1988), proves that one can construct charge-transfer salts of BEDT-TTF with quite different donor packing motifs in the presence of water, especially if the anion is small and alone cannot stabilize salts of BEDT-TTF.

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Studies in Werner Clathrates. 12.[*] Structures of Four Novel but Non-Clathrating Complexes

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Abstract

Compound (I), tetrakis(4-benzylpyridine)bis(isothiocyanato)nickel(II), $C_{50}H_{44}N_6NiS_2$, $[Ni(NCS)_2(C_{12}H_{11}N)_4]$, $M_r = 851{\cdot}8$, monoclinic, Cc, $a = 9{\cdot}686\,(6)$, $b = 25{\cdot}015\,(10)$, $c = 17{\cdot}728\,(9)$ Å, $\beta = 90{\cdot}29\,(8)^\circ$, $V = 4295{\cdot}2$ Å^3, $Z = 4$, $D_m = 1{\cdot}298$, $D_x = 1{\cdot}32$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 5{\cdot}47$ cm^{-1}, $F(000) = 2016$, $R = 0{\cdot}056$ for 2819 observed reflections. Compound (II), tetrakis(4-*tert*-butylpyridine)-

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[*] Part 11: Lavelle, Nassimbeni, Niven & Taylor (1989).

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bis(isothiocyanato)nickel(II), $C_{38}H_{52}N_6NiS_2$, $[Ni(NCS)_2(C_9H_{13}N)_4]$, $M_r = 715{\cdot}8$, tetragonal, $I4_1/a$, $a = 21{\cdot}501\,(6)$, $c = 18{\cdot}003\,(8)$ Å, $V = 8322{\cdot}7$ Å^3, $Z = 8$, $D_m = 1{\cdot}132$, $D_x = 1{\cdot}14$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 5{\cdot}53$ cm^{-1}, $F(000) = 3056$, $R = 0{\cdot}071$ for 1599 observed reflections. Compound (III), bis(dimethyl sulfoxide)bis(isothiocyanato)bis(4-phenylpyridine)nickel(II), $C_{28}H_{30}N_4NiO_2S_4$, $[Ni(NCS)_2(C_{11}H_9N)_2(C_2H_6OS)_2]$, $M_r = 640{\cdot}7$, monoclinic, $C2/c$, $a = 10{\cdot}016\,(1)$, $b = 23{\cdot}430\,(4)$, $c = 13{\cdot}290\,(9)$ Å, $\beta = 96{\cdot}94\,(4)°$, $V = 3096{\cdot}0$ Å^3, $Z = 4$, $D_m = 1{\cdot}364$, $D_x = 1{\cdot}37$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 8{\cdot}62$ cm^{-1}, $F(000) = 1256$, $R = 0{\cdot}035$ for 2034 observed reflections. Compound (IV), dichlorobis(dimethyl sulfoxide)bis(4-phenylpyridine)nickel(II), $C_{26}H_{30}Cl_2N_2NiO_2S_2$, $[NiCl_2(C_{11}H_9N)_2(C_2H_6OS)_2]$, $M_r = 595{\cdot}7$, monoclinic, $P2_1/c$, $a = 7{\cdot}800\,(1)$, $b = 8{\cdot}250\,(1)$, $c = 22{\cdot}138\,(2)$ Å, $\beta = 95{\cdot}15\,(1)°$, $V = 1418{\cdot}8$ Å^3, $Z = 2$, $D_m = 1{\cdot}394$, $D_x = 1{\cdot}39$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 9{\cdot}78$ cm^{-1}, $F(000) = 596$, $R = 0{\cdot}030$ for 1883 observed reflections. The four structures were investigated at 294 K as potential hosts in clathrate formation. They all consist of irregular octahedral nickel complexes with NiN_6 [(I) and (II)] or NiN_4O_2 [(III) and (IV)] coordination spheres. The NCS^- groups are in *trans* positions in structures (I)–(III) as are the dimethyl sulfoxide groups in compounds (III) and (IV). Possible reasons for the formation of non-clathrating complexes are discussed.

Introduction

Interest in the field of Werner clathrates was initiated in the late 1950's by Schaeffer, Dorsey, Skinner & Christian (1957) who showed that these compounds could be used to separate various aromatic hydrocarbons from petroleum fractions. Fine separation of mixtures of organic isomers was achieved by de Radzitzky & Hanotier (1962) using these host lattices. The host molecules have the general formula MX_2L_4 where M is a bivalent transition-metal cation *e.g.* Mn^{2+}–Cu^{2+}, X is an anion, *e.g.* NCS^-, NCO^-, NO_2^-, halide, and L is a substituted pyridine or α-alkylarylamine.

The most thoroughly studied compound thus far is $[Ni(NCS)_2(4\text{-Mepy})_4]$ (4-Mepy = 4-methylpyridine) which has the ability to include a wide variety of guest molecules in cavities of the channel, layer or cage types (Lipkowski, 1984). We have investigated the structural and stability changes occurring on variation of the pyridine ligand. An extremely versatile host complex is the 4-ethylpyridine (4-Etpy) derivative which forms inclusion compounds of varying stoichiometry with isomers of xylene, CCl_4 and CS_2 (Moore, Nassimbeni & Niven, 1987*a*).

