary cell dimensions and space group symmetry were determined photographically. Accurate cell parameters were then obtained by least-squares analysis of twenty five reflections measured in the range $16° < \theta < 17°$ on a Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7107 Å). During the intensity data collection of each structure three

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TABLE 1. Crystal Data and Experimental and Refinement Parameters for the Structures

Crystal data			
Compound	I	II	III
Molecular formula	$C_{32}H_{28}N_6NiS_2Cl_8$	$C_{31}H_{29}N_6NiS_2I_3$	$C_{59}H_{59}N_{11}ONi_2S_4I_6$
M_r (g mol^{-1})	902.31	988.41	1944.06
Space group	$C2/c$	$Pbca$	$P2_1/c$
a (Å)	10.112(3)	15.969	15.825(2)
b (Å)	20.226(2)	25.417	24.702(9)
c (Å)	20.604(6)	19.074	19.041(6)
β (°)	98.25	90	96.58
V (Å^3)	4170.5	7741.8	7394.3
Z	4	8	4
Host: guest ratio	1:2	1:1	1:2
D_m (g cm^{-3})	1.37	1.78	1.84
D_c (g cm^{-3})	1.44	1.70	1.75
μ (Mo Kα) (cm^{-1})	7.91	28.37	29.70
F(000)	1832	4144	3744
Data collection			
Crystal dimensions (mm)	0.25 × 0.27 × 0.35	0.25 × 0.28 × 0.30	0.43 × 0.45 × 0.50
Scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Scan width, Δw (°)	(0.89 + 0.35 tan θ)	(1.0 + 0.35 tan θ)	(0.90 + 0.35 tan θ)
Aperture width (mm)	(1.16 + 1.05 tan θ)	(1.20 + 1.05 tan θ)	(1.20 + 1.05 tan θ)
Max. recording time (s)	40	40	40
Total no. unique reflections	2591	4192	4689
Total no. reflections with $I_{rel} > 2\sigma I_{rel}$	1470	1835	2426
Crystal stability (%)	48.1[a]	25.7[a, b]	6.8[b]
Min. correction factor		0.9362	0.7234
Max. correction factor		0.9995	1.0000
Average correction factor		0.9785	0.8719
2θ range (°)	2–50	2–50	2–40
Final refinement			
No. variables	150	204	436
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.101	0.068	0.084
$R_w = \Sigma w^{1/2}\|\|F_o\| - \|F_c\|\|\Sigma w^{1/2}\|F_o\|$	0.117	0.068	0.089
Weighting scheme, w	$(\sigma^2 F)^{-1}$	unity	$(\sigma^2 F)^{-1}$

[a]Decay correction applied. [b]Absorption correction applied.

reference reflections were periodically monitored to check crystal stability. Crystal data and experimental details of the data collections are listed in Table 1.

All data were corrected by a Lorentz polarisation factor and for **II**, **III** also for absorption [5]. The structures were solved by the heavy atom method and refined by full-matrix least-squares using the SHELX76 [6] program system.

In compound **I**, the Ni atom lies on the diad at Wyckoff position 'e', such that two of the 4-vinylpyridine moieties lie along this axis. This resulted in the vinyl group being disordered as shown in Fig. 1, which shows the host molecule with atomic nomenclature. The guest CCl_4 molecules were easily located and refined.

The final refinement was carried out with the Ni, S and Cl atoms treated anisotropically, and with the H atoms constrained at 1.00 Å from their parent C atoms and with a common temperature factor. Compounds **II** and **III** were refined in a similar manner. In both cases the guest CHI_3 molecules were well ordered, and the iodine atoms were refined anisotropically. In compound **III**, the tetrahydrofuran has displaced one 4-vinylpyridine base in every alternate host molecule. However this has not greatly changed the geometry of the host molecule, which retains the Ni ion at the centre of an irregular octahedron. The Ni–N bond length of the structures reported here, and those of five other clathrates with the same host, all fall within the range 2.00 to 2.22 Å and there appears to be no significant *trans* effect of the Ni–N bond opposite the thf ligand. Figure 2 shows the conformation of the ligands about the nickel with a coordinated tetrahydrofuran.

