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**X-RAY CRYSTAL STRUCTURE OF THE CLATHRATE COMPOUND  
 TETRAKIS[(BENZONITRILE)(TRIPHENYLPHOSPHORANE)NICKEL(0)]  
 · 2 TOLUENE · ~1 n-HEXANE · ~1 CYCLOOCTA-1,5-DIENE**

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**Summary**

The preparation and the chemical properties of the clathrate compound tetrakis[(benzonitrile)(triphenylphosphorane)nickel(0)] · 2 toluene · ~1 n-hexane · ~1 cycloocta-1,5-diene are described. The crystal and molecular structure of this compound were determined from X-ray diffractometer data. The structure was solved by direct and Fourier methods and refined by least-squares techniques to  $R = 0.117$  for 3441 independent reflections. The crystals are monoclinic, space group  $P2_1$ , with  $Z = 2$ , in a unit cell of dimensions  $a$  14.680(7),  $b$  28.198(18),  $c$  15.432(8) Å,  $\beta = 118.43(8)^\circ$ . Eight  $(\text{NiP}(\text{C}_6\text{H}_5)_3 \cdot \text{NCC}_6\text{H}_5)$  formula units are present as two tetrameric molecules in the unit cell. Each Ni atom of the tetramer is linked by  $\sigma$  bonds to a P and N atom and by  $\pi$  bonds to the  $\text{N}\equiv\text{C}$  group of another benzonitrile molecule. The coordination of the nickel atoms is roughly trigonal. The nickel and N atoms form an eight-membered ring with a boat conformation. The  $\text{N}=\text{C}-\text{C}$  groups of the benzonitrile residues are bent and the  $\text{N}=\text{C}$  distances indicate a high degree of double bond character for all these bonds. The triphenylphosphorane groups adopt a "propeller"-like conformation. Four solvent molecules 2 toluene, 1 n-hexane, and ~1 cycloocta-1,5-diene per asymmetric unit are present in the unit cell.

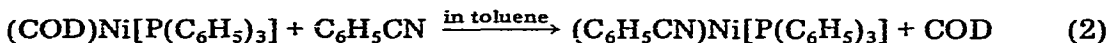
**Introduction**

We have recently described the synthesis and structure of a nickel(0) complex containing triphenylphosphine and benzonitrile, viz. (benzonitrile)tris(triphenylphosphorane)nickel(0) (II) [1]. We also reported the synthesis of another nickel(0) complex containing triphenylphosphine and benzonitrile and thought to contain one molecule of phosphine and of benzonitrile per nickel atom, and to have the nitrile  $\pi$ -complexed to the metal atom via its triple bonds.

We now report the crystal structure and composition of this clathrate complex, viz. tetrakis[(benzonitrile)(triphenylphosphorane)nickel(0)] · 2 toluene · ~1 n-hexane · ~1 cycloocta-1,5-diene (I).

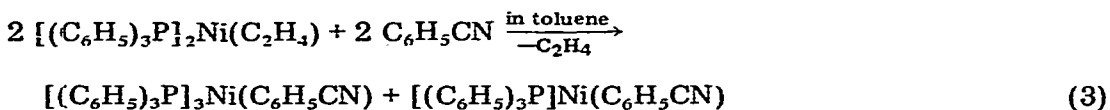
### Preparation

The preparation of  $[(C_6H_5)_3P]Ni(C_6H_5CN)$  (I) was by the route shown in equations 1 and 2.



(I)

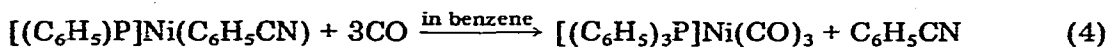
On addition of triphenylphosphine to a stirred suspension of dicycloocta-1,5-dienickel(0) (with a nickel/phosphine ratio 1/1) a bright yellow solid is obtained, which on addition of benzonitrile is converted into the bright red complex I. The IR spectrum of this extremely air sensitive compound, shows a strong band at  $1750\text{ cm}^{-1}$  in the region normally assigned to C=N stretching frequencies [2]. This band disappears on decomposition in air, while the  $\nu(CN)$  of the free nitrile appears. The position of the band at  $1750\text{ cm}^{-1}$  in complex I suggests that the nitrile must be  $\pi$ -complexed via its  $p_\pi-p_\pi$  bonds to the metal atom. This has been confirmed by X-ray crystal structure determination although it should be noted that one nitrile molecule is bound to two nickel atoms in two ways, i.e. through its triple bond and through the lone pair electrons of the nitrogen atom. Complex I can also be obtained, together with complex II which was described previously [1], starting from the complex  $[(C_6H_5)_3P]_2Ni(C_2H_4)$  (eq. 3).



(II)

(I)

The two complexes could be separated because complex I is insoluble and complex II quite soluble in toluene. This separation gave good crystals for the X-ray structure determination; when the filtered toluene solution was left for several days suitable red crystals of complex I were formed. This is probably due to slow displacement of equilibria in solution which leads to very slow formation of complex I. We were not able to obtain a satisfactory elemental analysis for complex I, perhaps because it contains many different molecules as clathrates. In order to confirm the composition of complex I we have decomposed it with CO (eq. 4).



(I)

(III)

Complex III was identified by its IR spectrum and the quantity of benzonitrile produced was determined by GC analysis. The nickel content was deter-

ined by usual analysis, and in several determinations we always found a nickel/benzonitrile ratio of 1/1. GLC analysis of the benzene layer also revealed a nickel/toluene ratio of 2/1, and the presence of substantial amounts of n-hexane (which was used for washing the precipitate) and cycloocta-1,5-diene, though not in constant ratio to nickel.

On this basis we have concluded that in the structure of complex I there are several holes into which fit several molecules other than toluene. The nitrile is very loosely bound, and using many different substrates we were unable to obtain any nitrile insertion products, but only those expected for typical reactions of nickel(0) complexes.

## Experimental

$\text{Ni}(\text{COD})_2$  [3] and  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ni}(\text{C}_2\text{H}_4)$  [4] were prepared by published methods. All experiments were carried out under pure argon. Solvents were freed from water and oxygen by distillation over sodium-potassium alloy. IR spectra were recorded on a Perkin-Elmer 225 spectrometer using Nujol mulls.

