Chapter 6

Crystal and molecular structure of bis[1,3-di(*p*-*n*-octylphenyl)propane -1,3-dionato] palladium(II) and bis[1,3-di(*p*-*n*-octylphenyl)propane -1,3-dionato] nickel(II)

6.1 Introduction

As mentioned in Chapter 1, the organo-metallic series studied by us includes two palladium complexes. In the previous chapter, the crystal structure analysis of one of them *viz.*, Pd-$C_{10}H_{21}$ was described. It was pointed out (section 5.4.3, Chaptcr 5) tliat similarities existed between the structural characteristics of Pd-$C_{10}H_{21}$ and the P-form of the copper complex, Cu-C_8H_{17} (Chapter 4), despite the presence of longer decyl chains in the former. These observations prompted us to analyse the crystal structure of the lower homolog of Pd-$C_{10}H_{21}$, *viz.*, bis[1,3-di(*p*-*n*-octylphenyl)propane -1,3-dionato] palladium(II), i.e., Pd-C_8H_{17}. Figure 6.1 shows the structural formula of Pd-C_8H_{17}. It could be expected tliat similarities between Pd-C_8H_{17} and Cu-C_8H_{17}, to be much closer than between Pd-$C_{10}H_{21}$ and Cu-C_8H_{17}. The results presented in tliis chapter show tliat the complexes Pd-C_8H_{17} and the P-form of Cu-C_8H_{17} are in fact isomorphous.

Giroud-Godquin and Billard [1983] mention that bis[1,3-di(*p*-*n*-octylphenyl) propane -1,3-dionato] nickel(II) *i.e.*, Ni-C_8H_{17} (Figure 6.1) is nonmesogenic. In contrast, its copper and palladium analogs are found to exhibit discotic mesomorphism [Giroud-Godquin and Billard, 1981; Sadashiva and Rao]. As the only difference between these three complexes concerns tlie metal atom, it was of interest to find out the differences, if any, between the crystal structure of the reportedly nonmesogenic Ni-C_8H_{17} aiid those of the mesogenic Pd-C_8H_{17} and Cu-C_8H_{17}. Very interestingly, the crystal structure analysis of Ni-C_8H_{17} presented along with tliat of Pd-C_8H_{17} in this chapter is found to be isomorphous with Pd-C_8H_{17} aiid consequently with the P-form of Cu-C_8H_{17}.

Of the two crystal structures described in tliis chapter, tlie analysis on the

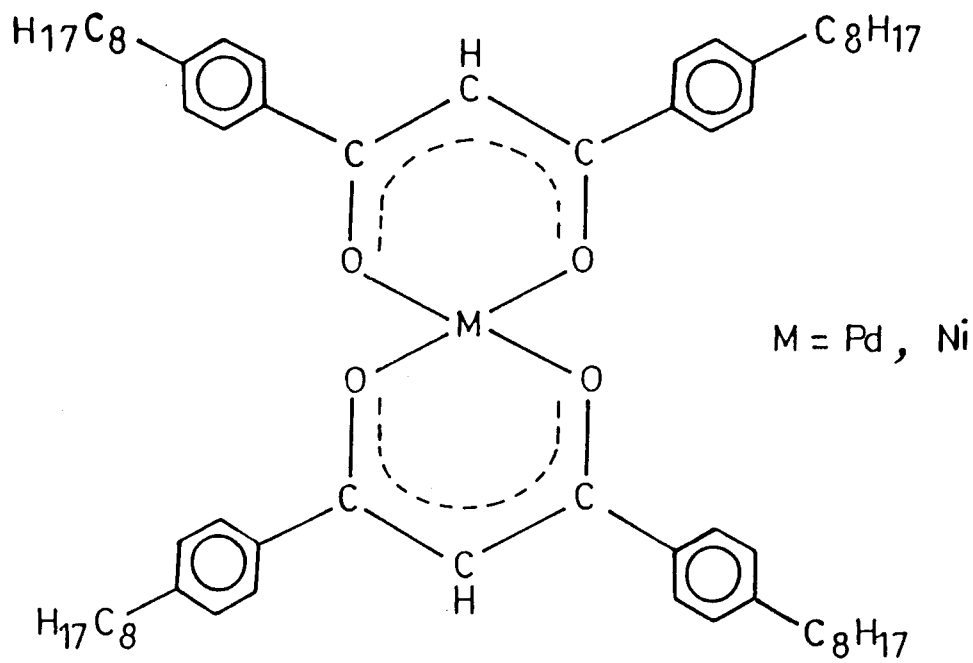


Figure 6.1: Structural formula.

palladium complex was carried out first and the study of the Ni-complex was carried out at a later stage.

6.2 Experimental details

Tlie transition temperatures observed for Pd-C_8H_{17} are as follows [Sadashiva and Rao]:

$$C \xrightarrow{120.5} D \xrightarrow{138^{\circ}C} I$$

Golden yellow, transparent, prismatic crystals of Pd-C_8H_{17} were grown by slow evaporation from a solution in butan-2-one. Red coloured, prismatic crystals of Ni-C_8H_{17} were also obtained by the same procedure but from a solution in acetone. Oscillation and Weissenberg photographs showed both tlie crystals to be triclinic. Tlie unit cell dimensions determined and refined on a diffractometer are listed in Table **6.1.** Tlie closeness of the unit cell constants suggest isomorphism between tlie two crystal structures. Comparison witli the unit cell constants of the P-form of Cu-C_8H_{17} (Table **4.1)** further suggests that botli Pd-C_8H_{17} and Ni-C_8H_{17} are isomorphous with the P-form of Cu-C_8H_{17}. Comparison of the intensities of reflections from the three crystals provided further evidence for their structural isomorphism. Tlie crystal data of Pd-C_8H_{17} and Ni-C_8H_{17} are presented in Table **6.1.**

Three dimensional intensity data from Pd-C_8H_{17} and Ni-C_8H_{17} were collected using a CAD4 diffractometer. Details of data collection are presented in Table 6.2.

Table 6.1: Crystal data of Pd-C_8H_{17} and Ni-C_8H_{17}.

	Pd-C_8H_{17}	Ni-C_8H_{17}
Molecular formula	$C_{62}H_{86}O_4Pd$	$C_{62}H_{86}O_4Ni$
Molecular weight	1001.7	954.0
a (Å)	10.318(2)	10.139(1)
b (Å)	11.537(1)	11.320(8)
c (Å)	13.089(2)	13.242(2)
α (°)	104.119(9)	101.919(8)
β (°)	94.73(1)	92.796(9)
γ (°)	108.88(1)	108.520(7)
V(Å^3)	1407	1399
Z	1	1
Space group	PI	P$\bar{1}$
ρ_{calc} (gm/cc)	1.174	1.125
μ_{CuK_α} (cm^{-1})	30.556	8.1136
$F_{(000)}$	536	518

Table 6.2: Details of data collection

Radiation used	CuK_α	CuK_α
Crystal size (mm^3)	0.25×0.13×0.2	0.23×0.18×0.08
Scan mode	$\omega/2\theta$	$\omega/2\theta$
Maximum Bragg angle	60^o	50^o
Unique reflections	4895	4105
Reflections with $I \geq 3\sigma(I)$	4099	1531
Ranges of h k l	0 to 12 -13 to 13 -15 to 15	0 to 11 -12 to 12 -14 to 14
Corrections applied	Lp and absorption	Lp

6.3 Structure solution

Although evidence from the unit cell dimensions and tlie intensity distributions was strongly in favour of structural isomorphism between Pd-C_8H_{17} and the P-form of Cu-C_8H_{17}, the isomorphous replacement method was not used to determine tlie crystal structure of Pd-C_8H_{17}. Conclusive and independent evidence for isomorphism was sought by solving the crystal structure of Pd-C_8H_{17} following procedures which do not depend on isomorphism.

The calculated density of Pd-C_8H_{17} (Table G.1) suggested **Z** to be 1. The palladium atom was placed at (0,0,0) and a difference Fourier map was computed. Positions of all the **33** other nonhydrogen atoms could be easily obtained from this map. Details of the subsequent refinement procedures are given in Figure 6.2.

In the case of the nickel complex, the isomorphous replacement method was used. Using the refined atomic coordinates of Pd-C_8H_{17} molecule as the starting set, the crystal structure of Ni-C_8H_{17} was refined by full matrix least squares method. Table **G.3** depicts the details concerning tlie weighting functions, R-factors, residual elcctron density, *etc.*

6.4 Results and discussion

Table **G.4** records tlie positional and the equivalent temperature factors (U_{eq}). Table G.5 lists the anisotropic thermal parameters U_{ij}'s . Parameters of the hydrogen atoms are given in Table 6.6. Their positional coordinates refer to tlie calculated values.