Final atomic coordinates and temperature factors for the three structures are given in Tables 2, 3 and 4. In all three structures the Ni atom is octahedrally coordinated with the thiocyanato groups in *trans* positions. The Ni–N bond lengths are within the

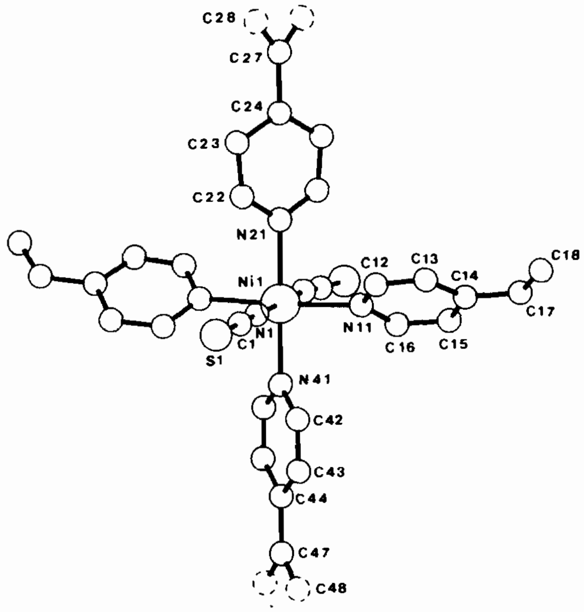


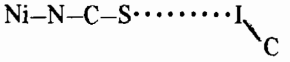
Fig. 1. Perspective view of the host molecule of structure I showing the disordered vinyl moiety.

limits found for these compounds, but bond lengths involving the vinyl carbon atoms are sometimes outside the usually quoted limits. The isotropic temperature factors of these vinyl carbons are consistently higher than those in the phenyl rings, indicating some possible disorder in these moieties. See also 'Supplementary Material'.

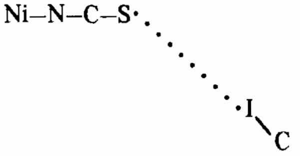
The packing of these structures is of interest. Structure **I** may be compared with its chloroform analogue, $[Ni(NCS)_2(4\text{-}ViPy)_4]\cdot 2CHCl_3$ which crystallises in $P2_1/n$ with cell dimensions a = 10.435(4), b = 19.787(6), c = 19.82(1) Å, β = 99.10(4)°, Z = 4 [2].

Figure 3 shows these two structures projected along [010]. The chloroform clathrate has symmetry $P2_1/n$ which is a subset of $C2/c$, and the host molecules are therefore not constrained to lie in special positions. Nevertheless the packings bear certain similarities, with the host and guest molecules lying in bands parallel to a. Structures **II** and **III** display even greater similarity in their packing. Structure **III** crystallises in $P2_1/c$ which is not a subset of $Pbca$. The two sets of cell dimensions are similar, however, with the angle β only 6.58° skewed from 90°, and the two structures retaining the inversion centres and the two-fold screw axes parallel to b in common. The positions of the host and guest molecules are essentially the same, showing that the substitution of a tetrahydrofuran for a 4-vinylpyridine ligand has little effect on the crystal packing, as shown in Fig. 4.

There are two ways in which secondary bonding can occur between the isothiocyanate sulphur and the iodines of the guest molecule.