### *Preparation of (triphenylphosphine)nickel(benzonitrile) (I)*

(a) *From  $\text{Ni}(\text{COD})_2 + (\text{C}_6\text{H}_5)_3\text{P}$ .* 0.60 g (2.3 mmol) of  $(\text{C}_6\text{H}_5)_3\text{P}$  was added to a stirred suspension of 0.64 g (2.3 mmol) of  $\text{Ni}(\text{COD})_2$  in 15 ml of toluene. The mixture was stirred until a bright yellow solid was obtained and 0.5 g (4.9 mmol) of  $\text{C}_6\text{H}_5\text{CN}$  were then added. Complex I was immediately formed as a bright red solid which was collected by filtration. After washing with n-hexane and drying for many hours at the vacuum pump, 0.85 g (2.0 mmol) of complex I were obtained.

(b) *From  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ni}(\text{C}_2\text{H}_4)$ .* 1.00 g (9.7 mmol) of  $\text{C}_6\text{H}_5\text{CN}$  was added to a stirred suspension of 4.28 g (7.0 mmol) of  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Ni}(\text{C}_2\text{H}_4)$  in 20 ml of toluene. A red precipitate of complex I formed immediately; this was filtered off and washed with toluene and n-hexane to give after drying 1.49 g (3.5 mmol) of complex I. Toluene solution after standing for several days deposited good crystals of complex I for X-ray study.

### *Decomposition of complex I*

A suspension of 1.61 g of complex I, prepared as described under (a) above and containing 11.6% of Ni (3.2 g-atom of Ni), in 20 cm<sup>3</sup> of toluene-free benzene was stirred under CO; 175 cm<sup>3</sup> (9.6 mmol) of gas were adsorbed in a few hours, as the red solid disappeared and a white solid was formed. The white solid was identified from its spectrum as  $(\text{C}_6\text{H}_5)_3\text{PNi}(\text{CO})_3$  (collected 1.20 g, 3.0 mmol). GLC analysis of the benzene solution revealed 0.32 g (3.2 mmol) of benzonitrile and 0.15 g (1.6 mmol) of toluene. This determination always showed constant amounts of n-hexane and cycloocta-1,5-diene.

## X-ray analysis

Preliminary space group and unit cell dimensions were obtained from Weissenberg photographs. The crystals often grow along the [101] axis. A crystal, essentially a parallelepiped having dimensions ca. 0.30 × 0.25 × 0.50 mm, was mount-

ed on a Picker FACS 1 four-circle computer-controlled diffractometer, equipped with a scintillation counter and a pulse-height analyser. The orientation matrix, and cell dimensions were obtained from a least-squares fit of  $\chi$ ,  $\phi$ ,  $\omega$  and  $2\theta$  values from 12 independent reflections.

### Crystal data

$C_{128}H_{112}N_4P_4Ni_4$ , mol. wt. 2065.04. Monoclinic:  $a$  14.680(7),  $b$  28.198(18),  $c$  15.432(8) Å,  $\beta$  118.43(8)°,  $U$  5617.8 Å<sup>3</sup>,  $D_m$  1.24 g cm<sup>-3</sup>,  $Z$  = 2,  $D_c$  1.22 g cm<sup>-3</sup>. Space group  $P2_1$  from systematic absences  $0k0$  with  $k$  odd and from structure determination. Mo- $K_\alpha$  radiation,  $\lambda$  0.71069 Å,  $\mu$ (Mo- $K_\alpha$ ) 7.6 cm<sup>-1</sup>. Intensity data were collected by use of zirconium filtered Mo- $K_\alpha$  radiation with  $2\theta \leq 45^\circ$ . The moving-crystal moving-counter technique was used, with a  $2\theta$  scan rate of 1° min<sup>-1</sup> and a scan range of  $(2.00^\circ + \Delta)$ , where  $\Delta$  is introduced to take into account the  $2\theta$  separation of the  $K_{\alpha_1}K_{\alpha_2}$  peaks at increasing values of  $2\theta$ . Background counts of 10 s duration were measured at each end of every  $2\theta$  scan. Three standard reflections were measured after every 50 reflections. The intensities of these monitoring reflections showed no relevant fluctuations (less than  $\pm 3\%$ ) during data collection. 7505 independent reflections were measured, of which 3441 were considered observed and has  $I \geq 3.2 \sigma I$ . An arbitrary intensity equal to 0.5, the observable limit, was assigned to the non-significant reflections. All intensities were corrected for Lorentz and polarization effects. No absorption correction was introduced.

### Determination and refinement of the structure

The structure was solved both by Patterson and direct methods, using the 1972 version of the Multan program written by Main, Woolfson and Germain [5]. The observed structure factors were automatically converted by the program into normalized structure factor amplitudes ( $|E|$ ). All the normalized structure factor amplitudes greater than 1.94 (150 reflections) were introduced into the calculations, further 50 reflections with very low  $|E|$  value were input to the program in order to define also the  $\psi_0$  figure of merit. The number of phase relationships found was 430. The starting set automatically chosen by the program is reported in Table 1.

TABLE 1

PHASE ANGLES OF THE STARTING SET FOR THE TANGENT FORMULA

The enantiomorph is fixed by the 020 reflection

$h$	$k$	$l$	$ E $	Phase	
3	0	0	3.82	360	
0	1	1	2.58	360	origin-fixing reflections
1	0	-1	2.24	360	
3	3	-3	2.43	A	
2	3	0	2.38	B	
0	2	0	2.70	C	

The program has furnished 32 solutions according to values ( $\pm\frac{\pi}{4}$ ,  $\pm\frac{3}{4}\pi$ ) of the phase angles A and B, and ( $\frac{\pi}{4}$ ,  $\frac{3}{4}\pi$ ) of the phase angle C.

The correct solution had the highest value of ABS FOM, the lowest value of RESID, while the  $\psi_0$  figure of merit had an intermediate value. The corresponding phase angles A, B and C were  $-\frac{\pi}{4}$ ,  $\frac{\pi}{4}$  and  $\frac{3}{4}\pi$  respectively.