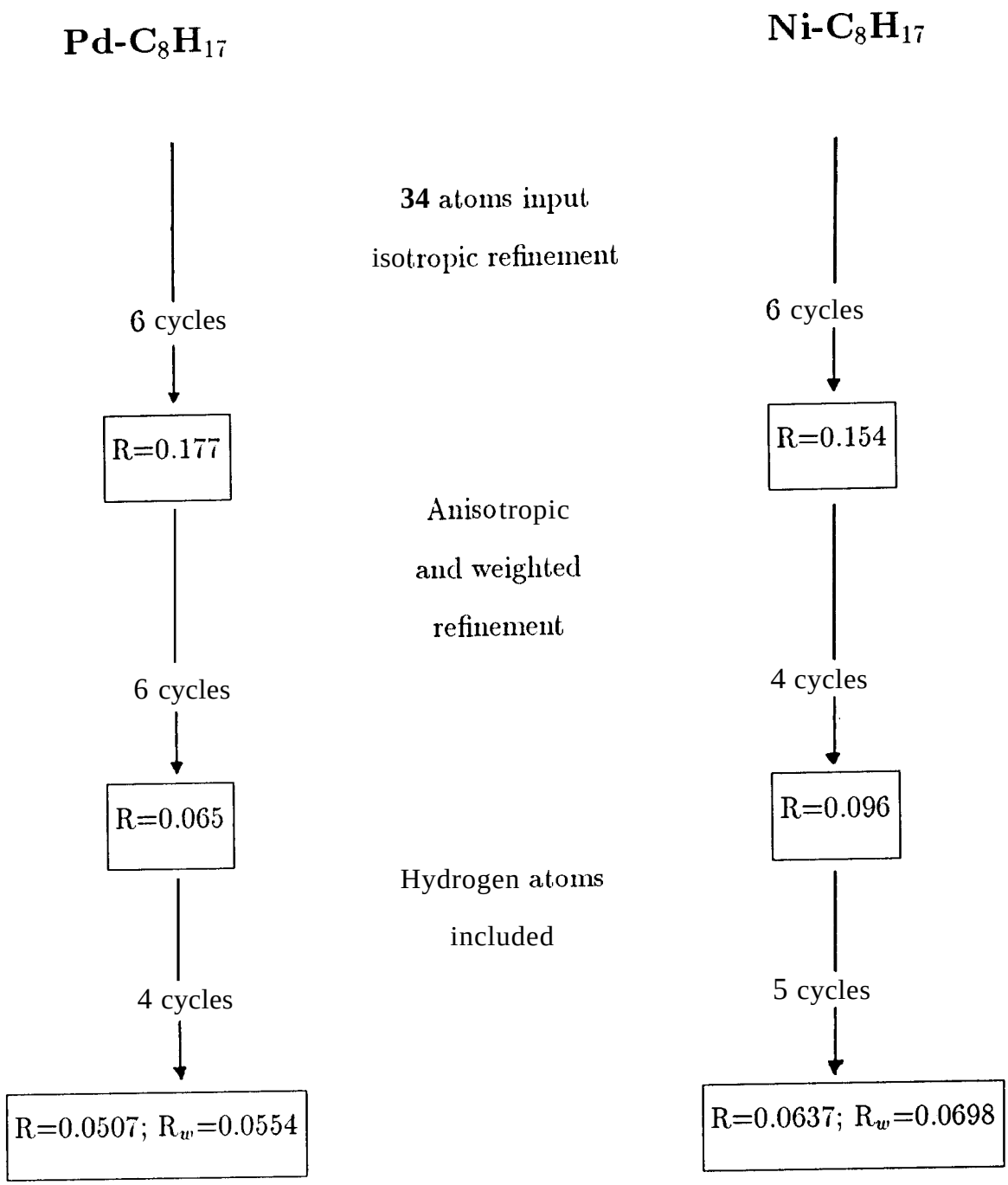


Figure 6.2: Details of the refinement procedure.

Table 6.3: Details of refinement

	Pd-C_8H_{17}	Ni-C_8H_{17}
Program used	SHELX-76	SHELX-76
Weighting scheme	$K/[\sigma^2(F) + g(F)^2]$	$K/[\sigma^2(F) + g(F)^2]$
K	18.1137	1.6927
g	0.00086	0.00193
R	0.0507	0.0637
R_w	0.0554	0.0693
Maximum shift/e.s.d	0.198	0.347
Residual electron density:		
ρ_{min} (el/Å^3)	-0.48	-0.29
ρ_{max} (el/Å^3)	0.59	0.19

Table 6.4: Final fractional atomic coordinates and $U_{eq}(Å)^2$ in Pd-C_8H_{17} and Ni-C_8H_{17}

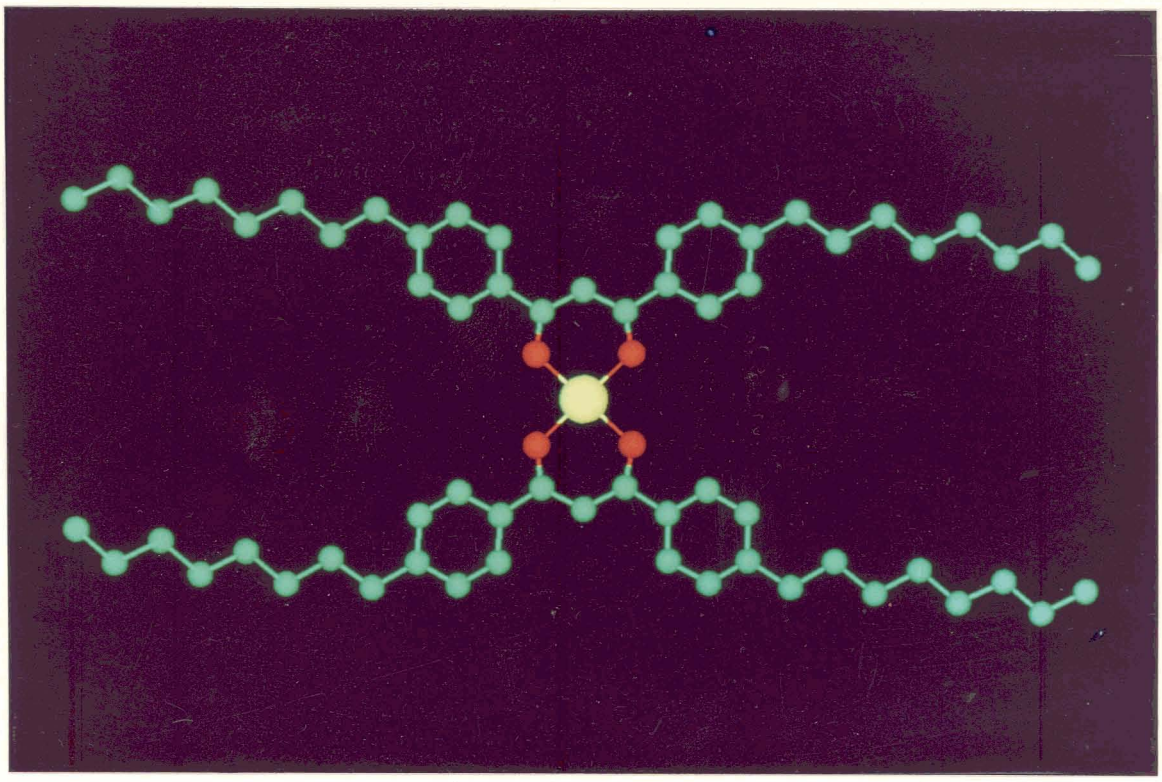
	Pd-C_8H_{17}				Ni-C_8H_{17}			
Atom	x	y	z	U_{eq}	x	y	z	U_{eq}
Pd/Ni	0.0000	0.0000	0.0000	0.0623(2)	0.0000	0.0000	0.0000	0.077(1)
O(1)	0.1953(3)	0.1103(3)	0.0145(3)	0.072(1)	0.1841(5)	0.1054(5)	0.0134(4)	0.079(3)
O(2)	0.0223(3)	-0.1481(3)	-0.0993(3)	0.072(1)	0.0246(5)	-0.1345(5)	-0.0910(4)	0.079(3)
C(3)	0.1327(5)	-0.1475(4)	-0.1361(4)	0.061(2)	0.1364(8)	-0.1385(9)	-0.1293(7)	0.073(4)
C(4)	0.2578(5)	-0.0407(4)	-0.1100(4)	0.064(2)	0.2621(8)	-0.036(1)	-0.1045(7)	0.075(4)
C(5)	0.2833(4)	0.0776(4)	-0.0374(4)	0.058(2)	0.2797(8)	0.076(1)	-0.0347(8)	0.070(4)
C(6)	0.4222(4)	0.1827(4)	-0.0157(4)	0.059(2)	0.4190(8)	0.1848(8)	-0.0114(7)	0.071(4)
C(7)	0.5372(5)	0.1627(5)	-0.0543(5)	0.076(2)	0.5390(9)	0.1696(8)	-0.0532(7)	0.088(4)
C(8)	0.6625(5)	0.2661(5)	-0.0338(5)	0.079(2)	0.6639(9)	0.272(1)	-0.0331(8)	0.091(5)
C(9)	0.6780(4)	0.3862(4)	0.0257(4)	0.064(2)	0.6754(8)	0.389(1)	0.0282(7)	0.075(4)
C(10)	0.5637(5)	0.4042(5)	0.0662(5)	0.071(2)	0.5567(9)	0.4038(8)	0.0707(7)	0.085(4)
C(11)	0.4378(5)	0.3045(4)	0.0462(4)	0.067(2)	0.4305(8)	0.301(1)	0.0509(7)	0.079(4)
C(12)	0.8175(5)	0.4942(5)	0.0438(5)	0.080(2)	0.8138(8)	0.4968(9)	0.0461(7)	0.085(4)
C(13)	0.8375(5)	0.6202(5)	0.1213(4)	0.069(2)	0.8301(8)	0.6196(9)	0.1219(7)	0.076(4)
C(14)	0.9873(5)	0.7156(5)	0.1372(5)	0.072(2)	0.9814(8)	0.7135(8)	0.1367(6)	0.076(4)
C(15)	0.0142(5)	0.8439(5)	0.2129(5)	0.073(2)	0.0051(8)	0.8418(9)	0.2102(7)	0.079(4)
C(16)	0.1659(5)	0.9348(5)	0.2282(5)	0.075(2)	0.1593(8)	0.9302(8)	0.2253(7)	0.081(4)
C(17)	0.1973(6)	0.0689(5)	0.2975(5)	0.082(2)	0.1843(9)	0.0618(9)	0.2947(7)	0.087(5)
C(18)	0.3467(7)	0.1576(6)	0.3127(6)	0.108(3)	0.337(1)	0.151(1)	0.3073(8)	0.117(5)
C(19)	0.3756(1)	0.2889(7)	0.3811(9)	0.144(5)	0.364(1)	0.281(1)	0.374(1)	0.153(7)
C(20)	0.1202(5)	-0.2682(4)	-0.2132(4)	0.065(2)	0.1205(8)	-0.2586(9)	-0.2044(7)	0.066(4)
C(21)	0.2305(5)	-0.3001(5)	-0.2501(5)	0.071(2)	0.2324(8)	-0.2894(9)	-0.2484(8)	0.076(4)
C(22)	0.2103(6)	-0.4180(5)	-0.3204(5)	0.079(2)	0.2102(8)	-0.404(1)	-0.3165(8)	0.086(5)
C(23)	0.0778(5)	-0.5093(5)	-0.3587(4)	0.070(2)	0.0768(9)	-0.4960(9)	-0.3485(8)	0.081(5)
C(24)	-0.0313(6)	-0.4755(5)	-0.3219(6)	0.090(3)	-0.0336(9)	-0.464(1)	-0.3050(8)	0.090(5)
C(25)	-0.0128(5)	-0.3629(5)	-0.2507(5)	0.085(2)	-0.0107(9)	-0.351(1)	-0.2352(8)	0.086(5)
C(26)	0.0553(6)	-0.6419(5)	-0.4340(5)	0.080(2)	0.0569(9)	-0.6193(9)	-0.4249(7)	0.083(4)
C(27)	-0.0921(6)	-0.7310(5)	-0.4670(5)	0.078(2)	-0.0935(9)	-0.7139(9)	-0.4506(7)	0.082(4)
C(28)	-0.111)	-0.8650(5)	-0.5381(5)	0.080(2)	-0.1083(9)	-0.840(1)	-0.5260(7)	0.091(5)
C(29)	-0.2630(7)	-0.9504(5)	-0.5649(5)	0.085(2)	-0.2580(9)	-0.9299(9)	-0.5498(7)	0.088(4)
C(30)	-0.2878(7)	-0.0875(5)	-0.6312(5)	0.083(2)	-0.277(1)	-0.060(1)	-0.6188(7)	0.097(5)
C(31)	- 0 4(7	-0.1723(6)	-0.6512(6)	0.094(3)	-0.427(1)	-0.150(1)	-0.6377(7)	0.100(5)
C(32)	-0.4641(8)	-0.3095(6)	-0.7171(6)	0.106(3)	-0.444(1)	-0.2823(1)	-0.7020(8)	0.115(6)
C(33)	-0.6084(1)	-0.3982(7)	-0.7258(8)	0.135(4)	-0.589(1)	-0.3730(1)	-0.715(1)	0.154(7)

Table 6.5(a): Anisotropic thermal parameters, U_{ij} of Pd-C_8H_{17}.