$Ni{-}N{-}C{-}S\cdots\cdots I{\diagdown}C$

I donor


$Ni{-}N{-}C{-}S\cdots\cdots I{\diagdown}C$

S donor

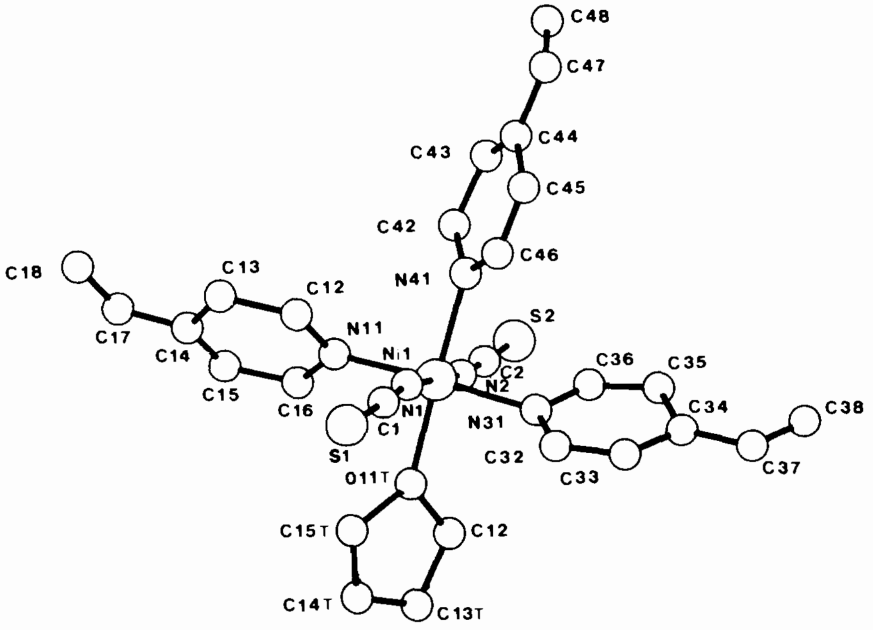


Fig. 2. Perspective view of a host molecule in structure III with a coordinated tetrahydrofuran.

TABLE 2. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (Å^2 × 10^3) for Structure I[a]

Atom	x/a	y/b	z/c	U_{iso}/U_{eq}[b]
Ni(1)	0(0)	3075(1)	2500(0)	66(1)*
N(21)	0(0)	4138(8)	2500(0)	78(5)
N(41)	0(0)	2037(8)	2500(0)	71(5)
N(11)	694(11)	3099(6)	1557(6)	73(3)
N(1)	1951(12)	3090(6)	2947(6)	77(3)
C(12)	1794(15)	3445(7)	1458(8)	79(4)
C(13)	2149(16)	3528(7)	871(8)	77(4)
C(14)	1449(15)	3247(7)	328(8)	80(4)
C(15)	315(17)	2864(8)	433(9)	91(5)
C(16)	23(15)	2795(7)	1056(8)	75(4)
C(17)	1786(22)	3324(11)	–342(11)	119(6)
C(18)	2732(25)	3678(12)	–509(13)	125(7)
C(22)	490(16)	4472(8)	3002(9)	89(5)
C(23)	507(16)	5161(8)	3062(9)	90(5)
C(24)	0(0)	5499(12)	2500(0)	91(7)
C(27)	0(0)	6281(18)	2500(0)	132(11)
C(28)	271(40)	6684(22)	2806(19)	104(12)
C(42)	1042(16)	1671(9)	2375(8)	89(5)
C(43)	1101(16)	1018(8)	2368(8)	89(5)
C(44)	0(0)	614(15)	2500(0)	110(8)
C(47)	0(0)	–108(18)	2500(0)	127(10)
C(48)	551(54)	–514(26)	2340(30)	106(19)
C(1)	2989(14)	3049(7)	3236(7)	75(4)
C(0)	2332(36)	800(17)	4600(18)	168(11)
Cl(1)	1063(11)	268(5)	4202(5)	211(6)*
Cl(2)	3693(12)	340(5)	4904(7)	218(6)*
Cl(3)	2782(12)	1400(5)	4096(5)	203(6)*
Cl(4)	1698(9)	1167(5)	5236(5)	189(5)*
S(1)	4473(5)	3018(4)	3649(3)	154(3)*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	45(1)	57(1)	90(2)	0(0)	–9(1)	0(0)
Cl(1)	214(10)	201(9)	193(10)	–45(7)	–59(8)	21(7)
Cl(2)	174(8)	186(9)	273(13)	34(8)	–36(8)	42(7)
Cl(3)	241(11)	176(9)	189(9)	36(7)	15(8)	24(8)
Cl(4)	158(7)	220(10)	185(9)	–32(7)	13(6)	10(7)
S(1)	73(3)	223(8)	149(5)	28(5)	–42(3)	11(4)

[a] e.s.d.s given in parentheses. [b] Anisotropic atoms (marked by asterisk) have thermal parameters (Å^2 × 10^3) of the form: $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^* + \ldots)\}$.