The corresponding *E*-map yielded the positional parameters of the Ni and P atoms. The correctness of this initial structure was tested by means of a three-dimensional Patterson map. The positional parameters of the carbon and nitrogen atoms were obtained by successive Fourier maps and on stereochemical considerations. The positional and the isotropic thermal parameters of the non-hydrogen atoms were refined by some cycles of block-diagonal least-squares by use of the program of Immirzi [6]. Atomic scattering factors were calculated from the expression in ref. 7 using the values for the parameters given in ref. 8. The weighting scheme of ref. 9 was adopted:  $1/w = A + B|F_o| + C|F_o|^2$ , where  $A = 2 F_o(\text{min})$ ,  $B = 1.00$ , and  $C = 2/F_o(\text{max})$ . At this point the conventional *R* was 0.13 for the 3441 non-zero reflections. A difference-Fourier map clearly revealed the presence of two clathrate toluene molecules. Further four cycles of block-diagonal least-squares were run, introducing into the calculations the two found toluene molecules. The refinement converged to  $R = 0.117$  for the 3441 significant reflections. A final difference-Fourier map showed residual electron densities in two different unit cell regions approximately centered at  $x = 1.00$ ,  $y = 0.10$ ,  $z = 0.30$  and at  $x = 0.50$ ,  $y = 0.42$ ,  $z = 1.10$ . In both cases no correlation could be found between the residual electron density peaks and acceptable solvent molecule models. (Toluene, n-hexane, or cycloocta-1,5-diene).

The possible presence in the unit cell of two associated disordered, solvent molecules, per independent unit, will be discussed below.

Table 2 lists the final fractional coordinates and the corresponding standard deviations of the atoms of the independent unit, including two toluene molecules only. A table of calculated and observed structure amplitudes can be obtained by application to the authors.

## Results and discussion

A view of the molecule of I is shown in Fig. 1. The figure was obtained by means of the ORTEP computing and drawing program [10]. The geometric parameters of the molecule with their estimated deviations are listed in Table 3.

In I eight formula units ( $\text{Ni} \cdot \text{P}(\text{C}_6\text{H}_5)_3 \cdot \text{NCC}_6\text{H}_5$ ) are contained in the unit cell as two tetrameric molecules. Every nickel atom of the tetramer is linked by  $\sigma$ -bonds to a P atom, and to a N atom of the  $\text{N}\equiv\text{C}$  group of benzonitrile. Four of these monomers form the tetramer using  $\pi$ -bonds from the  $\text{N}\equiv\text{C}$  groups as shown in the schematic drawing reported in Fig. 2. Each nickel atom is tetra-coordinated by two N atoms, a P atom and a C atom. The average values of the Ni-P and Ni-C distances are 2.136 and 1.85 Å, respectively, a little shorter than those reported in the literature [1,11-14]. The average value of the Ni-N distance of 1.91 Å is in good agreement with previous determinations [1,14,15].

(continued on p. 232)

TABLE 2

FINAL FRACTIONAL COORDINATES OF THE  $[\text{C}_6\text{H}_4\text{CN} \cdot \text{P}(\text{C}_6\text{H}_5)_3 \cdot \text{Ni}]_4 \cdot 2 \text{C}_7\text{H}_8$  INDEPENDENT UNIT

The e.s.d. (in parentheses) in this and in the following tables, occurs in the last significant digit.

Atom	$x/a$	$y/b$	$z/c$	$B (\text{Å}^2)$
Ni(1)	0.62685(25)	0.25675(13)	0.81345(24)	2.40
Ni(2)	0.63951(25)	0.23872(13)	0.60005(24)	2.35
Ni(3)	0.50042(25)	0.33885(13)	0.55897(24)	2.51
Ni(4)	0.72582(25)	0.35762(13)	0.77039(24)	2.35
P(1)	0.6110(6)	0.2668(3)	0.9433(5)	3.09
P(2)	0.7353(6)	0.1779(3)	0.6266(5)	3.02
P(3)	0.3550(6)	0.3275(3)	0.4289(5)	3.00
P(4)	0.8020(6)	0.4164(3)	0.7471(5)	2.96
N(1)	0.7385(16)	0.2963(8)	0.8362(15)	2.61
N(2)	0.5837(15)	0.2272(7)	0.6878(14)	2.43
N(3)	0.5909(15)	0.2985(7)	0.5378(14)	2.39
N(4)	0.5800(14)	0.3655(7)	0.6858(13)	2.01
C(1)	0.695(2)	0.3155(12)	1.032(2)	4.30
C(2)	0.640(3)	0.3577(15)	1.031(3)	6.29
C(3)	0.695(4)	0.3948(19)	1.087(3)	9.29
C(4)	0.810(3)	0.3903(15)	1.131(3)	6.29
C(5)	0.8600(3)	0.3502(13)	1.137(2)	5.60
C(6)	0.800(3)	0.3016(14)	1.075(3)	6.08
C(7)	0.474(2)	0.2834(10)	0.914(2)	2.98
C(8)	0.424(2)	0.3069(12)	0.830(2)	4.71
C(9)	0.315(3)	0.3241(14)	0.804(3)	6.10
C(10)	0.279(3)	0.3140(17)	0.877(3)	8.10
C(11)	0.332(3)	0.2921(16)	0.956(3)	7.43
C(12)	0.443(4)	0.2789(19)	0.981(4)	9.38
C(13)	0.644(2)	0.2157(12)	1.030(2)	4.26
C(14)	0.652(2)	0.2219(11)	1.124(2)	3.62
C(15)	0.684(3)	0.1801(14)	1.189(3)	5.76
C(16)	0.687(3)	0.1387(16)	1.152(3)	6.81
C(17)	0.681(3)	0.1337(16)	1.052(3)	7.39
C(18)	0.653(2)	0.1730(12)	0.998(2)	4.53
C(19)	0.694(2)	0.1320(12)	0.530(2)	4.82
C(20)	0.734(2)	0.0878(10)	0.535(2)	2.88
C(21)	0.697(3)	0.0561(13)	0.456(2)	5.17
C(22)	0.626(3)	0.0750(16)	0.366(3)	7.01
C(23)	0.589(2)	0.1159(12)	0.353(2)	4.62
C(24)	0.623(2)	0.1475(11)	0.432(2)	3.50
C(25)	0.871(2)	0.1896(9)	0.659(2)	2.49
C(26)	0.937(3)	0.1619(14)	0.633(3)	6.39
C(27)	1.040(2)	0.1793(12)	0.665(12)	4.25
C(28)	1.068(2)	0.2216(12)	0.718(2)	4.84
C(29)	1.010(2)	0.2463(13)	0.747(2)	5.30
C(30)	0.915(3)	0.2300(14)	0.714(2)	5.66
C(31)	0.755(2)	0.1369(10)	0.732(2)	3.10
C(32)	0.839(3)	0.1420(13)	0.825(2)	5.20
C(33)	0.854(4)	0.1147(19)	0.923(4)	9.78
C(34)	0.767(3)	0.0879(14)	0.890(3)	5.78
C(35)	0.679(3)	0.0834(15)	0.807(3)	6.25
C(36)	0.661(3)	0.1082(14)	0.713(3)	5.67
C(37)	0.903(2)	0.4007(10)	0.715(2)	2.86
C(38)	0.874(2)	0.3664(13)	0.643(2)	4.88
C(39)	0.944(2)	0.3508(12)	0.606(2)	4.70
C(40)	1.032(2)	0.3690(12)	0.640(2)	4.95
C(41)	1.065(3)	0.4050(13)	0.726(2)	5.52
C(42)	1.005(2)	0.4180(12)	0.760(2)	4.08
C(43)	0.866(2)	0.4562(11)	0.849(2)	3.70
C(44)	0.880(2)	0.4425(11)	0.945(2)	3.94