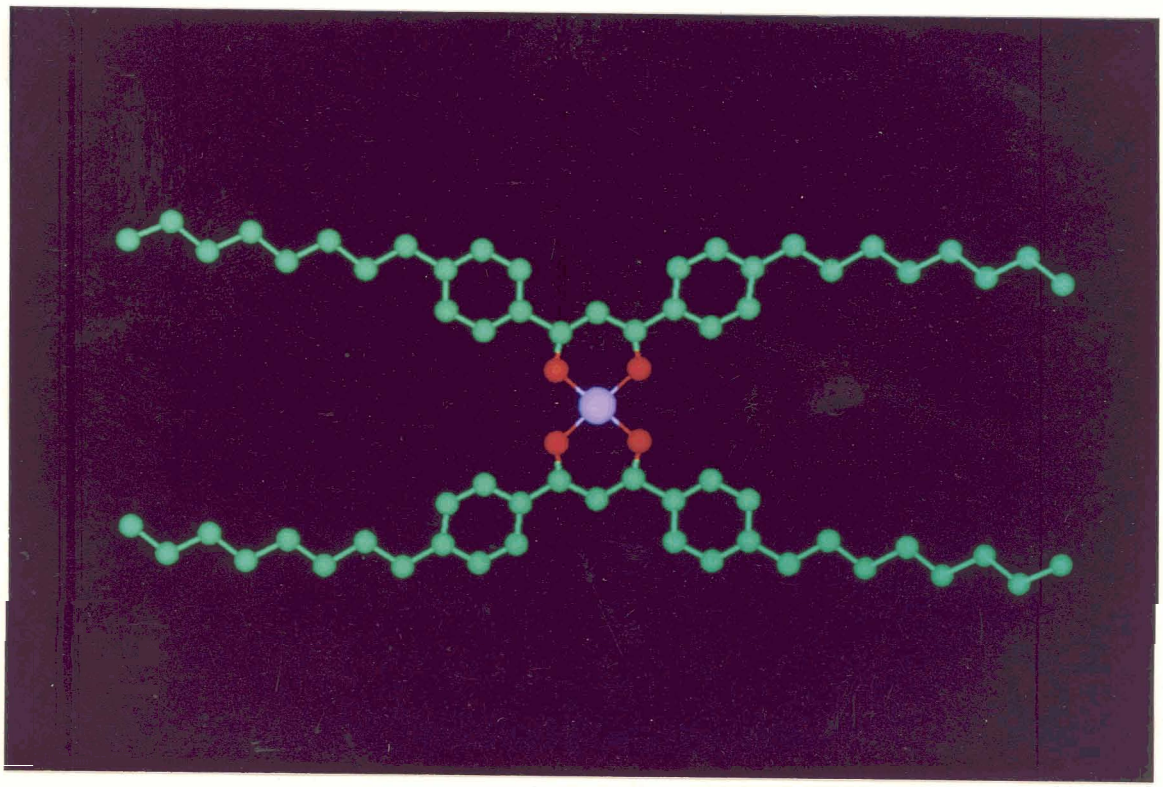
Atom	U_{11}	u 2 2	u 3 3	u 2 3	U_{13}	U_{12}
Pd	0.0392(3)	0.0507(3)	0.0822(4)	0.0134(2)	0.0113(2)	0.0009(2)
O(1)	0.047(2)	0.055(2)	0.098(3)	0.013(2)	0.016(2)	0.003(1)
O(2)	0.045(2)	0.048(2)	0.103(3)	0.010(2)	0.017(2)	-0.002(1)
C(3)	0.045(2)	0.053(2)	0.078(3)	0.019(2)	0.004(2)	0.010(2)
C(4)	0.044(2)	0.051(2)	0.089(3)	0.015(2)	0.011(2)	0.009(2)
C(5)	0.040(2)	0.050(2)	0.079(3)	0.022(2)	0.008(2)	0.007(2)
C(6)	0.037(2)	0.051(2)	0.079(3)	0.017(2)	0.004(2)	0.004(2)
C(7)	0.044(2)	0.053(3)	0.111(4)	0.009(3)	0.018(3)	0.001(2)
C(8)	0.042(2)	0.065(3)	0.108(4)	0.007(3)	0.022(2)	-0.001(2)
C(9)	0.041(2)	0.057(3)	0.079(3)	0.013(2)	0.006(2)	0.002(2)
C(10)	0.043(2)	0.052(2)	0.102(4)	0.013(2)	0.011(2)	0.004(2)
C(11)	0.042(2)	0.053(2)	0.097(4)	0.014(2)	0.012(2)	0.009(2)
C(12)	0.044(2)	0.067(3)	0.101(4)	0.006(3)	0.016(3)	-0.003(2)
C(13)	0.011(2)	0.056(3)	0.094(4)	0.022(2)	0.002(2)	-0.003(2)
C(14)	0.047(2)	0.055(3)	0.093(4)	0.015(2)	0.009(2)	-0.005(2)
C(15)	0.049(2)	0.061(3)	0.091(4)	0.019(3)	0.006(2)	0.005(2)
C(16)	0.054(3)	0.056(3)	0.093(4)	0.014(3)	0.009(3)	-0.001(2)
(1	0.066(3)	0.065(3)	0.096(4)	0.015(3)	0.002(3)	0.006(3)
C(18)	0.083(4)	0.075(4)	0.121(5)	0.004(4)	0.013(4)	-0.014(3)
C(19)	0.121(7)	0.071(4)	0.185(9)	0.006(5)	0.002(6)	-0.010(4)
C(20)	0.048(2)	0.049(2)	0.088(3)	0.018(2)	0.010(2)	0.005(2)
C(21)	0.046(2)	0.053(3)	0.099(4)	0.018(2)	0.005(2)	0.004(2)
C(22)	0.059(3)	0.072(3)	0.099(4)	0.018(3)	0.014(3)	0.018(3)
C(23)	0.058(3)	0.052(2)	0.090(4)	0.020(2)	0.007(3)	0.011(2)
C(24)	0.057(3)	0.064(3)	0.121(5)	-0.000(3)	0.010(3)	0.006(3)
C(25)	0.051(3)	0.055(3)	0.123(5)	0.000(3)	0.009(3)	0.004(2)
C(26)	0.077(3)	0.071(3)	0.084(4)	0.014(3)	0.012(3)	0.023(3)
C(27)	0.075(3)	0.057(3)	0.088(1)	0.009(3)	-0.001(3)	0.018(3)
C(28)	0.078(3)	0.061(3)	0.084(4)	0.010(3)	0.008(3)	0.014(3)
C(29)	0.080(4)	0.059(3)	0.097(4)	0.003(3)	0.004(3)	0.016(3)
C(30)	.	0.068(3)	0.088(4)	0.008(3)	0.006(3)	0.021(3)
C(31)	0.087(4)	0.068(3)	0.106(5)	0.001(3)	0.014(3)	0.014(3)
C(32)	0.094(5)	0.073(4)	0.119(5)	0.002(4)	0.020(4)	0.005(3)
C(33)	0.111(6)	0.081(1)	0.166(8)	0.003(5)	0.030(6)	-0.006(4)