TABLE 3. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (Å^2 × 10^3) for Structure II[a]

Atom	x/a	y/b	z/c	U_{iso}/U_{eq}[b]
I(1)	1984(2)	572(1)	1937(2)	98(1)*
I(2)	4(2)	701(1)	1162(2)	113(1)*
I(3)	1746(2)	504(1)	70(2)	106(1)*
C(0)	1233(25)	849(15)	1008(22)	105(14)
Ni(1)	2302(3)	3392(2)	–6(3)	87(2)*
N(11)	3409(19)	3515(13)	564(16)	88(10)
N(21)	1733(23)	4043(15)	526(21)	117(12)
N(31)	1184(20)	3280(12)	–581(17)	90(10)
N(41)	2811(19)	2756(12)	–548(17)	96(11)
N(1)	2752(17)	3911(11)	–769(14)	74(9)
N(2)	1849(18)	2886(11)	774(15)	80(9)

(continued)

TABLE 3. *(continued)*

Atom	x/a	y/b	z/c	$U_{\text{iso}}/U_{\text{eq}}$[b]
S(1)	2917(7)	4816(4)	−1538(6)	98(5)*
S(2)	1320(9)	2185(5)	1721(7)	134(7)*
C(1)	2828(18)	4290(12)	−1117(17)	61(9)
C(2)	1649(19)	2584(13)	1184(18)	63(10)
C(12)	3806(27)	3134(18)	921(22)	106(15)
C(13)	4490(27)	3148(18)	1304(23)	112(15)
C(14)	4987(28)	3652(17)	1331(22)	103(13)
C(15)	4585(25)	4041(17)	976(21)	104(14)
C(16)	3680(26)	3995(17)	611(21)	103(14)
C(17)	5712(27)	3777(18)	1710(22)	108(15)
C(18)	6111(28)	3405(18)	2057(23)	118(16)
C(22)	1711(30)	4070(19)	1216(27)	138(18)
C(23)	1188(29)	4475(20)	1581(27)	133(18)
C(24)	921(28)	4847(19)	1250(26)	107(15)
C(25)	949(26)	4820(18)	591(25)	103(14)
C(26)	1279(27)	4439(19)	195(25)	123(16)
C(27)	289(35)	5240(21)	1698(31)	156(22)
C(28)	−362(49)	5498(30)	1680(40)	240(35)
C(32)	408(26)	3319(15)	−239(22)	99(14)
C(33)	−337(23)	3240(14)	−611(20)	81(12)
C(34)	−388(24)	3220(15)	−1319(21)	82(12)
C(35)	394(25)	3278(15)	−1662(21)	95(14)
C(36)	1136(25)	3286(14)	−1282(21)	92(13)
C(37)	−1205(29)	3238(16)	−1695(24)	111(15)
C(38)	−1296(32)	3251(20)	−2380(31)	149(19)
C(42)	2414(26)	2259(15)	−550(21)	95(13)
C(43)	2837(24)	1831(17)	−899(20)	103(14)
C(44)	3689(27)	1895(18)	−1226(23)	104(14)
C(45)	4039(24)	2368(16)	−1206(21)	93(13)
C(46)	3707(26)	2784(17)	−849(20)	103(14)
C(47)	3966(39)	1425(23)	−1624(30)	182(25)
C(48)	3465(36)	939(23)	−1663(30)	176(24)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	81(2)	104(2)	109(2)	0(2)	−12(2)	13(2)
I(2)	73(2)	150(3)	116(2)	−18(2)	−5(2)	25(2)
I(3)	107(2)	106(2)	104(2)	18(2)	23(2)	16(2)
Ni(1)	97(4)	72(3)	93(4)	15(3)	13(3)	−8(3)
S(1)	103(9)	101(8)	89(8)	28(7)	−16(7)	−40(7)
S(2)	146(12)	114(10)	143(13)	43(10)	51(10)	14(9)

[a] e.s.d.s given in parentheses. [b] Anisotropic atoms (marked by asterisk) have thermal parameters (Å² × 10³) of the form: $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^* + \ldots)\}$.