The $[Ni(NCS)_2(4\text{-Vipy})_4]$ (4-Vipy = 4-vinylpyridine) complex has recently received much attention (Moore, Nassimbeni, Niven & Taylor, 1986; Nassimbeni, Niven & Suckling, 1989) and this complex can entrap a wide variety of guest molecules in cavities of the channel type. The mixed-base complex $[Ni(NCS)_2(4\text{-Mepy})_2(4\text{-Phpy})_2]$ (4-Phpy = 4-phenylpyridine) is suitable for enclathrating aliphatic compounds with a five-atom skeleton in channels which undulate through the lattice (Nassimbeni, Niven & Taylor, 1989*b*; Bond, Jackson & Nassimbeni, 1983). These channels are of the 'hour-glass' shape whilst the cavities for the derivative containing four 4-Phpy ligands form large holes which are interconnected *via* narrow channels (Nassimbeni, Niven & Taylor, 1987, 1989*a*).

The 4-Mepy complex is readily soluble in, and forms very stable compounds with, a wide variety of organic solvents. Both the solubility and stability decrease with variation from 4-Mepy to 4-Vipy to 4-Etpy and to the 4-Phpy derivative. For the 4-Phpy complex, solubility of the host powder is so low in a wide variety of solvents that use of a co-solvent has to be made in order to form crystals. The solvent in which the host powder is most soluble ($\sim 0{\cdot}15$ g ml^{-1}) is dimethyl sulfoxide (dmso) which as a co-solvent has the double disadvantage that it can firstly be included as a guest molecule, either exclusively or in addition to the intended guest, and secondly, with time, it can substitute the pyridine ligands.

In our search for host compounds which can include guest molecules with a high guest:host ratio, we have varied the substituent on the base to increase the bulkiness. The hope was that an increase in size of the ligand would cause the host to pack less efficiently and therefore leave large cavities in which the guest molecules could be accommodated.

We now report the structures of two compounds of the type $[Ni(NCS)_2L_4]$, where L = 4-benzylpyridine (4-Bzpy) (I) and 4-*tert*-butylpyridine (4-*t*-Bupy) (II), and two compounds of the type $[NiX_2(\text{dmso})_2(4\text{-Phpy})_2]$ where $X = NCS^-$ (III) and Cl^- (IV).

Experimental

The host powder complex [4-Bzpy (I), 4-*t*-Bupy (II) and 4-Phpy (III) and (IV) derivatives] was prepared by treating an aqueous solution of nickel(II) isothiocyanate [(I), (II) and (III)] or nickel(II) chloride [(IV)] with a stoichiometric quantity of the substituted pyridine. The dried precipitate was then dissolved in the prospective guest solvent [$CHCl_3$ for (I) and (II), and dmso for (III) and (IV)]. Blue needle-shaped crystals grew within 72 h for (I) and (II) but only after 3 months for (III) and (IV) on slow

Table 1. *Experimental data and structure refinement parameters*

	(I)	(II)	(III)	(IV)
Crystal dimensions (mm)	0·19 × 0·31 × 0·31	0·25 × 0·25 × 0·31	0·15 × 0·16 × 0·24	0·25 × 0·25 × 0·28
θ range scanned (°)	1–25	1–20	1–20	1–25
Range of indices *h*	−11→11	−16→16	−11→11	−9→9
k	0→29	−17→17	0→27	0→9
l	0→21	0→17	0→15	0→26
Transmission factors, min., max. (%)	98·6→99·9	97·6→99·9	96·9→99·9	95·4→99·9
Standard reflections (*hkl*)	$\bar{5}$,13,1 $\bar{7}$91 6,12,2	8$\bar{1}\bar{2}$ 83$\bar{2}$ 7$\bar{5}\bar{4}$	$\bar{4}$,10,8 771 $\bar{1}$,17,5	535 $\bar{1}$,5,12 1,1,17
Stability (%)	0·5	1·1	0·5	2·3
Scan width*	0·64	0·44	0·80	0·84
Aperture width†	1·13	1·12	1·20	1·11
Total No. of reflections	4003	8072	2917	2762
Total No. observed‡	2819	1599	2034	1883
No. of variables	252	159	191	168
R_{int}	0·001	0·024	0·013	0·016
$\Delta\rho$(min., max.) (e Å^{-3})	−0·34, 0·45	−0·34, 0·42	−0·38, 0·40	−0·45, 0·68
Δ/σ(final)	< 0·02	< 0·05	< 0·009	< 0·02
R	0·056	0·071	0·035	0·032
wR	0·057	0·101	0·037	0·030
Weighting scheme, *w*	$(\sigma^2F)^{-1}$	$(\sigma^2F+0·01)^{-1}$	$(\sigma^2F)^{-1}$	$(\sigma^2F)^{-1}$
S	3·0	3·6	2·7	1·0

* Scan width, $\Delta\omega = (y + 0·35\tan\theta)°$.
† Aperture width $= (x + 1·05\tan\theta)$ mm.
‡ $I_{\text{rel}} > 2\sigma I_{\text{rel}}$.

evaporation of the resulting solution at room temperature. Crystals of the clathrate [Ni(NCS)$_2$(4-Phpy)$_4$].4dmso formed in the solution of (III) after 1 week (Nassimbeni, Papanicolaou & Moore, 1986), but on further standing the distinctly different crystals of (III) formed. Suitable single crystals were selected for the structural determinations and were mounted in Lindemann capillaries with mother liquor to prevent deterioration in the atmosphere. Density measurements of crystals were obtained by flotation in a water/saturated KI solution and measuring the density of the resulting solution by means of a PAAR DMA 35 density meter.