Table 6.5(b): Anisotropic thermal parameters U_{ij} of Ni-C_8H_{17}.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	0.039(1)	0.081(2)	0.092(2)	0.019(1)	0.012(1)	-0.005(1)
O(1)	0.040(3)	0.070(4)	0.105(5)	0.008(3)	0.014(3)	-0.003(3)
O(2)	0.041(3)	0.074(4)	0.099(5)	0.004(4)	0.016(3)	-0.002(3)
C(3)	0.040(5)	0.078(7)	0.095(7)	0.024(6)	0.009(5)	0.007(5)
C(4)	0.045(5)	0.077(7)	0.085(7)	0.003(6)	0.019(4)	0.005(5)
C(5)	0.044(5)	0.071(6)	0.092(7)	0.032(6)	0.014(5)	0.004(5)
C(6)	0.011(5)	0.078(7)	0.083(7)	0.021(6)	0.007(5)	0.006(5)
C(7)	0.052(6)	0.073(6)	0.120(8)	-0.001(6)	0.018(5)	0.007(5)
C(8)	0.055(6)	0.086(7)	0.112(8)	0.004(7)	0.022(5)	0.004(6)
C(9)	0.042(5)	0.088(7)	0.087(7)	0.019(6)	0.006(5)	0.012(5)
C(10)	0.051(5)	0.064(6)	0.122(8)	0.008(5)	0.010(5)	0.005(5)
C(11)	0.044(5)	0.076(7)	0.104(8)	0.015(6)	0.014(5)	0.006(5)
C(12)	0.050(5)	0.065(6)	0.111(7)	0.000(6)	0.019(5)	-0.008(4)
C(13)	0.045(5)	0.073(6)	0.094(7)	0.028(6)	0.001(5)	-0.003(4)
C(14)	0.056(5)	0.058(6)	0.095(7)	0.011(5)	0.012(5)	-0.003(4)
C(15)	0.045(5)	0.087(7)	0.098(7)	0.031(6)	0.008(5)	0.006(5)
C(16)	0.061(6)	0.068(6)	0.100(7)	0.019(5)	0.015(5)	0.004(5)
C(17)	0.062(6)	0.079(7)	0.108(8)	0.015(6)	0.009(5)	0.011(5)
C(18)	0.093(8)	0.085(8)	0.132(9)	0.024(7)	-0.003(7)	-0.020(6)
C(19)	0.12(1)	0.092(9)	0.187(2)	0.013(9)	-0.005(9)	-0.026(8)
C(20)	0.044(5)	0.069(7)	0.085(7)	0.024(6)	0.010(5)	0.013(5)
C(21)	0.051(5)	0.065(6)	0.101(7)	0.014(6)	0.005(5)	0.007(5)
C(22)	0.053(6)	0.089(8)	0.107(8)	0.021(7)	0.027(5)	0.011(6)
C(23)	0.063(6)	0.072(7)	0.098(8)	0.024(6)	0.008(6)	0.008(5)
C(24)	0.050(5)	0.078(8)	0.120(8)	0.003(7)	0.011(6)	0.005(5)
C(25)	0.045(5)	0.077(7)	0.118(8)	0.012(7)	0.013(5)	0.004(5)
C(26)	0.072(6)	0.077(7)	0.090(7)	0.019(6)	0.018(5)	0.008(5)
C(27)	0.071(6)	0.073(7)	0.090(7)	0.018(6)	0.010(5)	0.014(5)
C(28)	0.083(7)	0.094(8)	0.082(7)	0.011(6)	0.009(5)	0.018(6)
C(29)	0.070(6)	0.072(7)	0.105(7)	0.001(6)	0.005(5)	0.014(5)
C(30)	0.082(7)	0.096(8)	0.101(8)	0.007(7)	0.016(6)	0.023(6)
C(31)	0.078(7)	0.090(8)	0.109(8)	-0.007(7)	0.014(6)	0.014(6)
C(32)	0.097(8)	0.100(9)	0.121(9)	-0.009(7)	0.022(7)	0.017(7)
C(33)	0.108(9)	0.113(9)	0.19(1)	-0.021(9)	0.030(8)	-0.003(8)



(a)



(b)

Figure 6.6: Molecular conformation in (a) Pd-C_8H_{17} (b) Ni-C_8H_{17}.

Table 6.6: Fractional atomic coordinates and the values of $U_{iso}(Å^2)$ of hydrogen atoms in Pd-C_8H_{17} and Ni-C_8H_{17}.

	Pd-C_8H_{17}				Ni-C_8H_{17}			
Atom	x	y	z	U_{iso}	x	y	z	U_{iso}
H(4)	0.3367	-0.0576	-0.1540	0.063	0.3507	-0.0485	-0.1479	0.072
H(7)	0.5313	0.0664	-0.0993	0.072	0.5361	0.0746	-0.1027	0.088
H(8)	0.7500	0.2500	-0.0709	0.081	0.7545	0.2554	-0.0684	0.089
H(10)	0.5737	0.4979	0.1172	0.069	0.5581	0.4999	0.1196	0.077
H(11)	0.3503	0.3233	0.0774	0.067	0.3425	0.3174	0.0898	0.076
H(21)	0.3345	-0.2296	-0.2225	0.070	0.3425	-0.2210	-0.2249	0.080
H(22)	0.3003	-0.4393	-0.3467	0.081	0.3000	-0.4252	-0.3502	0.084
H(24)	-0.1362	-0.5457	-0.3526	0.090	-0.1450	-0.5329	-0.3260	0.087
H(25)	-0.1026	-0.3436	-0.2205	0.085	-0.1046	-0.3317	-0.2031	0.082
H(121)	0.8420	0.5084	-0.0333	0.080	0.8427	0.5168	-0.0305	0.091
H(122)	0.9020	0.4616	0.0660	0.080	0.8995	0.4603	0.0656	0.091
H(131)	0.8148	0.6059	0.1974	0.074	0.8046	0.5989	0.1977	0.081
H(132)	0.7659	0.6603	0.0913	0.074	0.7594	0.6646	0.0941	0.081
H(141)	1.0130	0.7267	0.0604	0.076	1.0092	0.7260	0.0586	0.082
H(142)	1.0606	0.6745	0.1653	0.076	1.0521	0.6658	0.1628	0.082
H(1510	0.9898	0.8328	0.2903	0.075	0.9760	0.8276	0.2865	0.081
H(152)	0.9454	0.8870	0.1835	0.075	0.9395	0.8904	0.1807	0.081
H(161)	1.1945	0.9373	0.1508	0.080	1.1917	0.9396	0.1478	0.088
H(162)	1.2353	0.8938	0.2624	0.080	1.2260	0.8839	0.2574	0.088
H(171)	1.1699	1.0663	0.3759	0.085	1.1546	1.0529	0.3706	0.095
H(172)	1.1292	1.1102	0.2633	0.085	1.1181	1.1079	0.2613	0.095
H(181)	1.3742	1.1620	0.2338	0.115	1.3716	1.1593	0.2296	0.114
H(182)	1.4160	1.1155	0.3466	0.115	1.4072	1.1074	0.3411	0.114
H(261)	0.1179	-0.6871	-0.3972	0.085	0.1207	-0.6747	-0.3998	0.092
H(262)	0.1000	-0.6308	-0.5058	0.085	0.0936	-0.6063	-0.5007	0.092
H(271)	-0.1524	-0.6889	-0.5073	0.083	-0.1581	-0.6665	-0.4845	0.090
H(272)	-0.1360	-0.7417	-0.3949	0.083	-0.1320	-0.7321	-0.3777	0.090
H(281)	-0.0503	-0.9079	-0.4981	0.084	-0.0428	-0.8865	-0.4916	0.090
H(282)	-0.0719	-0.8553	-0.6131	0.084	-0.0672	-0.8206	-0.5981	0.090
H(291)	-0.3226	-0.9095	-0.6094	0.093	-0.3216	-0.8851	-0.5875	0.097
H(292)	-0.3037	-0.9536	-0.4916	0.093	-0.3007	-0.9423	-0.4770	0.097
H(301)	-0.2239	-1.1272	-0.5903	0.088	-0.2089	-1.1028	-0.5819	0.099
H(302)	-0.2523	-1.0853	-0.7086	0.088	-0.2370	-1.0477	-0.6923	0.099
H(311)	-0.5009	-1.1341	-0.6959	0.102	-0.4918	-1.1100	-0.6774	0.107
H(312)	-0.4732	-1.1738	-0.5766	0.102	-0.4662	-1.1588	-0.5639	0.107
H(321)	-0.3886	-1.3430	-0.6796	0.114	-0.3750	-1.3264	-0.6661	0.123
H(322)	-0.4383	-1.3097	-0.7967	0.114	-0.4156	-1.2808	-0.7811	0.123
H(191)	1.4811	1.3513	0.3929	0.151	1.4711	1.3443	0.3815	0.150
H(102)	1.3074	1.3321	0.3486	0.151	1.2976	1.3282	0.3386	0.150
H(193)	1.3493	1.2853	0.4618	0.151	1.3333	1.2762	0.4503	0.150
H(331)	-0.6226	-1.4955	-0.7719	0.152	-0.6010	-1.4664	-0.7570	0.150
H(332)	-0.6321	-1.4010	-0.6467	0.152	-0.6187	-1.3775	-0.6346	0.150
H(333)	-0.6824	-1.3673	-0.7650	0.152	-0.6591	-1.3322	-0.7487	0.150

6.4.1 Thermal parameters

Figure 6.3 shows tlie thermal ellipsoids of tlie atoms of both tlie complexes. As in the crystal structures described in tlie preceding chapters, thermal parameters of the terminal atoms in tlie chains are tlie liighest. In Table 6.7, average U_{eq} values of tlie core, the phenyl rings and tlie chains of both tlie crystal structures are compared. Tlie corresponding value observed for the P-form of Cu-C_8H_{17} have also been included in Table 6.7 to enable comparison.

It is observed that although tlie U_{eq} values characterizing the nickel complex are marginally higher than tliose of Pd-C_8H_{17}, the observed differences are not statistically significant,. In contrast, tlie average U_{eq} values of the core of the nickel and copper complexes exhibit significant differences. On moving towards the phenyl rings and the octyl chains, the differences tend to be less significant. Comparison of the thermal parameters of the homologous Pd-C_8H_{17} and Pd-$C_{10}H_{21}$ also shows (Table 6.8) that despite the increase in tlie chain length, tlie thermal parameters of the latter arc lower than tliose of tlie former.

6.4.2 Molecular dimensions

Tlie dimensions of the square planar coordination polyhedron around the metal atoms are presented in Figure 6.4. The Pd-O lengths average to 1.9695(5)Å and Ni-O lengths average to 1.837(8)Å. Tlie observed reduction in the latter value is commensurate with the corresponding reduction in tlie single bond metallic radii (Single bond metallic radii for palladium and nickel are 1.283Å and 1.154Å [Pauling, 1967].