TABLE 4. Fractional Atomic Coordinates (×10⁴) and Thermal Parameters (Å² × 10³) for Structure III[a]

Atom	x/a	y/b	z/c	$U_{\text{iso}}/U_{\text{eq}}$[b]
C(0A)	3874(31)	9122(22)	8862(25)	91(17)
C(0B)	1167(39)	810(27)	3696(31)	131(24)
I(1B	1739(3)	485(2)	4697(2)	114(2)*
I(1A)	3396(3)	9341(1)	9852(2)	83(2)*
I(2A)	3207(2)	9434(1)	7971(2)	71(1)*
I(3A)	5223(2)	9293(2)	8923(2)	101(2)*
I(2B)	1689(3)	485(2)	2806(2)	102(2)*
1(3B)	−202(3)	597(2)	3623(2)	106(2)*
Ni(1A)	1873(4)	1421(2)	−279(3)	62(3)*

(continued)

TABLE 4. *(continued)*

Atom	*x/a*	*y/b*	*z/c*	$U_{\mathrm{iso}}/U_{\mathrm{eq}}$[b]
Ni(1B)	7252(4)	1678(2)	4884(3)	69(3)*
S(1A)	2681(12)	-8(6)	1351(8)	108(9)*
S(2A)	905(10)	2806(6)	-1923(9)	105(8)*
S(1B)	7717(11)	106(5)	3557(8)	102(8)*
S(2B)	6256(11)	2703(6)	6736(8)	98(8)*
N(1A)	2377(21)	898(14)	479(18)	55(11)
N(11A)	815(22)	1511(13)	268(19)	51(10)
N(2B)	6890(22)	2244(14)	5621(20)	66(11)
N(2A)	1324(24)	1934(15)	-1029(20)	71(12)
N(11B)	6066(24)	1747(15)	4320(20)	71(12)
N(21B)	6763(23)	1024(14)	5525(21)	62(11)
N(1B)	7551(26)	1086(18)	4134(22)	88(14)
N(31B)	7717(24)	2322(14)	4266(18)	58(11)
N(41A)	2567(27)	2056(16)	291(20)	80(13)
N(31A)	2877(23)	1309(15)	-869(19)	63(11)
N(41B)	8454(22)	1569(14)	5415(18)	59(11)
C(1A)	2525(23)	514(16)	838(20)	38(11)
C(2A)	1144(26)	2306(17)	-1422(22)	48(12)
C(1B)	7612(34)	687(23)	3902(27)	90(18)
C(32A)	3368(38)	886(24)	-859(29)	94(19)
C(33A)	4129(34)	871(22)	-1169(26)	84(17)
C(34A)	4479(31)	1261(19)	-1523(25)	70(15)
C(35A)	3889(34)	1763(21)	-1546(27)	87(17)
C(36A)	3181(36)	1702(23)	-1211(27)	90(18)
C(37A)	5265(31)	1182(20)	-1853(25)	68(15)
C(38A)	5652(41)	1519(28)	-2118(27)	116(23)
C(12A)	895(29)	1513(17)	963(25)	62(13)
C(13A)	148(31)	1544(18)	1407(26)	74(15)
C(14A)	-669(25)	1536(14)	1048(22)	38(12)
C(15A)	-719(30)	1523(17)	388(26)	66(14)
C(16A)	10(28)	1490(16)	-21(23)	54(12)
C(17A)	-1337(30)	1582(17)	1466(26)	71(15)
C(18A)	-1395(35)	1656(22)	2084(33)	103(19)
C(42A)	2167(31)	2578(19)	290(23)	66(14)
C(43A)	2721(35)	3024(21)	583(27)	86(18)
C(44A)	3442(29)	2978(17)	855(23)	53(13)
C(45A)	3808(34)	2427(21)	861(26)	87(17)
C(46A)	3319(29)	2009(17)	561(22)	61(13)
C(47A)	4063(50)	3366(29)	1239(37)	146(27)
C(48A)	3830(49)	3867(35)	1198(43)	174(33)
C(2B)	6643(27)	2432(17)	6118(24)	52(13)
C(32B)	8368(30)	2250(19)	3916(24)	65(14)
C(33B)	8643(38)	2657(24)	3590(29)	107(20)
C(34B)	8258(32)	3185(19)	3445(26)	67(15)
C(35B)	7656(31)	3181(19)	3837(25)	72(15)
C(36B)	7304(28)	2815(18)	4235(23)	60(14)
C(37B)	8480(37)	3722(24)	3007(29)	108(20)
C(38B)	9065(45)	3687(31)	2661(37)	180(34)
C(12B)	5298(39)	1774(21)	4591(31)	99(19)
C(13B)	4552(37)	1810(21)	4222(30)	101(19)
C(14B)	4424(28)	1806(17)	3491(24)	56(13)
C(15B)	5160(29)	1740(17)	3207(24)	61(14)
C(16B)	5943(28)	1768(16)	3603(23)	47(12)
C(17B)	3537(35)	1812(20)	3125(29)	89(18)
C(18B)	3286(48)	1776(32)	2441(46)	186(36)
C(22B)	6931(30)	1081(20)	6213(27)	74(16)
C(23B)	6627(39)	641(25)	6595(35)	127(21)
C(24B)	6133(37)	268(23)	6243(34)	95(19)