(continued)

TABLE 2 (continued)

Atom	$x/a$	$y/b$	$z/c$	$B$ (Å <sup>2</sup> )
C(45)	0.945(3)	0.4697(15)	1.035(3)	6.38
C(46)	0.970(3)	0.5134(13)	1.017(3)	5.41
C(47)	0.964(3)	0.5293(14)	0.924(3)	6.42
C(48)	0.901(2)	0.5022(12)	0.835(2)	4.35
C(49)	0.720(3)	0.4615(13)	0.649(2)	5.18
C(50)	0.742(3)	0.4698(14)	0.573(3)	5.74
C(51)	0.691(4)	0.5067(20)	0.496(4)	10.29
C(52)	0.596(3)	0.5240(17)	0.499(3)	8.43
C(53)	0.580(3)	0.5114(16)	0.577(3)	7.77
C(54)	0.639(3)	0.4777(14)	0.657(13)	5.82
C(55)	0.350(2)	0.2789(10)	0.343(2)	3.38
C(56)	0.311(2)	0.2341(13)	0.345(2)	4.86
C(57)	0.328(3)	0.1986(16)	0.279(3)	7.25
C(58)	0.389(3)	0.2077(17)	0.237(3)	7.88
C(59)	0.425(3)	0.2459(17)	0.242(3)	7.56
C(60)	0.412(3)	0.2934(14)	0.297(3)	5.72
C(61)	0.250(2)	0.3079(11)	0.456(2)	3.70
C(62)	0.139(4)	0.3226(19)	0.389(4)	9.61
C(63)	0.067(3)	0.3027(15)	0.423(3)	6.41
C(64)	0.092(3)	0.2752(16)	0.504(3)	7.88
C(65)	0.195(3)	0.2624(14)	0.557(2)	5.82
C(66)	0.273(3)	0.2816(13)	0.539(2)	5.17
C(67)	0.306(2)	0.3797(10)	0.348(2)	3.01
C(68)	0.345(2)	0.4234(10)	0.386(2)	3.19
C(69)	0.314(3)	0.4648(14)	0.323(3)	5.83
C(70)	0.231(3)	0.4604(14)	0.234(3)	5.74
C(71)	0.189(3)	0.4184(14)	0.194(3)	5.65
C(72)	0.224(2)	0.3735(12)	0.248(2)	4.84
C(73)	0.830(2)	0.3157(10)	0.861(2)	2.98
C(74)	0.931(2)	0.2971(11)	0.928(2)	3.62
C(75)	0.946(2)	0.2548(11)	0.972(2)	3.18
C(76)	1.050(3)	0.2428(14)	1.041(2)	5.87
C(77)	1.130(3)	0.2771(14)	1.052(3)	5.65
C(78)	1.013(2)	0.3330(11)	0.941(2)	3.30
C(79)	1.113(3)	0.3190(14)	1.005(3)	5.87
C(80)	0.651(2)	0.2749(9)	0.515(2)	2.21
C(81)	0.688(2)	0.2904(11)	0.447(2)	3.50
C(82)	0.757(2)	0.2610(11)	0.430(2)	3.61
C(83)	0.797(2)	0.2757(12)	0.364(2)	4.38
C(84)	0.769(3)	0.3187(14)	0.320(3)	5.82
C(85)	0.710(2)	0.3505(13)	0.341(2)	5.37
C(86)	0.667(2)	0.3374(13)	0.401(2)	5.17
C(87)	0.532(2)	0.2130(11)	0.724(2)	3.72
C(88)	0.443(2)	0.1827(10)	0.690(2)	3.04
C(89)	0.403(2)	0.1741(12)	0.752(2)	4.45
C(90)	0.314(3)	0.1438(17)	0.714(3)	8.11
C(91)	0.255(3)	0.1248(16)	0.611(3)	7.03
C(92)	0.302(3)	0.1380(16)	0.562(3)	6.85
C(93)	0.392(2)	0.1630(12)	0.591(2)	4.56
C(94)	0.492(2)	0.3793(11)	0.651(2)	4.06
C(95)	0.433(2)	0.4051(10)	0.681(2)	2.75
C(96)	0.484(2)	0.4256(12)	0.780(2)	4.35
C(97)	0.436(3)	0.4540(17)	0.818(3)	7.77
C(98)	0.332(3)	0.4587(16)	0.761(3)	7.06
C(99)	0.281(2)	0.4444(12)	0.660(2)	4.54
C(100)	0.327(2)	0.4168(11)	0.624(2)	3.64
C(101)	0.393(3)	0.1369(15)	1.014(3)	6.15
C(102)	0.313(3)	0.1624(17)	0.953(3)	7.91
C(103)	0.224(3)	0.1570(17)	0.944(3)	8.18

(continued)