Tlie bond lengths and valence angles and their average values are listed in

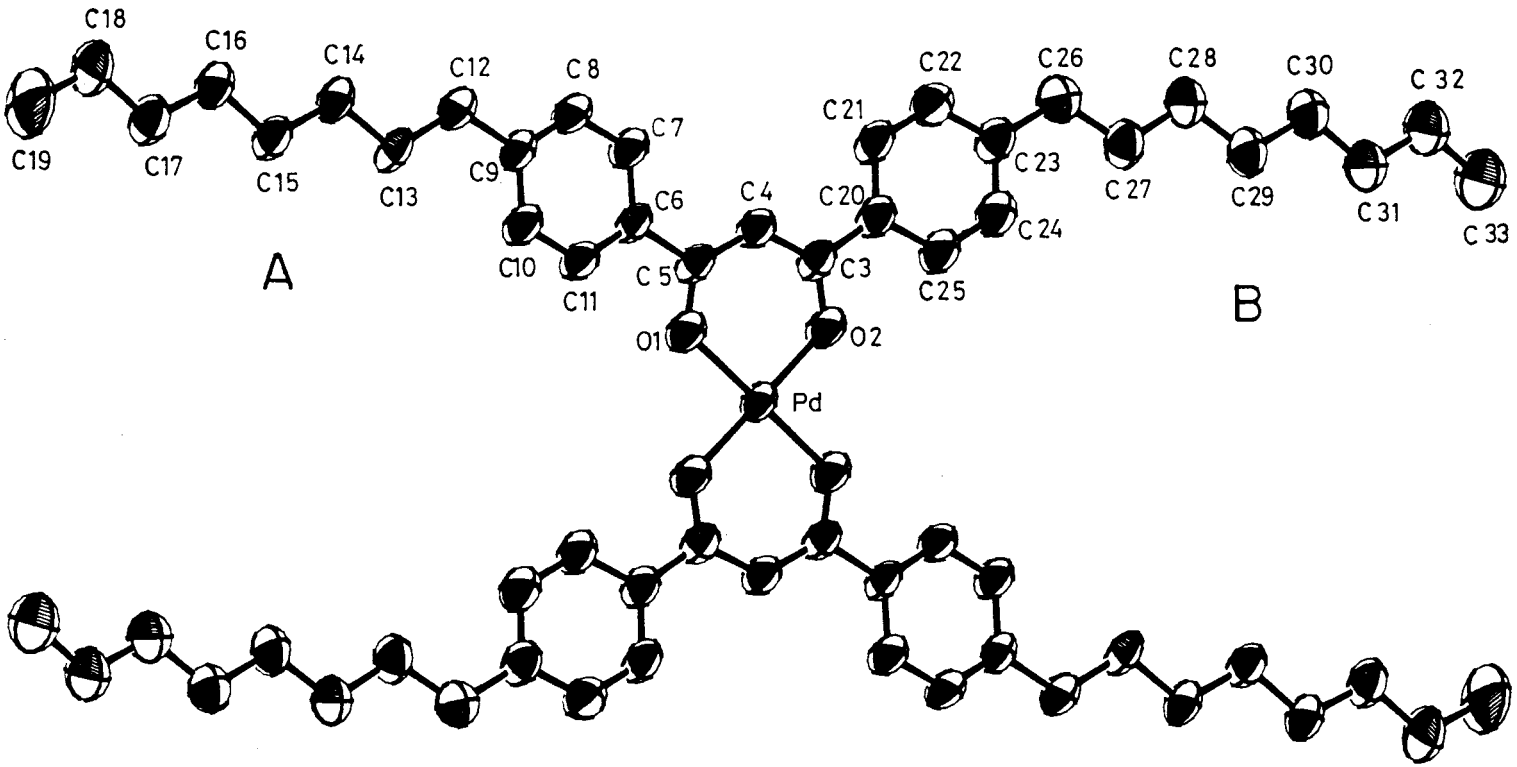


Figure 6.3(a): ORTEP diagram of the thermal ellipsoids drawn with 50% probability for Pd-C_8H_{17}.

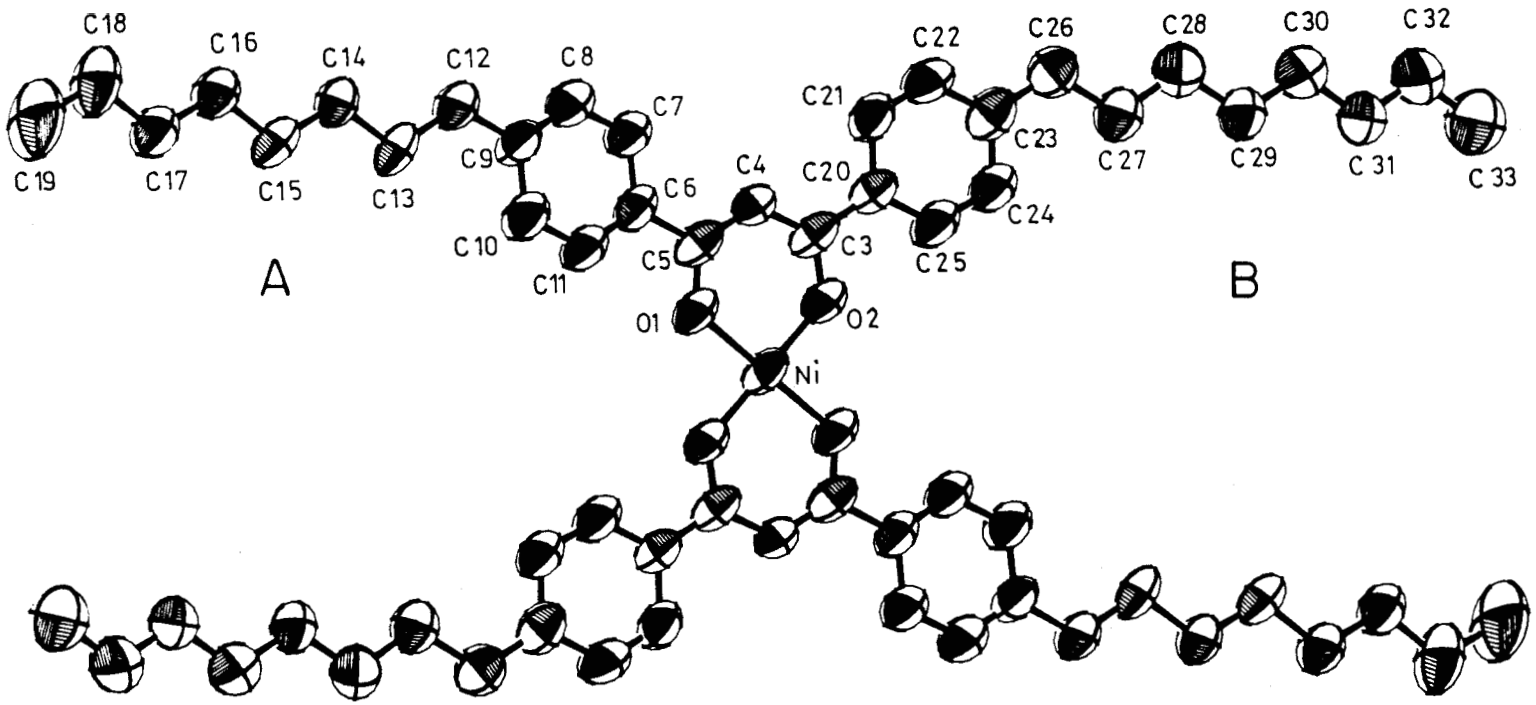


Figure 6.3(b): ORTEP diagram of the thermal ellipsoids drawn with 50% probability for Ni-C_8H_{17}.

Table 6.7: Average $U_{eq}(Å^2)$ values in Pd-C_8H_{17}, Ni-C_8H_{17} and P form of Cu-C_8H_{17}.

	Pd-C_8H_{17}	Ni-C_8H_{17}	P-form of Cu-C_8H_{17}
Core	0.065(5)	0.075(3)	0.061(6)
Phenyl ring A	0.069(7)	0.082(7)	0.062(7)
B	0.077(9)	0.081(8)	0.069(7)
Chain **A**	0.09(2)	0.09(3)	0.08(2)
B	0.09(2)	0.10(2)	0.09(2)

Table 6.8: Average $U_{eq}(Å^2)$ values in Pd-C_8H_{17} and Pd-$C_{10}H_{21}$.

	Pd-C_8H_{17}	Pd-$C_{10}H_{21}$
Core	0.065(5)	0.048(5)
Phenyl ring A	0.069(7)	0.059(9)
B	0.077(9)	0.053(4)
Chain A	0.09(2)	0.07(2)
B	0.09(2)	0.07(2)

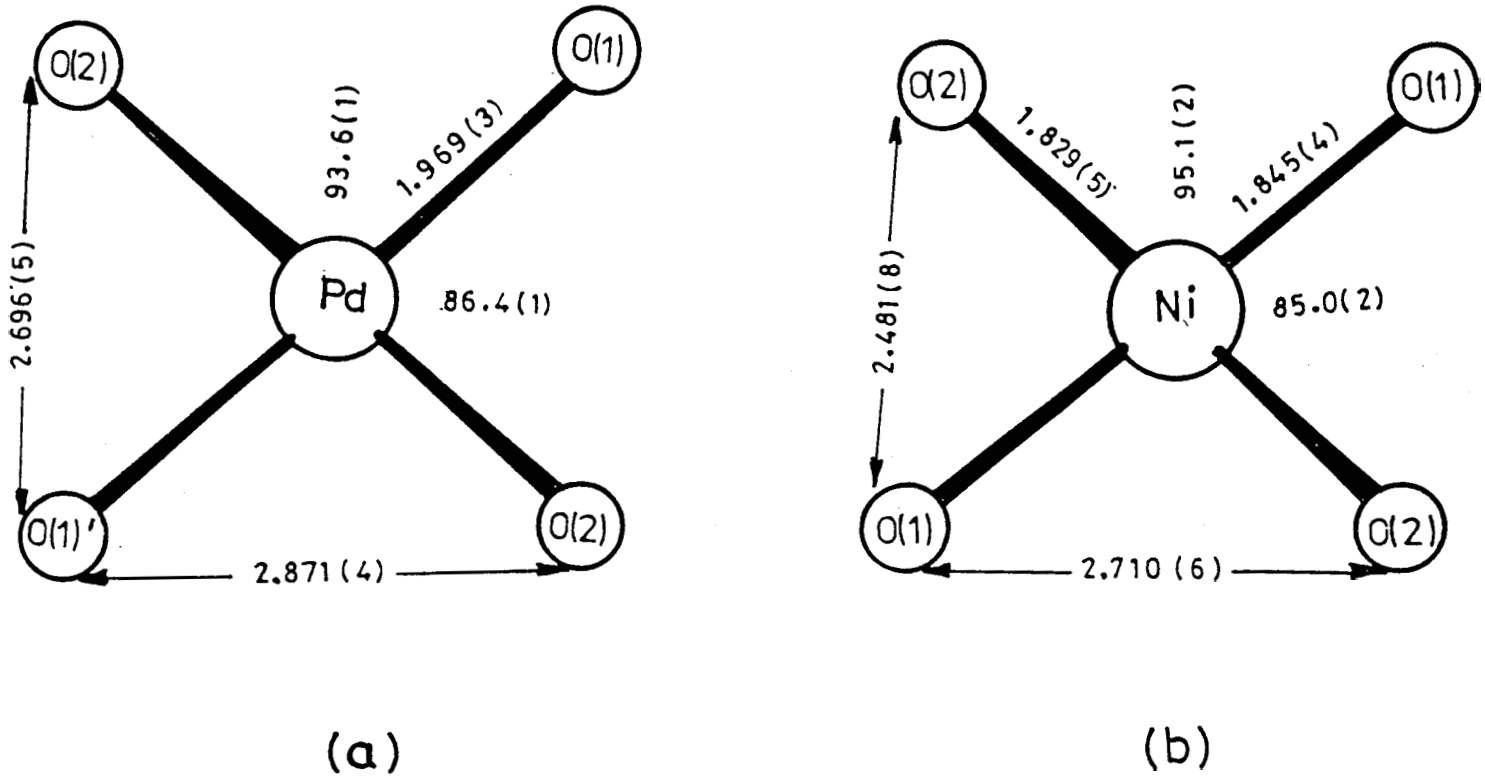


Figure 6.4: Coordination polyhedron around the copper atom in (a) Pd-C_8H_{17} (b) Ni-C_8H_{17}

Table 6.9(a), (b) and (c) respectively. Within the limits of experimental errors, the dimensions coultl be considered normal.