(continued)

TABLE 4. *(continued)*

C(25B)	6014(43)	294(28)	5574(39)	133(24)
C(26B)	6348(35)	643(24)	5156(31)	106(19)
C(27B)	5784(50)	−145(28)	6803(39)	153(28)
C(28B)	5166(63)	−343(29)	6767(44)	194(35)
C(42B)	8879(33)	1993(21)	5782(27)	87(17)
C(43B)	9742(36)	1959(22)	6105(28)	94(18)
C(44B)	10108(30)	1445(19)	6191(24)	68(14)
C(45B)	9644(32)	1025(19)	5835(25)	77(16)
C(46B)	8871(31)	1084(19)	5473(24)	74(15)
C(47B)	11027(41)	1349(25)	6565(31)	116(22)
C(48B)	11445(58)	1669(33)	6913(43)	179(34)
O(11T)	1256(20)	772(13)	−848(18)	84(10)
C(12T)	1185(43)	696(25)	−1587(33)	132(23)
C(13T)	679(49)	202(32)	−1840(40)	176(31)
C(14T)	471(36)	−34(23)	−1212(30)	104(19)
C(15T)	870(43)	222(27)	−581(34)	149(26)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1B)	136(4)	79(3)	119(4)	−12(2)	−19(3)	12(3)
I(1A)	116(3)	58(2)	75(3)	12(2)	17(2)	1(2)
I(2A)	81(3)	63(2)	69(3)	−1(2)	7(2)	−2(2)
I(3A)	77(3)	98(3)	125(4)	−5(3)	6(3)	24(2)
I(2B)	112(3)	85(3)	111(3)	11(2)	22(3)	12(3)
I(3B)	101(3)	105(3)	111(3)	−5(3)	7(3)	17(3)
Ni(1A)	75(5)	38(4)	73(5)	8(3)	5(4)	7(3)
Ni(1B)	85(5)	51(4)	74(5)	−11(3)	26(4)	−3(4)
S(1A)	165(17)	68(11)	95(13)	32(9)	37(12)	30(10)
S(2A)	99(13)	73(11)	139(15)	34(10)	−2(11)	13(9)
S(1B)	159(16)	28(8)	111(13)	−10(7)	−13(12)	10(9)
S(2B)	127(14)	69(10)	109(13)	−17(9)	53(11)	8(9)

[a] e.s.d.s given in parentheses. [b] Anisotropic atoms (marked by asterisk) have thermal parameters (Å^2 × 10^3) of the form: $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^* + \ldots)\}$.