TABLE 2 (continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å <sup>2</sup> )
C(104)	0.211(3)	0.1227(16)	1.005(3)	7.50
C(105)	0.319(3)	0.0903(18)	1.068(3)	8.62
C(106)	0.396(3)	0.0997(15)	1.050(3)	7.03
C(107)	0.481(3)	0.0630(17)	1.092(3)	7.97
C(108)	0.048(3)	0.4586(17)	0.364(3)	7.80
C(109)	0.022(3)	0.4970(15)	0.315(3)	6.80
C(110)	-0.077(3)	0.5105(16)	0.300(3)	7.62
C(111)	-0.104(4)	0.4842(19)	0.359(4)	9.28
C(112)	-0.070(3)	0.4552(16)	0.424(3)	7.31
C(113)	0.003(3)	0.4346(16)	0.420(3)	7.66
C(114)	-0.120(3)	0.5474(16)	0.227(3)	7.51

There are no significant differences between  $\sigma$  and  $\pi(\text{Ni}-\text{N})$  bond lengths in I. Each nickel atom and the atoms linked to it (the  $\sigma$ -bonded P and N atoms, and the  $\pi$ -bonded N and C atoms of a benzonitrile group) are nearly coplanar.

(continued on p. 235)

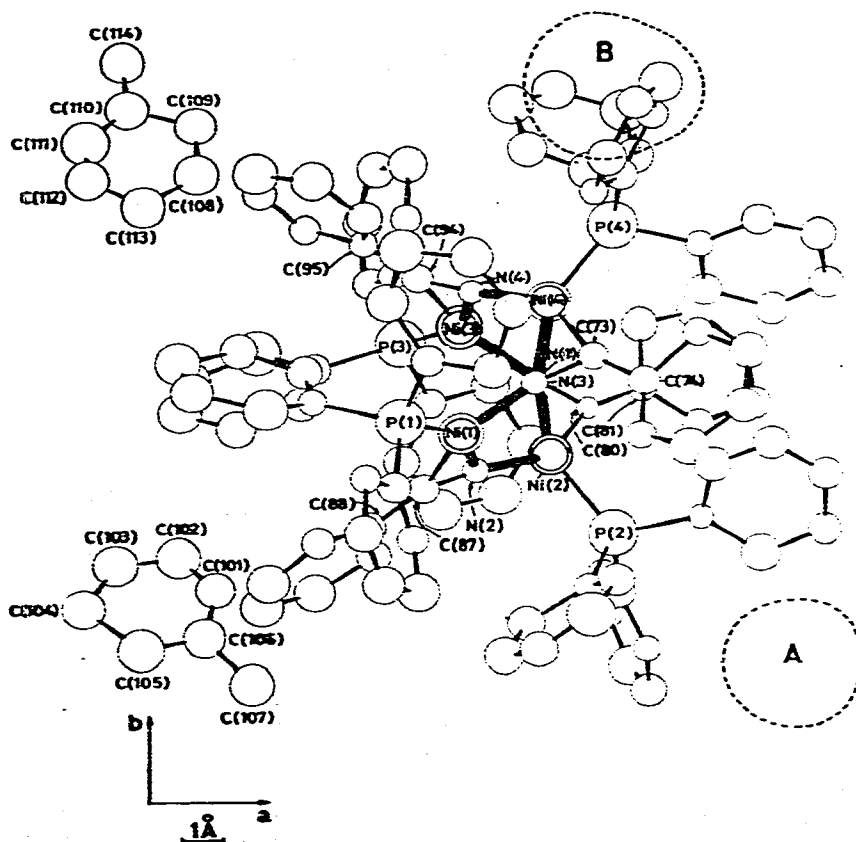


Fig. 1. The molecule of  $[\text{C}_6\text{H}_5\text{CN} \cdot \text{P}(\text{C}_6\text{H}_5)_3 \cdot \text{Ni}]_4 \cdot 2 \text{C}_7\text{H}_8$  as viewed down the  $c^*$  axis. For sake of clarity only the ring atoms are labelled. A and B denote the positions of the empty regions.



TABLE 3

GEOMETRICAL PARAMETERS OF THE  $[\text{C}_6\text{H}_5\text{CN} \cdot \text{P}(\text{C}_6\text{H}_5)_3 \cdot \text{Ni}]_4 \cdot 2\text{C}_7\text{H}_8$  MOLECULE IN THE CRYSTALS

The average C—C bond length and C—C—C bond angle for the phenyl groups are 1.40 Å and 120° respectively. The greatest discrepancies from the average values were found for the toluene molecules.