Tlie angle, η, between the M-O-C-C groups in each half of tlie molecular core is 2.8° in Pd-C_8H_{17} and 3.1" in Ni-C_8H_{17}. Figure 6.5 shows tlie displacements δ's of atoms from the planes through tlie respective cores.

6.4.3 Molecular conformation

Figure 6.6(a) and (11) depict the molecular conformations of Pd-C_8H_{17} and Ni-C_8H_{17} respectively. Tlie phenyl rings in both tlie molecules are tilted with respect to tlie core. Tlie angles of the tilt being 8 and 12" in the palladium complex and 5 and 7" in tlie nickel complex. Tlie corresponding tilts for tlie octyl chains are 3 and 12° in the palladium complex and 3 and 7° in the nickel complex. Tlie octyl chains are fully extended in an all-*trans* conformation (Table 6.10). In this conformation, the end-to-end dimensions of the molecules (Table 6.11) resemble model B of Ohta et *al*, [1986]. Table 6.11 includes the dimensions of the isomorphous P-form of Cu-C_8H_{17} also. A superposition of tlie molecular conformations of tlie three isomorphous complexes *i*.e., P-form of Cu-C_8H_{17}, Pd-C_8H_{17} and Ni-C_8H_{17} is shown in Figure 6.7.

6.4.4 Molecular packing

In Figure 6.8, stereo views of tlie molecular packing as seen down the respective crystallographic a-axes are presentcd. As in tlie case of P-form of Cu-C_8H_{17}, tlie molecular arrangement is essentially layer-like (Figure 6.9). Tlie layer structure is stabilized by nonbonded interactions of the type core...chain, phenyl

Table 6.9(a): Bond lengths (Å) in in Pd-C_8H_{17} and Ni-C_8H_{17}.

	Pd-C_8H_{17}	Ni-C_8H_{17}		Pd-C_8H_{17}	Ni-C_8H_{17}
M-O(1)	1.969(3)	1.829(5)	C(15)-C(16)	1.541(6)	1.54(1)
M-O(2)	1.970(3)	1.845(4)	C(16)-C(17)	1.504(7)	1.52(1)
O(1)-C(5)	1.276(6)	1.28(1)	C(17)-C(18)	1.513(8)	1.54(1)
O(2)-C(3)	1.272(6)	1.27(1)	C(18)-C(19)	1.48(1)	1.49(2)
C(3)-C(4)	1.412(6)	1.39(1)	C(20)-C(21)	1.393(8)	1.39(1)
C(3)-C(20)	1.466(6)	1.47(1)	C(20)-C(25)	1.406(6)	1.41(1)
C(4)-C(5)	1.388(6)	1.36(1)	C(21)-C(22)	1.384(8)	1.36(1)
C(5)-C(6)	1.497(5)	1.52(1)	C(22)-C(23)	1.388(6)	1.40(1)
C(6)-C(11)	1.391(6)	1.37(1)	C(23)-C(24)	1.390(9)	1.40(1)
C(6)-C(7)	1.392(8)	1.41(1)	C(23)-C(26)	1.538(7)	1.49(1)
C(7)-C(8)	1.398(6)	1.39(1)	C(24)-C(25)	1.346(8)	1.36(1)
C(8)-C(9)	1.365(7)	1.37(1)	C(26)-C(27)	1.491(7)	1.53(1)
C(9)-C(10)	1.388(8)	1.40(1)	C(27)-C(28)	1.537(8)	1.52(1)
C(9)-C(12)	1.523(6)	1.51(1)	C(28)-C(29)	1.510(8)	1.51(1)
C(10)-C(11)	1.382(6)	1.40(1)	C(29)-C(30)	1.534(8)	1.52(1)
C(12)-C(13)	1.496(7)	1.49(1)	C(30)-C(31)	1.502(9)	1.51(1)
C(13)-C(14)	1.543(6)	1.54(1)	C(31)-C(32)	1.531(9)	1.52(1)
C(14)-C(15)	1.491(8)	1.51(1)	C(32)-C(33)	1.49(1)	1.48(1)

Table 6.9(b): Bond angles(°) of Pd-C_8H_{17} and Ni-C_8H_{17}.

	Pd-C_8H_{17}	Ni-C_8H_{17}		Pd-C_8H_{17}	Ni-C_8H_{17}
O(1)-M-O(2)′	86.4(1)	88.5(2)	C(12)-C(13)-C(14)	111.6(5)	111.5(7)
O(1)-M-O(2)	93.6(1)	95.1(2)	C(15)-C(14)-C(13)	114.4(5)	114.6(7)
O(2)-M-O(2)′	180.0(1)	180.0(2)	C(14)-C(15)-C(16)	112.6(5)	112.4(7)
O(1)-M-O(1)′	180.0(1)	180.0(2)	C(17)-C(16)-C(15)	115.3(5)	113.4(7)
C(5)-O(1)-M	124.5(3)	124.8(6)	C(16)-C(17)-C(18)	115.1(5)	113.1(8)
C(3)-O(2)-M	125.0(3)	127.4(6)	C(19)-C(18)-C(17)	114.3(7)	114.0(9)
O(2)-C(3)-C(4)	124.7(5)	123.0(8)	C(21)-C(20)-C(25)	116.2(5)	115.8(9)
O(2)-C(3)-C(20)	114.4(4)	114.4(8)	C(21)-C(20)-C(3)	125.5(5)	124.2(8)
C(4)-C(3)-C(20)	120.9(4)	122.7(8)	C(25)-C(20)-C(3)	118.3(5)	120.1(9)
C(5)-C(4)-C(3)	126.4(5)	123.8(9)	C(22)-C(21)-C(20)	122.0(5)	121.0(9)
O(1)-C(5)-C(4)	125.6(4)	125.8(9)	C(21)-C(22)-C(23)	121.0(6)	122.9(9)
O(1)-C(5)-C(6)	113.3(4)	112.5(8)	C(22)-C(23)-C(24)	116.3(5)	123.3(9)
C(4)-C(5)-C(6)	121.0(4)	121.6(9)	C(22)-C(23)-C(26)	121.2(5)	115.7(9)
C(11)-C(6)-C(7)	118.5(5)	118.3(9)	C(24)-C(23)-C(26)	122.5(5)	121.1(9)
C(11)-C(6)-C(5)	119.1(4)	120.5(8)	C(25)-C(24)-C(23)	123.3(6)	121(1)
C(7)-C(6)-C(5)	122.4(4)	121.2(8)	C(24)-C(25)-C(20)	121.1(6)	123(1)
C(6)-C(7)-C(8)	119.3(5)	120.0(9)	C(27)-C(26)-C(23)	115.3(5)	116.0(8)
C(9)-C(8)-C(7)	122.5(5)	122.0(9)	C(26)-C(27)-C(28)	114.5(5)	114.2(8)
C(8)-C(9)-C(10)	117.7(5)	118.2(9)	C(29)-C(28)-C(27)	111.1(5)	112.5(8)
C(8)-C(9)-C(12)	119.4(5)	119.4(9)	C(28)-C(29)-C(30)	113.3(5)	114.4(8)
C(10)-C(9)-C(12)	122.9(5)	122.4(8)	C(31)-C(30)-C(29)	112.2(6)	113.1(8)
C(11)-C(10)-C(9)	121.3(5)	120.3(9)	C(30)-C(31)-C(32)	112.7(6)	112.8(9)
C(10)-C(11)-C(6)	120.7(5)	121.3(9)	C(33)-C(32)-C(31)	113.3(7)	112.9(9)
C(13)-C(12)-C(9)	118.1(5)	119.1(8)			

Table 6.9(c): Average bond lengths(Å) and valence angles(°) along with the values given by Allen et *al*, [1987].

	bond lengths		values given by Allen et *al*		bond angles	
	Pd-C_8H_{17}	Ni-C_8H_{17}			Pd-C_8H_{17}	Ni-C_8H_{17}
Core:						
M-O	1.9695(5)	1.837(8)		O-M-O	93.6(1)	95.1(2)
O-C_{ar}(core)	1.274(2)	1.275(5)		M-O-C_{ar}	124.8(4)	126(1)
Car-Car (core)	1.4(1)	1.38(2)		O-C_{ar}-C_{ar}	125.2(5)	124(1)
				Car-Car-Car	126.4(5)	123.8(9)
Phenyl ring:						
A	1.39(1)	1.39(2)	1.380(13)		120(2)	120(1)
B	1.38(2)	1.39(2)			120(3)	120(3)
Chain:						
A	1.52(2)	1.52(2)	1.530(15)		114(1)	113(1)
B	1.52(2)	1.518(7)			113(1)	113.3(7)
C_{core}-C_{phenyl}	1.48(2)	1.50(3)		C_{phenyl}-C_{sp^3}-C_{sp^3}	117(1)	118(2)
C_{sp^3}-C_{phenyl}	1.531(8)	1.50(1)	1.513(14)			