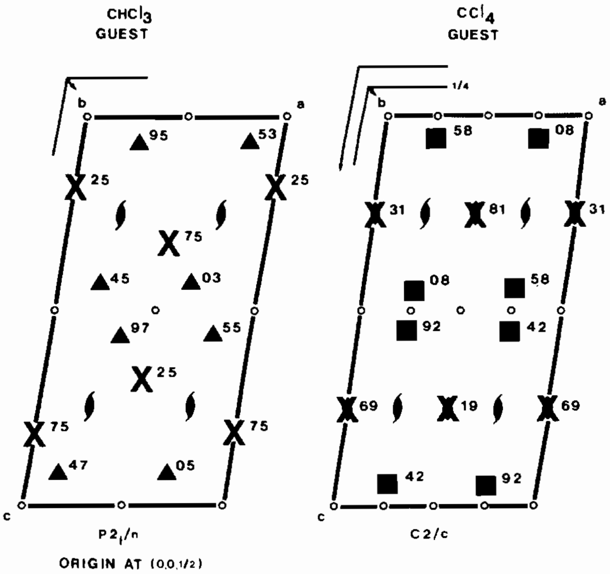


Fig. 3. Structures containing $CHCl_3$ and CCl_4 guests viewed along [010].

As illustrated the secondary bond is represented by a broken line. With iodine as donor we expect the (NiNC)–S...I angle to be in the vicinity of 180° while with sulphur as donor we expect linearity in the S...I–CHI_2 bond. We consider a secondary bond to occur when the S...I distances are less than the sum of their van der Waals radii. These are taken to be $r_w(\mathrm{I})$ = 1.98 Å and $r_w(\mathrm{S})$ = 1.80 Å [7]. In all these structures S acts as the donor atom. In structure **II** we have three S...I interactions with interatomic distances <3.78 Å occurring with only one of the S atoms of the host molecules. This pattern is repeated in structure **III** where we again find the two different molecules of the host each involving one NCS moiety in secondary bonding.

The details of these secondary bonds are listed in Table 5 which also gives the values for these interactions in the related compound $[Co(NCS)_2(py)_4]\cdot 2CHI_3$ [8].

The geometry of the S atom in structure **II** is shown in Fig. 5. The sulphur atom is surrounded

TABLE 5. Details of Secondary Bonds

	d (S...I)	Δ(*d* − 3.78) (Å)	S...I–C angle	I moved through symmetry element
Structure II				
S1...I1	3.36	−0.42	172.83	(i) $x, y + \frac{1}{2}, z - \frac{1}{2}$
S1...I2	3.63	−0.15	170.44	(ii) $x + \frac{1}{2}, y + \frac{1}{2}, -z$
S1...I3	3.42	−0.36	168.04	(iii) $x + \frac{1}{2}, y + \frac{1}{2}, z$
Structure III				
S1A...I1A	3.57	−0.21	168.19	(i) $x, y - 1, z - 1$
S1A...I3A	3.84	0.06	160.74	(ii) $x + 1, y + 1, z + 1$
S1A...I2B	3.55	−0.23	170.04	(iii) x, y, z
S1B...I1B	3.64	−0.14	168.64	(iv) $x + 1, y, z + 1$
S1B ...I3B	3.50	−0.23	173.82	(v) $x + 1, y, z$
$Co(NCS)_2(Py)_4 \cdot 2CHI_3$				
S...I1	3.36	−0.12	173.4	(i) $x, y + \frac{1}{2}, z + \frac{1}{2}$
S...I2	3.51	−0.27	176.5	(ii) $x, y + \frac{1}{2}, z + \frac{1}{2}$
S...I3	3.46	−0.32	170.3	(iii) x, y, z