All intensity data were collected at 294 K on a Nonius CAD-4 diffractometer with graphite-monochromated Mo *Kα* radiation ($\lambda = 0·7107$ Å). Preliminary cell parameters and space-group symmetry were obtained photographically whilst accurate cell parameters were obtained by least-squares analysis of 25 reflections in the range $16 < \theta < 17°$. In all cases, scans were in the ω–2θ mode with a final acceptance limit of 20σ at 20° min^{-1} in ω and a maximum recording time of 40 s. During the intensity data collection of each structure three reference reflections were periodically monitored to check crystal stability and centring. All intensities were corrected for Lorentz and polarization factors and an empirical absorption correction (North, Phillips & Mathews, 1968) applied to all compounds. Table 1 lists the experimental and refinement parameters for the compounds.

The structures were all solved by the heavy-atom method and refined by full-matrix least squares using the *SHELX76* program system (Sheldrick, 1978). Complex neutral-atom scattering factors for H were taken from Stewart, Davidson & Simpson (1965) and for all other atoms from Cromer & Mann (1968). Molecular parameters were obtained from *PARST* (Nardelli, 1983) and drawings from *PLUTO* (Motherwell, 1974).

For compound (I), the systematic absences indicated the space group *C*2/*c* or *Cc*, and the density measurements were indicative of a non-clathrating (α-phase) complex with $Z = 4$. Thus, the host molecule could either lie on a special position in the centrosymmetric space group, or on a general position for the noncentrosymmetric space group. Refinement of the structure in *C*2/*c*, with the Ni on the diad at Wyckoff position *c*, was however unsuccessful with the conventional *R* failing to converge to beneath a value of 0·20. For the noncentrosymmetric space group, with the Ni at 0,*y*,0, the refinement converged satisfactorily to an *R* of 0·056 and thus the latter space group was confirmed.

For compound (II), data were collected for a triclinic cell and transformed *via* 1$\bar{1}$0, 11$\bar{1}$, 001 to the tetragonal cell. Comparison of the equivalences *hkl*, $\bar{h}\bar{k}l$, *khl* and $k\bar{h}l$ confirmed the validity of the tetragonal cell.

For compound (III), the density measurement was incompatible with a host [Ni(NCS)$_2$(4-Phpy)$_4$] and guest dmso. The Patterson vector map indicated clearly that the Ni was located on the diad at Wyckoff position *e*. Further refinement yielded two 4-Phpy ligands lying on this diad with the two remaining pyridines being replaced by dmso molecules which were coordinated to the Ni *via* the O atom.

Compound (IV) was easily solved once it was recognized that substitution had also occurred. Den-

Table 2. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (Å^2 × 10^3) *with e.s.d.'s in parentheses for compound* (I)