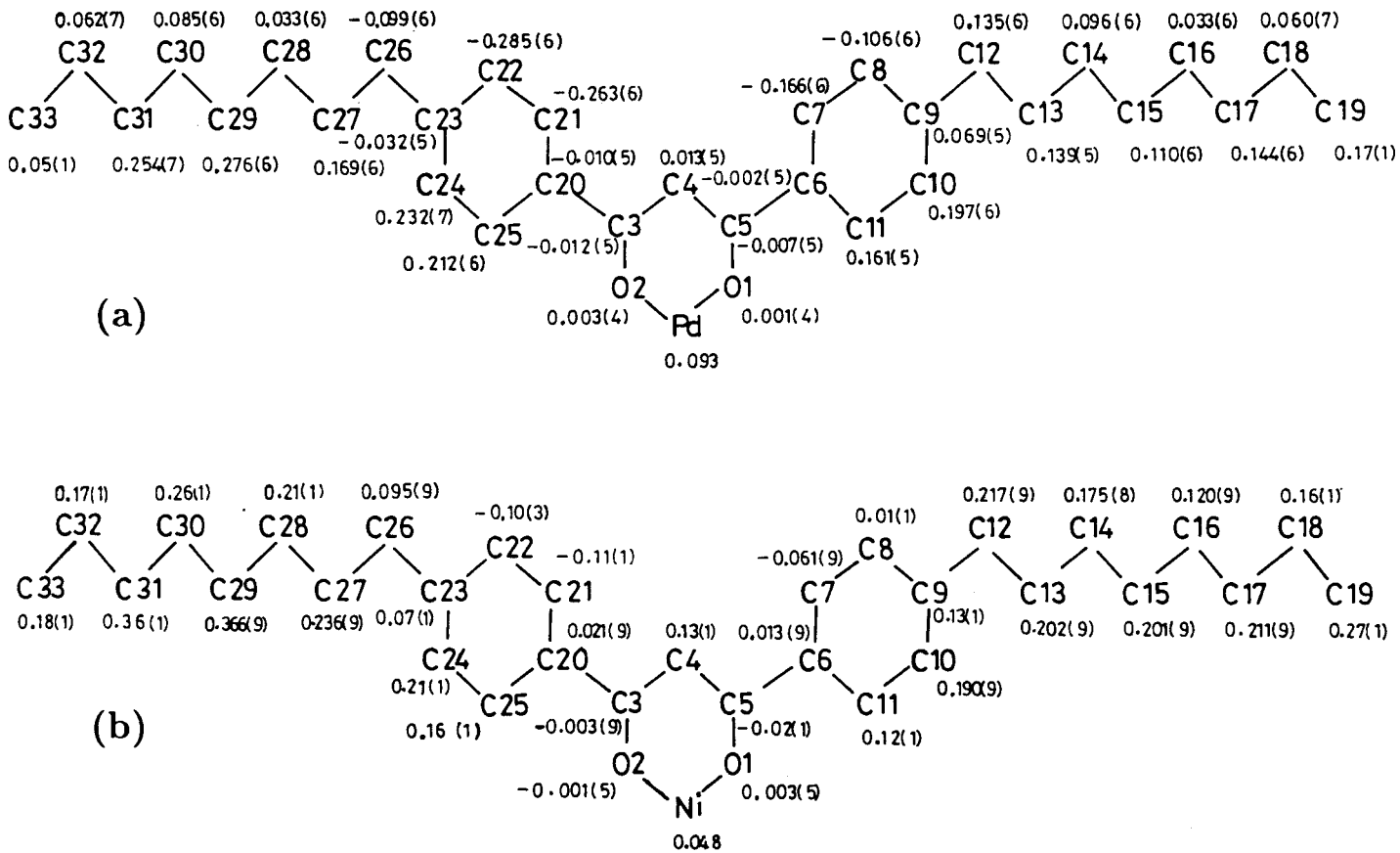


Figure 6.5: Displacements, δ's, of all the nonhydrogen atoms of the molecule from the plane through the crystallographically independent half of the core. (a) Pd-C_8H_{17} (b) Ni-C_8H_{17}.

Table 6.10: Observed torsional angles(°) in the chains of Pd-C_8H_{17} and Ni-C_8H_{17}.

	Pd-C_8H_{17}	Ni-C_8H_{17}
C(9)-C(12)-C(13)-C(14)	175.5(5)	175.0(8)
C(12)-C(13)-C(14)-C(15)	179.5(5)	178.3(7)
C(13)-C(14)-C(15)-C(16)	178.7(5)	177.9(7)
C(14)-C(15)-C(16)-C(17)	175.7(5)	177.2(7)
C(15)-C(16)-C(17)-C(18)	179.7(5)	-178.6(8)
C(16)-C(17)-C(18)-C(19)	-179.9(6)	179.1(9)
C(23)-C(26)-C(27)-C(28)	-177.3(5)	-178.0(8)
C(26)-C(27)-C(28)-C(29)	178.1(5)	-179.6(8)
C(27)-C(28)-C(29)-C(30)	-177.2(5)	-176.1(8)
C(28)-C(29)-C(30)-C(31)	176.6(6)	177.7(8)
C(29)-C(30)-C(31)-C(32)	-179.8(6)	-176.9(8)
C(30)-C(31)-C(32)-C(33)	172.7(7)	176.1(9)

Table 6.11: Comparison of the end-to-elid molecular dimensions in the three isomorphous crystals.

	Length(Å)	Width(Å)
Pd-C_8H_{17}	30.2	9.7
Ni-C_8H_{17}	30.3	9.5
P-form of Cu-C_8H_{17}	30.3	9.6

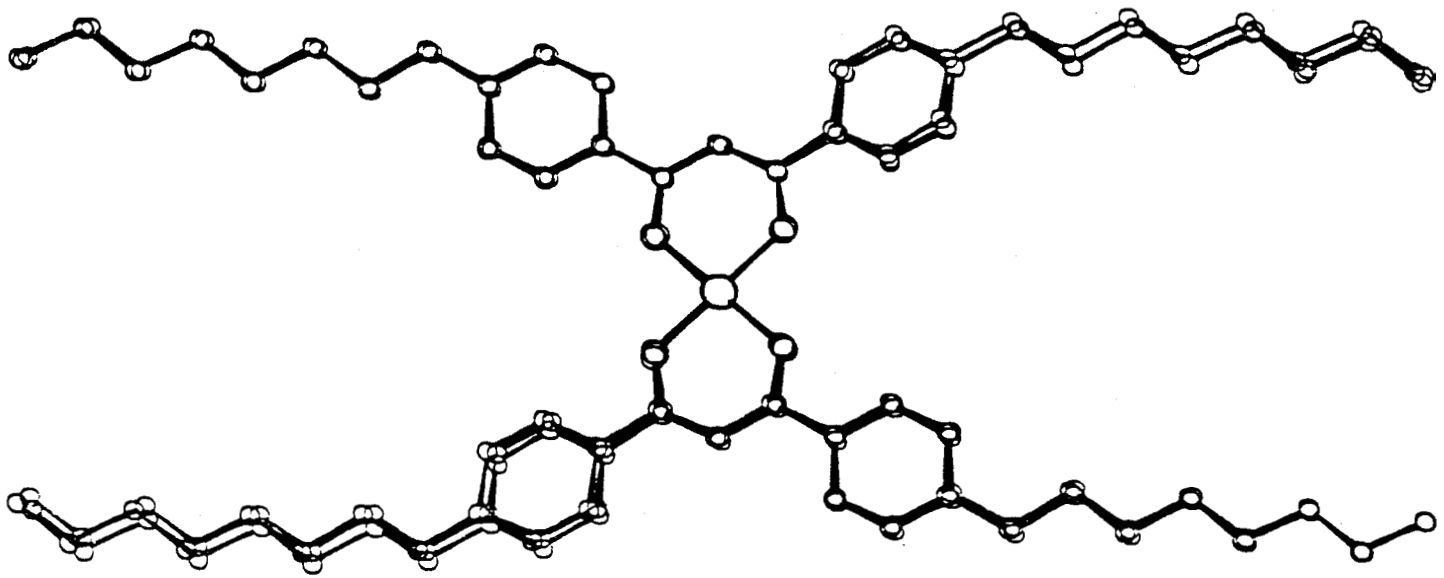
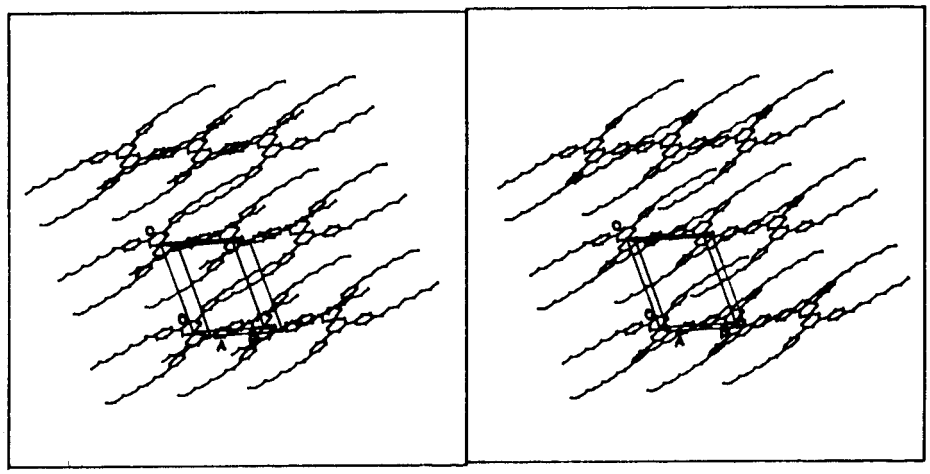
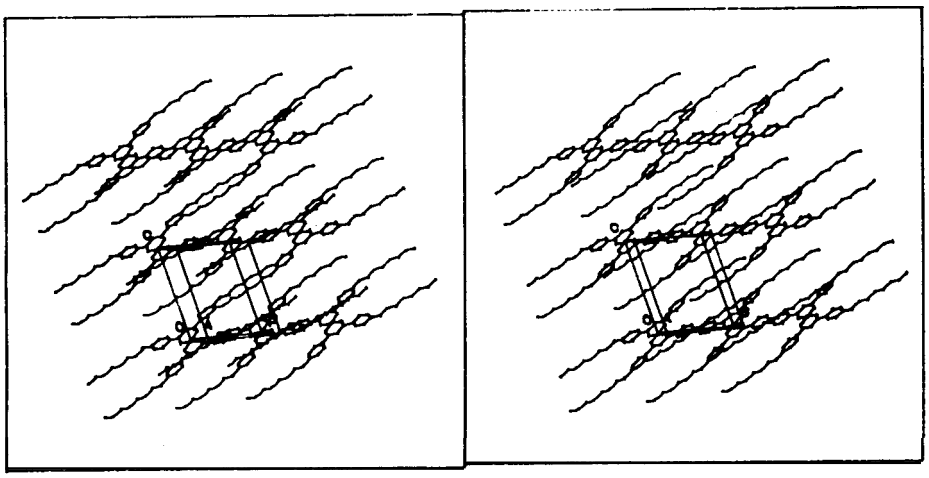


Figure 6.7: Superposition of the three isomorphous structures.