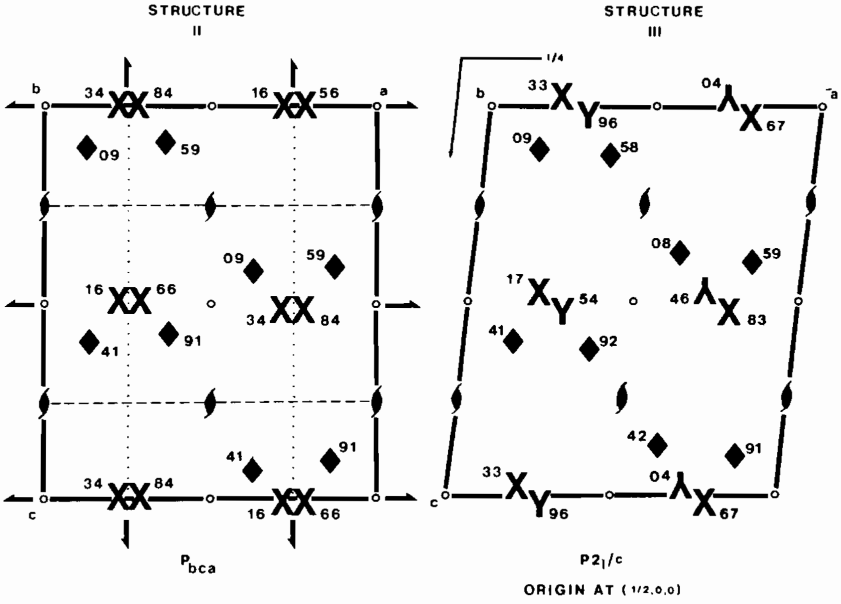


Fig. 4. Structures II and III viewed along [010].

by the three symmetry-related iodines and is almost coplanar with them. It lies 0.03 Å from the plane defined by the iodines. Similar geometries are exhibited by the S atoms which are involved in secondary interaction in structure **III**. Structure **I** does not display significant secondary bonding in that all S...Cl distances are on the limit or greater than the sum of the van der Waals radii.

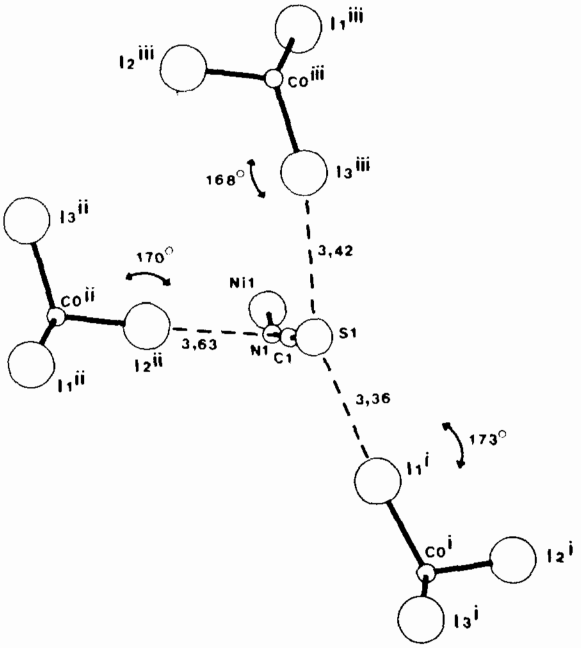


Fig. 5. Perspective view of the secondary interaction about the S in structure II.

Supplementary Material

A full list of bond lengths and angles of the three structures is available from the authors on request.

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References

1 M. H. Moore, L. R. Nassimbeni, M. L. Niven and M. W. Taylor, *Inorg. Chim. Acta, 115* (1986) 211.
2 M. H. Moore, L. R. Nassimbeni and M. L. Niven, *Inorg. Chim. Acta, 131* (1986) 45.
3 M. H. Moore, L. R. Nassimbeni and M. L. Niven, *J. Chem. Soc., Dalton Trans.*, (1987) 2125.
4 N. W. Alcock, *Adv. Inorg. Radiochem., 15* (1972) 2.
5 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.
6 G. M. Sheldrick, in H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld and G. C. Bassi (eds.), *Computing in Crystallography*, Delft University Press, Delft, The Netherlands, 1978, p. 34.
7 A. Bondi, *J. Phys. Chem., 68* (1964) 441.
8 Van Hans Hartl and S. Steidel, *Acta. Crystallogr., Sect. B, 36* (1980) 65.