	x	*y*	*z*	U_{iso}/U_{eq}
Ni(1)	0	3737 (0)	0	36 (0)*
N(1)	1831 (9)	3799 (3)	608 (5)	44 (2)
C(1)	2908 (10)	3779 (3)	871 (6)	37 (3)
S(1)	4448 (4)	3760 (1)	1232 (2)	70 (1)*
N(2)	-1844 (9)	3676 (3)	-570 (5)	42 (2)
C(2)	-2908 (10)	3687 (3)	-861 (6)	37 (3)
S(2)	-4384 (4)	3706 (1)	-1298 (2)	62 (1)*
N(11)	-822 (8)	4395 (3)	646 (4)	41 (2)
C(12)	-2139 (10)	4417 (4)	833 (5)	40 (2)
C(13)	-2690 (10)	4824 (4)	1271 (5)	42 (2)
C(14)	-1879 (11)	5231 (4)	1481 (6)	46 (3)
C(15)	-468 (11)	5219 (4)	1313 (6)	54 (3)
C(16)	-6 (10)	4794 (3)	880 (5)	44 (2)
C(17)	-2404 (11)	5692 (4)	1982 (6)	50 (3)
C(111)	-2013 (11)	6242 (4)	1741 (6)	50 (3)
C(112)	-2459 (11)	6424 (4)	1042 (6)	63 (3)
C(113)	-2102 (13)	6952 (5)	823 (7)	77 (4)
C(114)	-1347 (12)	7267 (4)	1290 (6)	62 (3)
C(115)	-943 (13)	7084 (5)	1976 (7)	76 (3)
C(116)	-1270 (12)	6569 (4)	2215 (7)	66 (3)
N(21)	745 (8)	4325 (3)	-790 (4)	38 (2)
C(22)	-171 (10)	4613 (3)	-1193 (5)	45 (2)
C(23)	186 (10)	5056 (4)	-1612 (6)	52 (3)
C(24)	1509 (10)	5232 (4)	-1651 (6)	42 (2)
C(25)	2478 (12)	4935 (4)	-1251 (6)	57 (3)
C(26)	2081 (11)	4490 (4)	-839 (6)	51 (3)
C(27)	1876 (13)	5728 (4)	-2071 (7)	61 (3)
C(211)	1702 (11)	6239 (4)	-1610 (6)	49 (3)
C(212)	1292 (10)	6239 (5)	-838 (6)	62 (3)
C(213)	1072 (13)	6721 (5)	-451 (8)	76 (4)
C(214)	1284 (12)	7195 (5)	-843 (7)	68 (3)
C(215)	1701 (12)	7202 (4)	-1596 (7)	61 (3)
C(216)	1909 (12)	6726 (4)	-1961 (7)	65 (3)
N(31)	816 (8)	3075 (3)	-619 (4)	36 (2)
C(32)	2157 (10)	3051 (4)	-823 (5)	47 (3)
C(33)	2714 (11)	2635 (4)	-1224 (5)	52 (3)
C(34)	1887 (11)	2207 (4)	-1471 (6)	44 (3)
C(35)	543 (11)	2227 (4)	-1215 (6	55 (3)
C(36)	10 (11)	2659 (4)	-818 (6)	51 (3)
C(37)	2509 (13)	1749 (4)	-1907 (7)	65 (3)
C(311)	2126 (9)	1202 (4)	-1600 (5)	43 (2)
C(312)	2600 (11)	1043 (4)	-899 (6)	59 (3)
C(313)	2314 (11)	551 (4)	-617 (7)	67 (3)
C(314)	1557 (11)	190 (4)	-1036 (6)	55 (3)
C(315)	1092 (11)	328 (4)	-1725 (6)	56 (3)
C(316)	1348 (12)	839 (4)	-2010 (7)	64 (3)
N(41)	-773 (8)	3150 (3)	815 (5)	43 (2)
C(42)	157 (11)	2862 (4)	1216 (6)	54 (3)
C(43)	-194 (11)	2402 (4)	1623 (6)	57 (3)
C(44)	-1523 (12)	2237 (4)	1611 (6)	52 (3)
C(45)	-2496 (11)	2531 (4)	1227 (5)	47 (3)
C(46)	-2063 (10)	2987 (4)	827 (5)	44 (3)
C(47)	-1959 (11)	1710 (4)	2003 (6)	53 (3)
C(411)	-1638 (10)	1213 (4)	1542 (5)	47 (3)
C(412)	-1269 (10)	1235 (5)	800 (6)	57 (2)
C(413)	-1008 (13)	772 (4)	394 (7)	71 (3)
C(414)	-1131 (12)	285 (4)	744 (7)	68 (3)
C(415)	-1445 (13)	259 (5)	1436 (7)	70 (4)
C(416)	-1747 (12)	722 (4)	1883 (7)	62 (3)

* $U_{eq} = \frac{1}{3}$(trace of orthogonalized U_{ij} matrix).

Table 3. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (Å^2 × 10^3) *with e.s.d.'s in parentheses for compound* (II)

	x	*y*	*z*	U_{iso}/U_{eq}
Ni(1)	0	2500	3533 (1)	66 (1)*
N(1)	849 (3)	2947 (3)	3570 (3)	76 (2)
C(1)	1328 (4)	3104 (3)	3718 (3)	66 (2)
S(1)	2000 (1)	3361 (2)	3962 (2)	128 (1)*
N(11)	326 (2)	1882 (2)	2692 (3)	67 (2)
C(12)	767 (4)	2065 (4)	2201 (4)	84 (2)
C(13)	1039 (4)	1673 (4)	1708 (5)	84 (2)
C(14)	884 (3)	1052 (3)	1674 (3)	60 (2)
C(15)	417 (3)	881 (3)	2152 (4)	70 (2)
C(16)	168 (3)	1285 (3)	2644 (4)	70 (2)
C(17)	1211 (4)	589 (4)	1161 (4)	85 (2)
C(171)	1512 (4)	926 (5)	495 (5)	103 (4)*
C(172)	778 (7)	126 (6)	860 (9)	149 (6)*
C(173)	1743 (5)	305 (6)	1630 (7)	142 (6)*
N(21)	309 (3)	1866 (3)	4371 (3)	71 (2)
C(22)	870 (4)	1603 (4)	4334 (5)	86 (2)
C(23)	1064 (4)	1155 (4)	4844 (5)	96 (3)
C(24)	703 (4)	965 (3)	5405 (4)	79 (2)
C(25)	126 (4)	1245 (4)	5452 (5)	93 (2)
C(26)	-59 (4)	1690 (4)	4934 (4)	82 (2)
C(27)	921 (4)	463 (5)	5945 (6)	100 (3)
C(271)	1465 (8)	707 (8)	6398 (8)	162 (7)*
C(272)	425 (9)	304 (9)	6480 (10)	226 (11)*
C(273)	1124 (16)	-67 (6)	5491 (10)	287 (16)*

$U_{eq} = \frac{1}{3}$(trace of orthogonalized U_{ij} matrix).