<i>(a) Bond lengths (Å)</i>		N(1)—Ni(4)—N(4)	104.9(6)
Ni(1)—P(1)	2.144(9)	N(4)—Ni(4)—P(4)	107.5(6)
Ni(2)—P(2)	2.130(10)	P(4)—Ni(4)—C(73)	107.8(8)
Ni(3)—P(3)	2.146(12)	C(73)—Ni(4)—N(1)	40(3)
Ni(4)—P(4)	2.122(9)		
Ni(1)—N(1)	1.87(2)	Ni(1)—N(1)—C(73)	167(7)
Ni(2)—N(2)	1.91(2)	Ni(1)—N(2)—C(87)	70(2)
Ni(3)—N(3)	1.89(2)	Ni(2)—N(2)—C(87)	164(6)
Ni(4)—N(4)	1.91(3)	Ni(2)—N(3)—C(80)	63(2)
Ni(1)—N(2)	1.92(2)	Ni(3)—N(3)—C(80)	172(10)
Ni(2)—N(3)	1.90(3)	Ni(3)—N(4)—C(94)	70(2)
Ni(3)—N(4)	1.90(3)	Ni(4)—N(4)—C(94)	163(8)
Ni(4)—N(1)	1.97(3)	Ni(4)—N(1)—C(73)	68(2)
Ni(1)—C(87)	1.88(4)	N(1)—C(73)—C(74)	128(2)
Ni(2)—C(80)	1.74(3)	N(2)—C(87)—C(88)	134(1)
Ni(3)—C(94)	1.87(3)	N(3)—C(80)—C(81)	126(1)
Ni(4)—C(73)	1.91(4)	N(4)—C(94)—C(95)	137(2)
P(1)—C(1)	1.91(4)	Ni(1)—P(1)—C(1)	116.1(9)
P(1)—C(7)	1.90(4)	Ni(1)—P(1)—C(7)	112.5(7)
P(1)—C(13)	1.87(4)	Ni(1)—P(1)—C(13)	117(1)
P(2)—C(19)	1.85(4)	C(1)—P(1)—C(7)	104.1(8)
P(2)—C(25)	1.82(3)	C(7)—P(1)—C(13)	104(1)
P(2)—C(31)	1.90(4)	C(13)—P(1)—C(1)	100.6(9)
P(3)—C(55)	1.89(3)	Ni(2)—P(2)—C(19)	118.4(9)
P(3)—C(61)	1.86(3)	Ni(2)—P(2)—C(25)	115.8(9)
P(3)—C(67)	1.85(4)	Ni(2)—P(2)—C(31)	118(1)
P(4)—C(37)	1.82(3)	C(19)—P(2)—C(25)	104.2(8)
P(4)—C(43)	1.80(4)	C(25)—P(2)—C(31)	100.0(7)
P(4)—C(49)	1.90(5)	C(31)—P(2)—C(19)	97.2(8)
N(1)—C(73)	1.32(4)	Ni(3)—P(3)—C(55)	116.8(9)
N(2)—C(87)	1.21(4)	Ni(3)—P(3)—C(61)	113(1)
N(3)—C(80)	1.28(3)	Ni(3)—P(3)—C(67)	114(1)
N(4)—C(94)	1.21(5)	C(55)—P(3)—C(61)	100.6(7)
C(73)—C(74)	1.44(6)	C(61)—P(3)—C(67)	106.8(8)
C(87)—C(88)	1.44(5)	C(67)—P(3)—C(55)	103.2(8)
C(80)—C(81)	1.46(4)	Ni(4)—P(4)—C(37)	114.6(7)
C(94)—C(95)	1.36(4)	Ni(4)—P(4)—C(43)	116(1)
		Ni(4)—P(4)—C(49)	118(1)
		C(37)—P(4)—C(43)	103.3(8)
		C(43)—P(4)—C(49)	98(1)
		C(49)—P(4)—C(37)	103(1)
<i>(b) Bond angles (deg.)</i>		<i>(c) Torsion angles (deg.)</i>	
N(2)—Ni(1)—N(1)	106.7(6)	Ni(1)—P(1)—C(1)—C(6)	—68
N(1)—Ni(1)—P(1)	102.6(5)	Ni(1)—P(1)—C(7)—C(8)	—29
P(1)—Ni(1)—C(87)	113(1)	Ni(1)—P(1)—C(13)—C(18)	—15
C(87)—Ni(1)—N(2)	37(3)	Ni(2)—P(2)—C(19)—C(24)	22
		Ni(2)—P(2)—C(25)—C(30)	34
N(3)—Ni(2)—N(2)	108.9(6)	Ni(2)—P(2)—C(31)—C(36)	72
N(2)—Ni(2)—P(2)	101.1(4)	Ni(3)—P(3)—C(55)—C(60)	—69
P(2)—Ni(2)—C(80)	109.1(8)	Ni(3)—P(3)—C(61)—C(66)	—29
C(80)—Ni(2)—N(3)	41(2)	Ni(3)—P(3)—C(67)—C(68)	—18
		Ni(4)—P(4)—C(37)—C(38)	47
N(4)—Ni(3)—N(3)	106.1(5)	Ni(4)—P(4)—C(43)—C(44)	12
N(3)—Ni(3)—P(3)	102.5(6)	Ni(4)—P(4)—C(49)—C(54)	51
P(3)—Ni(3)—C(94)	113.8(9)		
C(94)—Ni(3)—N(4)	38(3)		

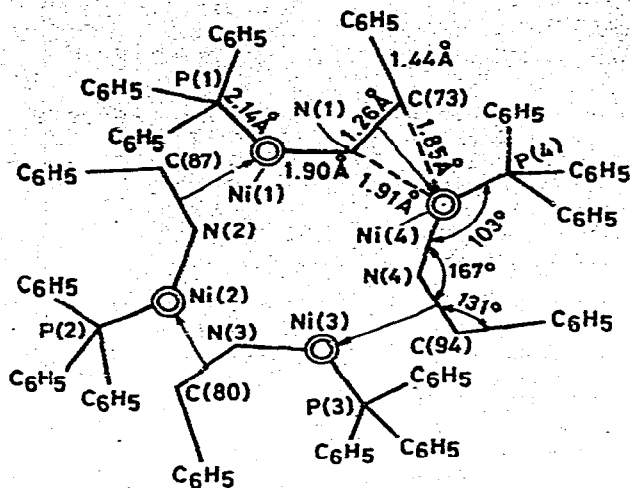


Fig. 2. Schematic drawing of the tetrameric molecule of I. Essential bond lengths and angles (averaged) are included.

TABLE 4

LEAST-SQUARES PLANES OF THE ATOMS BONDED TO THE Ni ATOMS AND OF BENZONITRILE RINGS. THE DIHEDRAL ANGLES BETWEEN THE PLANES ARE ALSO REPORTED

Each plane is represented by an equation of the type  $lx + my + nz - p = 0$ , referred to an orthogonal system of axes which has  $x$  along the  $a^*$  axis,  $y$  in the  $(b - c)$  plane and  $z$  along the  $c$  axis.

- (A) Ni(1), P(1), N(1), N(2), C(87).  
 $0.6404x - 0.7500y + 0.1654z + 1.1134 = 0$   
 root mean square distance 0.015 Å
- (B) Ni(2), P(2), N(2), N(3), C(80).  
 $0.7745x + 0.4725y + 0.4207z + 11.6135 = 0$   
 root mean square distance 0.029 Å
- (C) Ni(3), P(3), N(3), N(4), C(94).  
 $-0.2138x - 0.7673y + 0.6046z - 5.5751 = 0$   
 root mean square distance 0.029 Å
- (D) Ni(4), P(4), N(4), N(1), C(73).  
 $-0.0521x + 0.4801y + 0.8757z + 10.2901 = 0$   
 root mean square distance 0.027 Å
- (E) C(88), C(89), C(90), C(91), C(92), C(93).  
 $0.5599x - 0.8270y + 0.0509z - 0.6722 = 0$   
 root mean square distance 0.035 Å
- (F) C(81), C(82), C(83), C(84), C(85), C(86).  
 $0.8015x + 0.3857y + 0.4570z + 11.2620 = 0$   
 root mean square distance 0.037 Å
- (G) C(95), C(96), C(97), C(98), C(99), C(100).  
 $-0.2325x - 0.8266y + 0.5125z - 6.9329 = 0$   
 root mean square distance 0.061 Å
- (H) C(74), C(75), C(76), C(77), C(78), C(79).  
 $-0.0511x + 0.4351y + 0.8958z + 9.544 = 0$   
 root mean square distance 0.020 Å