(a)



(b)

Figure 6.8: Stereo view of the molecules seen down the a-axis. (a) Pd-C_8H_{17} (b) Ni-C_8H_{17}.

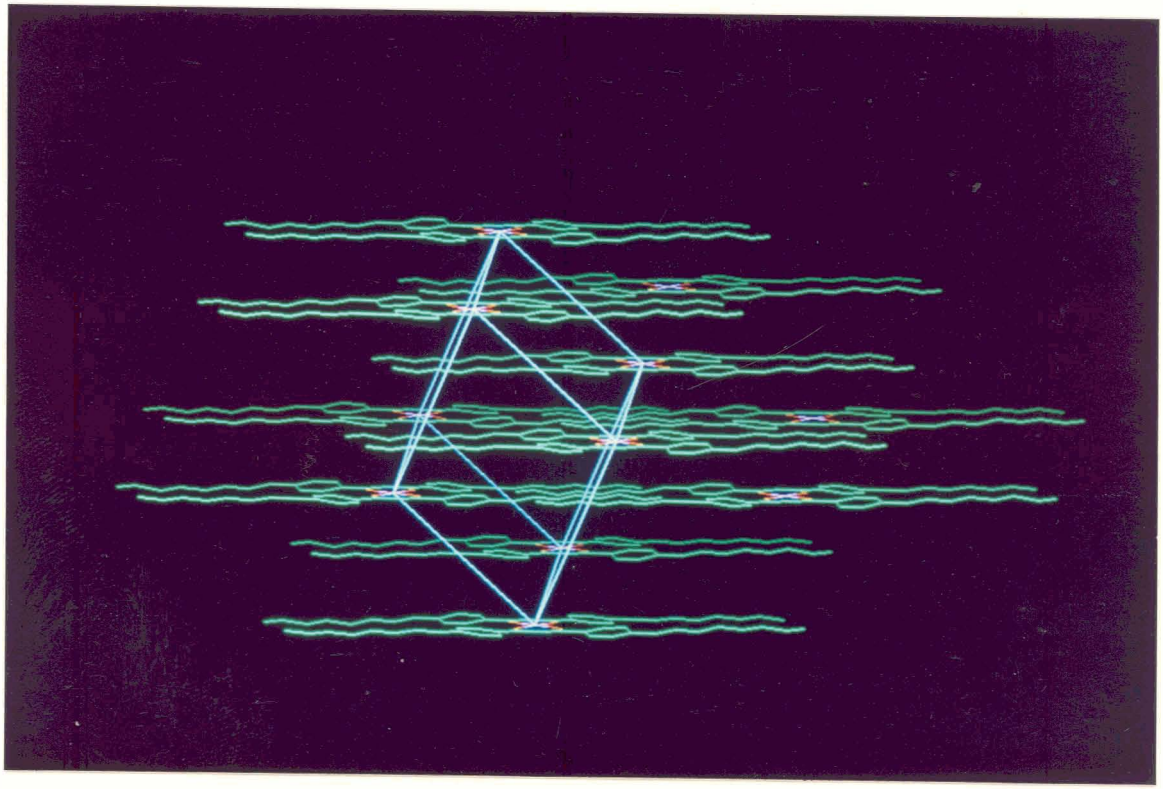


Figure 6.9: Layer structure observed in Ni-C_8H_{17}.

ring...phenyl ring, phenyl ring..l i i i and l i i i . ..chain. Regular stacking of the layers along the crystallographic a-axis introduces the columnar structure (Figure 6.10). The lilts of the cores of the palladium and nickel complexes with respect to the column axis are 112 and 111° respectively (Figure 6.11). The columnar structure is stabilized by nonbonded interactions which are of tlie core...phenyl ring, phenyl ring...phenyl ring, phenyl ring...chain and chain...chain type. Each column in the crystal is surrounded by six others situated at $\pm\vec{b}$, $\pm(\overrightarrow{b+c})$ and $\pm(\overrightarrow{2b+c})$.

However, tlie crystal structure analysis of Pd-C_8H_{17} and Ni-C_8H_{17} have conclusively established their isomorphism with the P-form of Cu-C_8H_{17}. It is quite intriguing that only two of these complexes are mesogenic. It must be pointed out that tlie absence of mesomorphism in salicylaldimine complex of nickel [Galyametdinov et al, 1988] has been associated with tlie tetrahedral coordination of the metal atom . In tlie case of llie complex Ni-C_8H_{17}, tliere is clearly no evidence for such tetrahedral coordination.

It is generally observed that tlie structure and properties are closely correlated. If (lie isomorphous copper and palladium complexes could be mesogenic, why not tlie isomorphous nickel complex? From preliminary thermal studies on the nickel complex, it was found that on heating the crystal, there is a strong peak, in tlie DSC scan at $\sim 80°$ followecl by a weak peak at $\sim 110°$. Implications of these peaks are being examined.

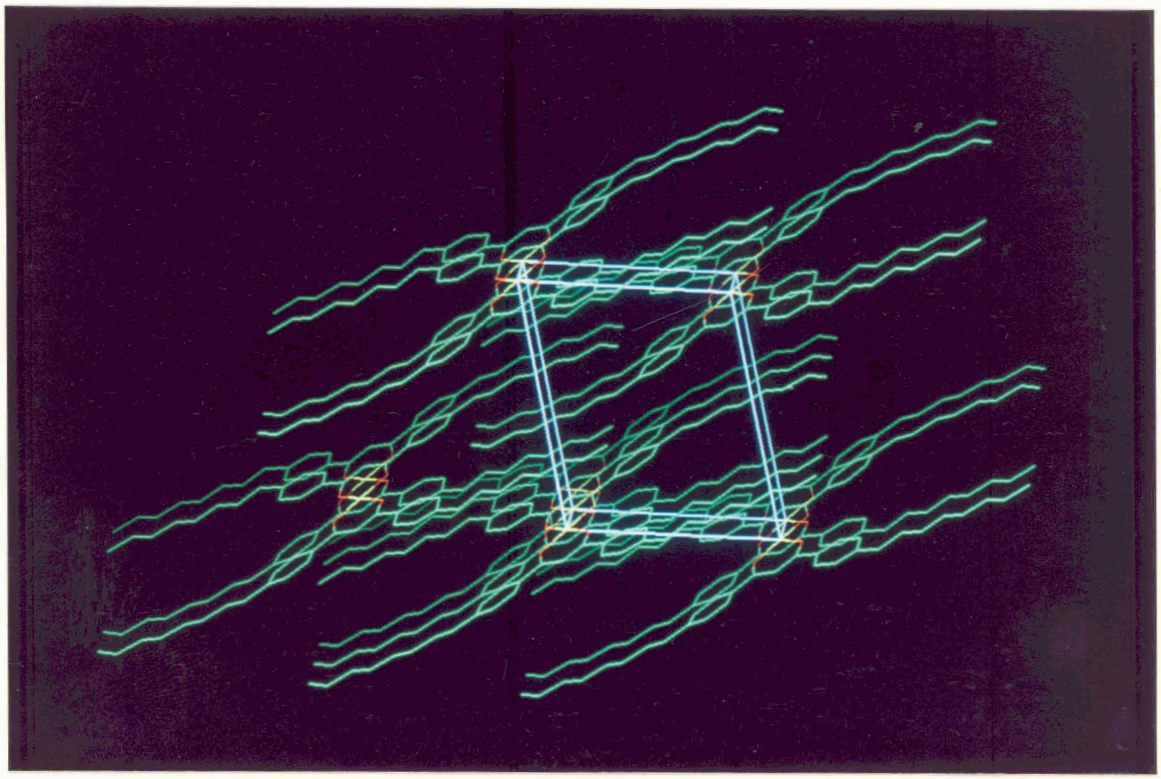


Figure 6.10: Columnar arrangement in Pd-C_8H_{17}.

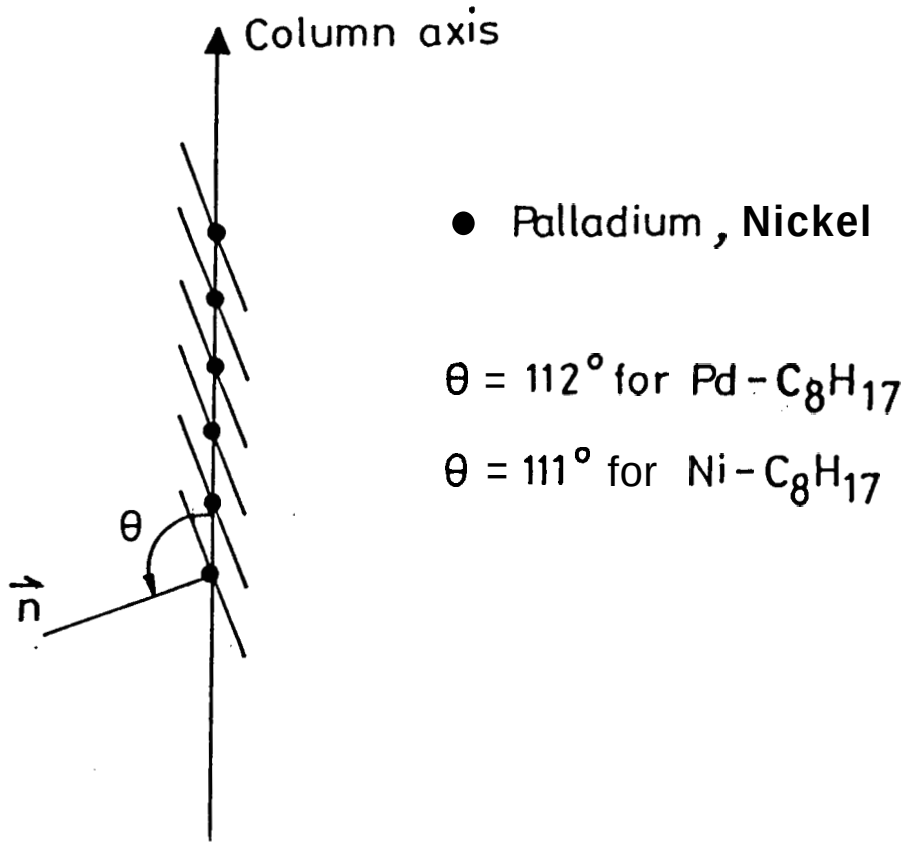


Figure 6.11: Comparison of the tilts of the core with respect to the column axis.