Table 4. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (Å^2 × 10^3) *with e.s.d.'s in parentheses for compound* (III)

	x	*y*	*x*	U_{eq}*
Ni(1)	0	1035 (0)	2500	39 (0)
N(1)	-1651 (2)	1021 (1)	3258 (2)	50 (1)
C(1)	-2331 (3)	1028 (1)	3889 (2)	42 (1)
S(1)	-3282 (1)	1043 (0)	4796 (1)	75 (0)
O(2)	1134 (2)	1034 (1)	3933 (2)	54 (1)
S(2)	2659 (1)	1069 (0)	4074 (1)	57 (0)
C(2)	3176 (4)	581 (2)	5050 (3)	82 (2)
C(3)	3007 (5)	1707 (2)	4759 (5)	131 (3)
N(21)	0	1948 (1)	2500	46 (1)
C(22)	-614 (3)	2248 (1)	3163 (2)	57 (1)
C(23)	-641 (3)	2833 (1)	3178 (3)	55 (1)
C(24)	0	3152 (2)	2500	42 (1)
C(211)	0	3779 (2)	2500	42 (1)
C(212)	-1130 (3)	4085 (1)	2710 (2)	49 (1)
C(213)	-1130 (4)	4677 (1)	2699 (2)	59 (1)
C(214)	0	4972 (2)	2500	62 (2)
N(41)	0	135 (1)	2500	46 (1)
C(42)	22 (3)	-160 (1)	1644 (2)	51 (1)
C(43)	13 (3)	-746 (1)	1609 (3)	56 (1)
C(44)	0	-1056 (2)	2500	58 (2)
C(411)	0	-1690 (2)	2500	73 (2)
C(412)	-611 (4)	-1993 (2)	1666 (4)	90 (2)
C(413)	-608 (5)	-2582 (2)	1681 (5)	123 (3)
C(414)	0	-2870 (3)	2500	141 (6)

* $U_{eq} = \frac{1}{3}$(trace of orthogonalized U_{ij} matrix).

sity measurements had indicated that $Z = 2$ and the Ni was located on the centre of inversion at Wyckoff position *a*.

For compounds (I) and (II), a paucity of data enabled only the Ni and S atoms, and the methyl C atoms of compound (II), to be refined with anisotropic thermal parameters with all other atoms treated isotropically. For compounds (III) and (IV), there were sufficient data to allow anisotropic thermal parameters for all non-H atoms. In all compounds, the H atoms were geometrically positioned and linked in groups with common temperature factors.

Final atomic coordinates are listed in Tables 2–5 for compounds (I)–(IV) respectively.*

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* Lists of structure factors, anisotropic thermal parameters bond lengths and angles, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52523 (65 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (Å^2 × 10^3) *with e.s.d.'s in parentheses for compound* (IV)

	x	y	z	U_{eq}*
Ni(1)	0 (0)	0 (0)	0 (0)	33 (0)
Cl(1)	1199 (1)	−2131 (1)	−581 (0)	45 (0)
S(1)	−1413 (1)	−3460 (1)	447 (0)	39 (0)
O(1)	1603 (2)	1623 (2)	−424 (1)	40 (1)
C(1)	2813 (5)	4028 (4)	−1009 (2)	56 (1)
C(2)	2661 (5)	4217 (4)	200 (2)	56 (1)
N(11)	−1942 (3)	350 (3)	−705 (1)	38 (1)
C(12)	−1655 (4)	740 (4)	−1275 (1)	48 (1)
C(13)	−2936 (4)	873 (4)	−1736 (2)	51 (1)
C(14)	−4649 (4)	572 (4)	−1634 (1)	38 (1)
C(15)	−4941 (4)	168 (4)	−1041 (1)	45 (1)
C(16)	−3585 (4)	80 (4)	−602 (1)	44 (1)
C(111)	−6071 (4)	630 (4)	−2126 (1)	42 (1)
C(112)	−5957 (5)	1568 (5)	−2635 (2)	65 (2)
C(113)	−7302 (6)	1619 (5)	−3092 (2)	76 (2)
C(114)	−8753 (5)	734 (5)	−3046 (2)	69 (2)
C(115)	−8893 (5)	−213 (5)	−2540 (2)	63 (2)
C(116)	−7572 (4)	−263 (4)	−2079 (2)	51 (1)

* $U_{eq} = \frac{1}{3}$(trace of orthogonalized U_{ij} matrix).

Discussion

The structure of the complexes in all four compounds has the central Ni atom in an octahedral configuration with the anion moieties, and the dmso ligands for compounds (III) and (IV), in *trans* positions.

Compound (I) packs in 'ribbons' running parallel to b with the Ni atom alternating between $x = 0$ and $x = \frac{1}{2}$. The pyridine groups are all nearly perpendicular to the yz plane whilst the phenyl moieties are parallel to the same plane. Fig. 1 shows a perspective view of the molecule of compound (I) with atomic nomenclature, whilst Fig. 2 illustrates the packing as viewed along [100]. Attempts to grow crystals of a β-phase complex (*i.e.* one containing guest molecules) failed even after extensive variations to the crystallizing procedure. The following solvents were used as possible guest compounds: dmso, CCl_4, thf, 2-methoxyethanol and ethanol whilst layering with the xylenes, CS_2, benzene, 4-Phpy dissolved in methanol, and phenylacetylene also failed to produce crystals of a β-phase clathrate.