*Dihedral angles (deg.)*

A-B	77.8	A-E	9.2
B-C	105.9	B-F	5.6
C-D	80.1	C-G	6.4
A-D	104.4	D-H	3.5

The dihedral angles between the four planes of the tetramer are 77.8, 105.9, 80.1 and 104.4°, respectively (see Table 4). As a result the Ni and N atoms of the tetramer form an eight-membered ring with a boat conformation. The overall shape and conformation of the ring are shown in Fig. 3.

The dihedral angles between these four planes and the atoms of the corresponding benzonitrile residues (C=N groups  $\pi$ -bonded to the Ni atoms) are all small, so that also these atoms are roughly coplanar with the former ones.

It is assumed that the  $\pi(\text{Ni}-\overset{\text{N}}{\parallel}{\text{C}})$  bonds are directed along the straight line

joining the Ni atoms and the mid point of the N=C groups, the coordination at the Ni atoms is roughly trigonal. The average value of the N-Ni-P bond angles is 103.4°, while the average values of the P-Ni-NC<sub>MID</sub> and NC<sub>MID</sub>-Ni-N bond angles are 130.4 and 126.5°, respectively. Similar trigonal symmetries at the nickel(0) atoms have been quoted for several similar compounds [14,16-18].

The observed N=C bond lengths (average value 1.26 Å) are decidedly longer

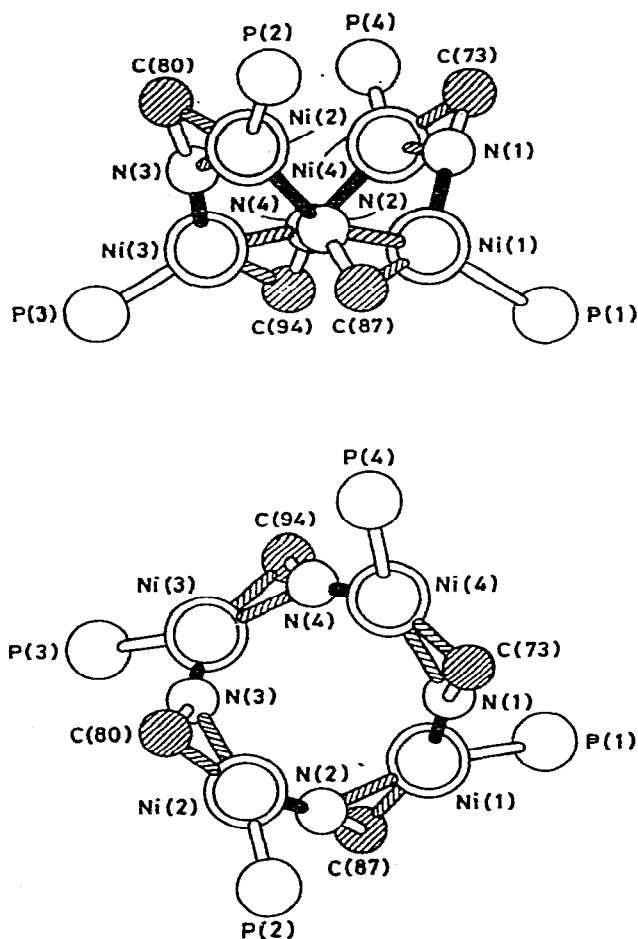


Fig. 3. Side and end views of the skeleton of the  $[\text{C}_6\text{H}_5\text{CN} \cdot \text{P}(\text{C}_6\text{H}_5)_3 \cdot \text{Ni}]_4 \cdot 2 \text{C}_7\text{H}_8$  molecule.

than the  $\text{N}=\text{C}$  triple bond of 1.158(2) Å [19], indicating a double bond nature for all these bonds. This is in accordance with the appearance in the IR spectrum of I, of a strong band in the region normally assigned to  $\text{C}=\text{N}$  double bond stretching frequencies ( $1750\text{ cm}^{-1}$ ) [1]. The average value of the  $\text{Ni}-\text{N}=\text{C}$  bond angles is  $167^\circ$ , while the average value of the  $\text{N}=\text{C}-\text{C}$  bond angles is  $131^\circ$  with a  $\text{C}-\text{C}$  average bond length of 1.44 Å.

With regard to the four-coordinated P atoms, there is a reduction of the local symmetry from tetrahedral to trigonal. The  $\text{Ni}-\text{P}-\text{C}(\text{Phen})$  angles are considerably greater than the tetrahedral ones (average value  $116^\circ$ ), while the  $\text{C}(\text{phen})-\text{P}-\text{C}(\text{Phen})$  angles are about  $102^\circ$ . Similar distortions of the tetrahedral symmetry at the P atoms have been noted for several analogous compounds [20].

The average values of the smallest  $\text{Ni}-\text{P}-\text{C}(\text{Phen})-\text{C}(\text{Phen})$  torsion angles are:  $-15^\circ$ ,  $-29^\circ$ ,  $-68^\circ$  when the benzene rings bonded to P(1) and P(3) are considered, and  $17^\circ$ ,  $40^\circ$ ,  $62^\circ$  when P(2) and P(4) are involved. The overall shape of the triphenylphosphorane groups is that of the well-known "propeller" like conformation [20].