The packing of compound (II), viewed along [001] is shown in Fig. 3 and is similar to that of the typical β phase of the [$Ni(NCS)_2(4\text{-}Etpy)_4$] complex (Moore, Nassimbeni & Niven, 1987*a*). A perspective view of the complex, with atomic nomenclature, is illustrated in Fig. 4. Like compound (I), attempts to grow suitable β-phase crystals using the same solvents as potential guest molecules also failed.

Compound (III) packs such that the Ni atom, the NCS^- moieties and the S and O atoms of the dmso ligands are all in a plane parallel to the xz plane. The two 4-Phpy ligands are thus perpendicular to this plane. The packing is similar to that of the mixed pyridine Werner clathrate [$Ni(NCS)_2(4\text{-}Mepy)_2$-$(4\text{-}Phpy)_2$] (Bond, Jackson & Nassimbeni, 1983). The reduced length of the dmso ligand compared with that of the 4-Mepy ligand, allows the Ni atoms to pack closer together and thus effectively close the channel present in the latter structure. A perspective diagram of the compound is shown in Fig. 5 with a packing diagram, viewed along [010], illustrated in

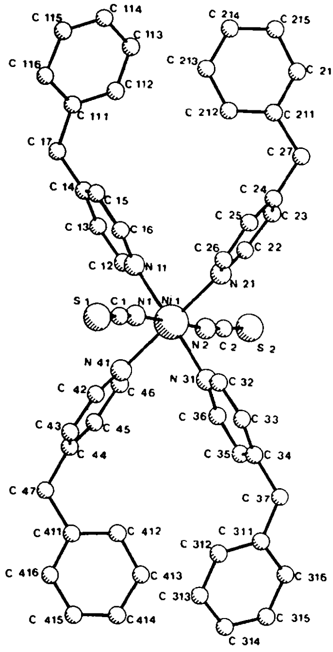

Fig. 1. Perspective view of compound (I) with atomic nomenclature.

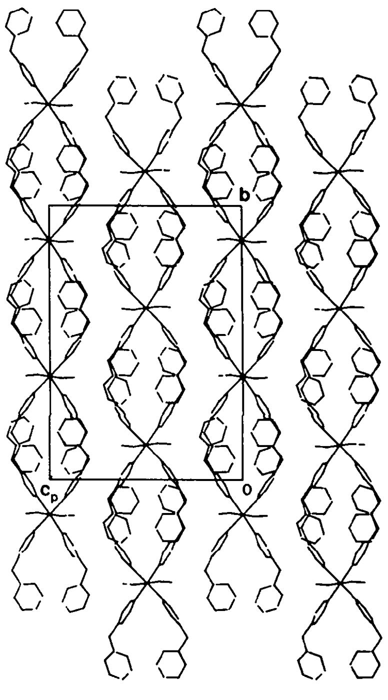

Fig. 2. Packing diagram of compound (I) viewed along [100].

Fig. 6. Fig. 7 illustrates the packing of compound (IV) viewed along [100] whilst Fig. 8 shows a perspective view of the molecule.

One of the possible reasons (Lipkowski, 1980) to explain the formation of clathrates by these kinds 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. It is interesting to compare the torsion angles of compounds (I) and (II) with those of the various *α* phases for the unsubstituted pyridine complex (Valach, Sivy & Koren, 1984) [py], the 4-Mepy derivative (Kerr & Williams, 1977) [Me], the two 4-Etpy derivatives (Moore, Nassimbeni & Niven, 1987*a*) [Et1, Et2] (each with two independent molecules per asymmetric unit), the 4-Vipy derivative

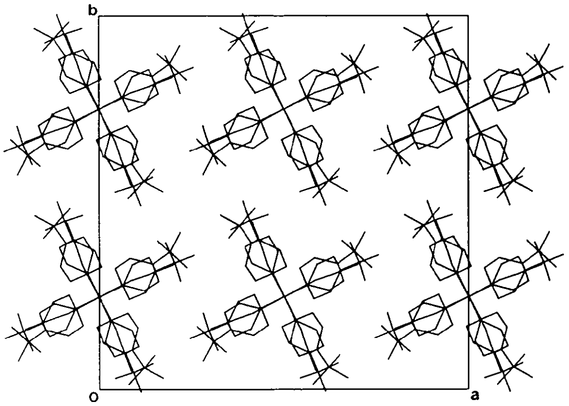

Fig. 3. Packing diagram of compound (II) viewed along [001].

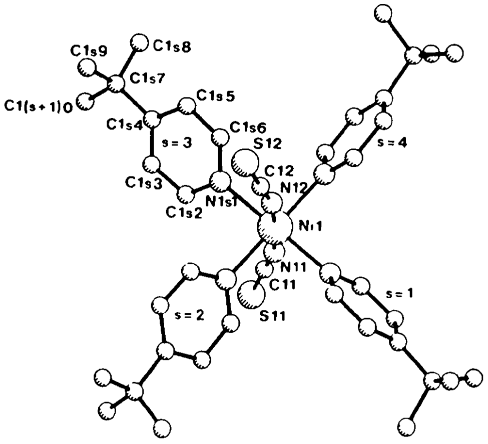

Fig. 4. Perspective view of compound (II) with atomic nomenclature.

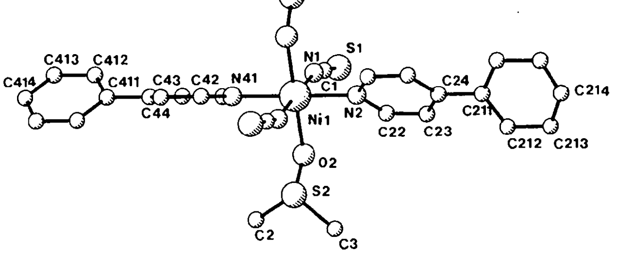

Fig. 5. Perspective view of compound (III) with atomic nomenclature.

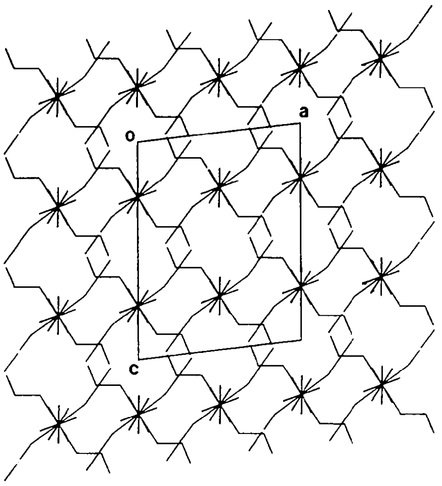

Fig. 6. Packing diagram of compound (III) viewed along [010].

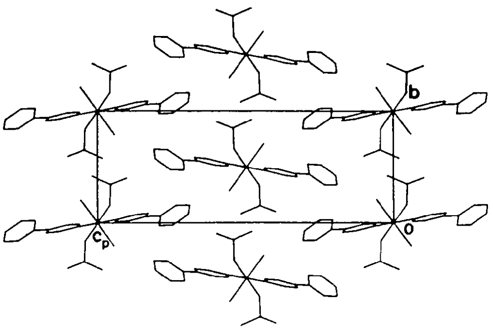

Fig. 7. Packing diagram of compound (IV) viewed along [100].

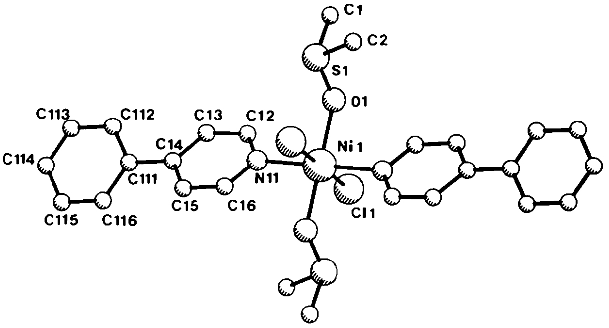

Fig. 8. Perspective view of compound (IV) with atomic nomenclature.

(Moore, Nassimbeni, Niven & Taylor, 1986) [Vi] and the 4-Phpy derivative (Nassimbeni, Niven & Taylor, 1987) [Ph].

We can define the following torsion angles: $\tau_x =$ min. [N(1)—Ni(1)—N(x1)—C(xy)] where $y = 2$ or 6 for $x = 1$–4. [For complexes with two independent molecules (a and b) per asymmetric unit we substitute N(11)—Ni(1)—N(1x1)—C(1xy) and N(21)—Ni(2)—N(2x1)—C(2xy) in the above formula.] If a molecule crystallizes in a centrosymmetric space group, the different enantiomers will have opposite signs for the same torsion angle. Thus the histogram illustrated in Fig. 9 compares the torsion angles for the ten α-phase host molecules with all angles quoted as positive. The exceptions are compound (I) which, because of the position of the pseudo-twofold axis, and the [py] complex, which because of the C_i symmetry of the host molecule, both have $\tau_1 \simeq -\tau_3$ and $\tau_2 \simeq -\tau_4$. Excluding the 4-Bzpy (I) and [py] complexes, the range of angles that the remaining compounds adopt is small (29–47°). They all have the + + + + propeller configuration common to many Werner clathrates (Lipkowski, 1981).

Table 6 indicates the packing efficiency of the eight α-phase complexes, defined as (cell volume)/(total No. of non-H atoms in the cell). Thus the order of packing efficiency is: (I) > [Ph] > [py] > (III) > [Vi] > (IV) > [Me] > [Et] > (II). For the tetrasubstituted pyridine complexes this indicates that derivatives containing planar substituents are able to pack closer together than the non-planar analogues.

For clathrate formation, it is reasonable to assume that one requires four substituted pyridine ligands to give the host sufficient flexibility to accommodate a guest molecule. However, this is clearly not a sufficient condition. It appears that the solubility of the host complex, in a guest solvent, is also responsible for the formation of clathrates. There is apparently a narrow range of solubility where clathration can result. Below this range, insufficient host dissolves to form crystals, whilst above it, the host is too soluble and will not crystallize out. This solubility range is not well defined and varies from host to host.