The measured density of I is  $1.24\text{ g cm}^{-3}$ . The calculated density reaches a comparable value ( $1.22\text{ g cm}^{-3}$ ) only where eight solvent molecules (toluene) are assumed to be present in the unit cell. This assumption brings the  $K$  "molecular packing coefficient", calculated according to Kitaigorodskii [21], to 0.67. The  $K$  value obtained for I is in good agreement with that calculated for (benzonitrile)tris(triphenylphosphorane)nickel(0) [1], viz. 0.66, and with the average value of 0.70 given in ref. 21 for organic compounds containing phenyl groups. The number of toluene molecules surely present in the unit cell of I is four, but

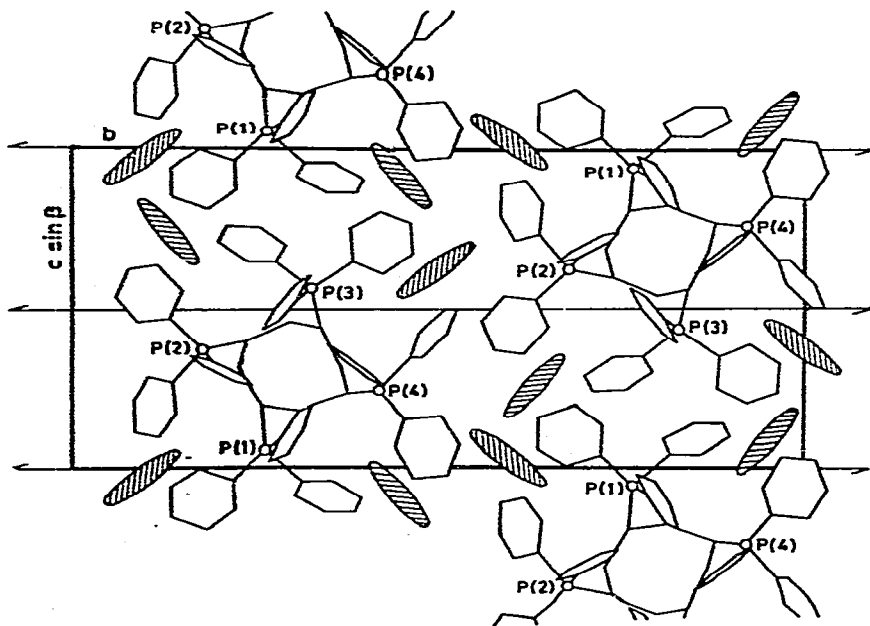


Fig. 4. Packing of the molecules of I as viewed down the  $a$  axis. Only the triphenylphosphorane groups are shown in addition to the skeleton of the molecules. Dashed areas indicate the toluene molecules.

as we have seen before, there are some difference-Fourier data which indicate the presence of other four associated solvent molecules.

It was also possible to deduce from packing considerations, that two empty regions with a volume of about 500 Å<sup>3</sup> each (A and B of Fig. 1) are present in the asymmetric unit cell of I. The fact that the residual electron densities evidenced from the difference-Fourier map in the same A and B regions of the unit cell could not be matched with stereochemically acceptable toluene molecules is in line with the results of the GLC analysis, which shows that in addition to 2 toluene molecules significant amounts of n-hexane and of cycloocta-1,5-diene are also present in the crystals. The results may be an indication of positional disorder and/or of statistical distribution of these three types of molecules in the holes present in the unit cell.

The four solvent molecules per asymmetric unit present in I are interlocked between two adjacent triphenylphosphorane groups of the same tetramer as shown in Fig. 4.

The intramolecular distances observed in I reach acceptable values, the C...C separations between atoms four or more bonds apart are  $\geq 3.40$  Å, except for the C(12)...C(14) and C(42)...C(48) distances which are 3.22 and 3.32 Å, respectively. The intramolecular Van der Waals separations are also good, no C...C distance being lower than 3.35 Å.

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## References

- 1 I.W. Bassi, C. Benedicenti, M. Calcaterra and G. Rucci, *J. Organometal. Chem.*, **117** (1976) 285.
- 2 W.S. Blond, R.D.W. Kemmitt and R.D. Moore, *J. Chem. Soc. Dalton, Trans.*, (1973) 1292.
- 3 F. Guerrieri, *Ital. Pat. Appl. class. 20878 A/70*, 1970.
- 4 G. Wilke and G. Herrman, *Angew. Chem.*, **74** (1962) 693.
- 5 G. Germain, P. Main and M.M. Woolfson, *Acta Crystallogr. A*, **27** (1971) 368.
- 6 A. Immirzi, *Ricerca Sci.*, **37** (1967) 743.
- 7 V. Vand, P.E. Eiland and R. Pepinsky, *Acta Crystallogr.*, **10** (1957) 303.
- 8 F.H. Moore, *Acta Crystallogr.*, **16** (1963) 1169.
- 9 D.W. Cruickshank, D.E. Pilling, A. Bujosa, F.M. Lovell and M.R. Truter, *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*, Pergamon Press, Oxford, 1961, p. 32.
- 10 C.K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A., 1970.
- 11 B. Barnett, B. Büssemeir, P. Heimbach, P.W. Jolly, C. Krüger, I. Tkatchenko and G. Wilke, *Tetrahedron Lett.*, **15** (1972) 1460.
- 12 P.W. Jolly, K. Jonas, C. Krüger and Y.H. Tsay, *J. Organometal. Chem.*, **33** (1971) 109.
- 13 C. Krüger and Y.H. Tsay, *Acta Crystallogr.*, **B**, **28** (1972) 1941.
- 14 I.W. Bassi and M. Calcaterra, *J. Organometal. Chem.*, **110** (1976) 129.
- 15 K. Krogmann and R. Mattes, *Angew. Chem. Internat. Edit.*, **5** (1966) 1046.
- 16 C. Fischer, K. Jonas and G. Wilke, *Angew. Chem.*, **85** (1973) 620.
- 17 K. Jonas, P. Heimbach and G. Wilke, *Angew. Chem.*, **80** (1968) 1033; *Angew. Chem., Int. Ed. Engl.*, **7** (1968) 949.
- 18 R.S. Dickson and J.A. Ibers, *J. Amer. Chem. Soc.*, **94** (1972) 2988.
- 19 O. Kennard, D.G. Watson, F.H. Allen, N.W. Isaacs, W.D.S. Motherwell, R.C. Pettersen and W.G. Town, *Molecular Structures and Dimensions*, Oosthoek, Utrecht, **1** (1972) S2.
- 20 J.D. Dunitz and J.A. Ibers, *Perspectives in structural chemistry*, vol. 3, Wiley, New York, 1960, p. 165-228.
- 21 A.I. Kitaigorodskii, *Organic Chemical Crystallography*, Consultants Bureau, New York, 1961, p. 107.