Table 6. *Comparison of α-phase structures*

Compound	τ_1 (°)	τ_2 (°)	τ_3 (°)	τ_4 (°)	Packing efficiency (Å^3 atom^{-1})
(I)	34	14	−37	−25	18·2
(II)	30	46	36	42	22·1
[py]	25	36	−25	−36	18·7
[Me]	34	38	29	34	20·6
[Et1*a*]	39	45	38	38	20·8
[Et1*b*]	36	33	41	36	
[Et2*a*]	44	35	33	41	20·8
[Et2*b*]	33	47	35	37	
[Vi]	36	40	38	43	19·9
[Ph]	41	46	31	38	18·6
(III)					19·8
(IV)					20·3

Table 7. *Solubilities of host compounds* (I) *and* (II) *at* 329 K *expressed as* 10^3X_{host}

Guest	Host (I)	Host (II)
Dmso	35·3	8·6
Thf	23·3	5·2
$CHCl_3$	17·6	3·7
EtOH	2·7	1·7

We have measured the solubilities of the two host compounds (I) and (II) in various potential guest solvents, and these are reported in Table 7. The solubilities, expressed as mole fraction of host at saturation at 329 K, show that the *tert*-butyl host (II) is only sparingly soluble, but that the benzyl host (I) can reach solubilities of $X_{\text{host}} = 35{\cdot}5 \times 10^{-3}$. These values are similar to those found for the 4-vinyl host in chloroform, which yielded an inclusion compound (Moore, Nassimbeni & Niven, 1987*b*). Solubility is therefore not the decisive factor which precludes clathrate formation for these host compounds.

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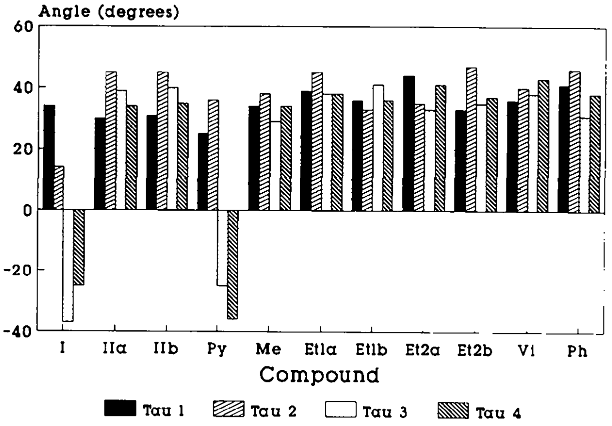

Fig. 9. Histogram of the torsion angles of the 11 α-phase host molecules.

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An Experimental Electron Density Study of $NaHC_2O_4.H_2O$ at 120 K*

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Abstract

Sodium hydrogen oxalate monohydrate, M_r = 130·03, triclinic, $P\bar{1}$, a = 6·4235 (7), b = 6·6580 (8), c = 5·6941 (10) Å, α = 85·048 (9), β = 110·100 (13), γ = 104·963 (14)°, V = 220·94 Å^3, Z = 2, D_x = 1·954 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·293 mm^{-1}, $F(000)$ = 132, T = 120 K, R = 0·0279 for conventional refinement based on 3971 reflections with $F_o^2 > 3\sigma(F^2)$. The deformation electron density of $NaHC_2O_4.H_2O$ has been measured at 120 K using X-ray and neutron diffraction techniques. *X–X* (high order) and *X–N* difference density maps are compared with deformation maps derived from a multipole model. Deformation densites in the covalent bonds of the $HC_2O_4^-$ ion are correlated with bond order. Deformation densities in the three independent hydrogen bonds are consistent with an electrostatic model for bonds of weak to intermediate strength in which polarization and other contributions become more important as the proton–acceptor distance decreases. The hydrogen bonding affects both the covalent bonds and the lone-pair electron density of the acceptor oxygen atoms.

Introduction

The effect of the crystalline field on the charge density of the water molecule has been the subject of a series of investigations at this institute (*cf.* Hermansson, 1984, and references therein). Studies of the electron density in solids by diffraction techniques include numerous examples containing hydrogen bonds (Olovsson, 1980); however, the number of accurate low-temperature investigations remains limited. The extensive electron density studies of oxalic acid dihydrate (Coppens *et al.*, 1984) permit detailed comparison with the corresponding density distribution in the hydrogen oxalate ion. In addition to both single and double C—O bonds, the $HC_2O_4^-$ ion contains two intermediate C—O bonds with the oxygen atoms in rather different environments.

The crystal structure and deformation electron density of $NaHC_2O_4.H_2O$ have been investigated previously at 295 K using X-ray and neutron diffraction (Tellgren, Thomas & Olovsson, 1977). The electron density of the H_2O molecule and $HC_2O_4^-$ ion including the crystal field effects in $NaHC_2O_4.H_2O$ was studied theoretically using *ab initio* MO–LCAO–SCF calculations by Lunell (1984). We present here an experimental study of the charge density distribution in $NaHC_2O_4.H_2O$ at 120 K using three different procedures for calculating dynamic deformation density maps: *X–N* difference densities, *X–X* (high-order) refinements and multipole model refinements. Details of the neutron diffraction study at 120 K have previously been reported (Delaplane, Tellgren & Olovsson, 1984).

Experimental

Data collection and reduction

Crystals of sodium hydrogen oxalate monohydrate were grown by slow evaporation of an aqueous solution. The crystal selected for data collection was

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* Hydrogen Bond Studies. 155. Part 154: Fernandes, Tellgren & Olovsson (1988).

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