Crystal and Molecular Structures of Isomorphous 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)

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Crystal structures of the transition metal complexes 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) have been solved and refined to R = 0.051 and 0.064 respectively, using diffractometer collected X-ray data. The palladium and the nickel complexes are found to be isomorphous with the P-form of the copper complex bis[1,3-di(*p-n*-octylphenyl propane-1,3-dionato] copper(II). Despite the unambiguous structural isomorphism, only the palladium and the copper complexes are mesogenic; the nickel complex is reportedly non-mesogenic. In the crystal structures, the metal atoms are surrounded by four oxygen atoms in a square planar arrangement. The octyl chains are fully extended in an all-*trans* conformation. The crystal structures are characterized by both layer-like and columnar arrangement of molecules.

Keywords: discotic, crystal structure, isomorphous, Ni complex, Pd complex

1 INTRODUCTION

The organo-metallic series (I) studied by us[1-5] includes two palladium complexes. Comparison of the crystal structures showed that similarities existed between the structural characteristics of bis[1,3-di(*p-n*-decylphenyl)propane-1,3-dionato] palladium(II) i.e. Pd-$C_{10}H_{21}$,[2] (iv) in (I) and the P-form of the copper complex bis[1,3-di(*p-n*-octylphenyl)propane-1,3-dionato] copper(II) i.e. Cu-C_8H_{17},[3] (iii) in (I), 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}, (v) in (I).
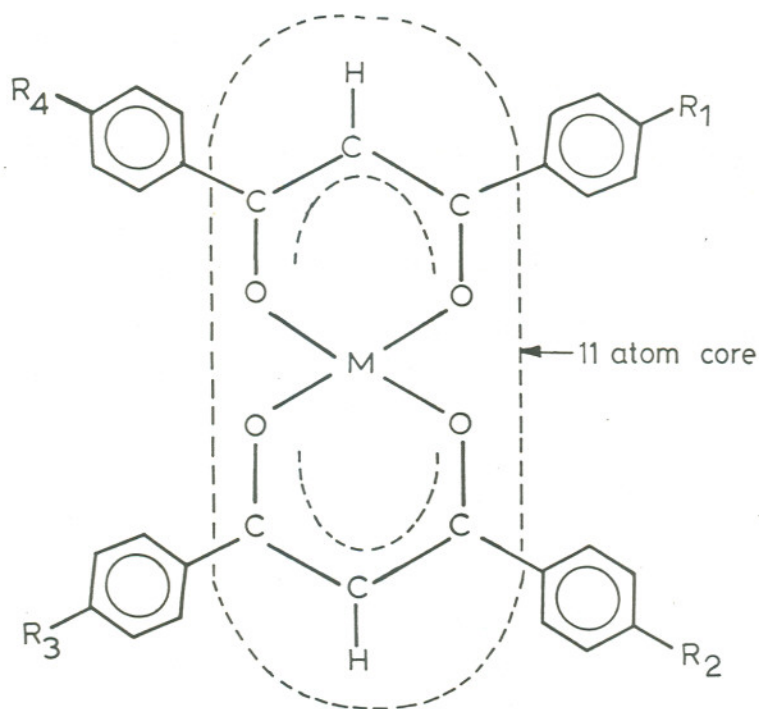
(i) M = Cu $R_1 = R_2 = R_3 = R_4 = OC_8H_{17}$

(ii) M = Cu $R_1 = R_2 = OC_7H_{15}, R_3 = R_4 = C_7H_{15}$

(iii) M = Cu $R_1 = R_2 = R_3 = R_4 = C_8H_{17}$

(iv) M = Pd $R_1 = R_2 = R_3 = R_4 = C_{10}H_{21}$

(v) M = Pd $R_1 = R_2 = R_3 = R_4 = C_8H_{17}$

(vi) M = Ni $R_1 = R_2 = R_3 = R_4 = C_8H_{17}$

SCHEME I

The results presented in this paper show that the complexes Pd-C_8H_{17} and the P-form of Cu-C_8H_{17} are in fact isomorphous.

The crystal structure analysis of the nickel complex bis[1,3-di(*p-n*-octyl-phenyl)propane-1,3-dionato] nickel(II) i.e., Ni-C_8H_{17}, (vi) in (I) is also described in this paper. It has been reported that Ni-C_8H_{17} is nonmesogenic.[6] In contrast, its copper and palladium analogs are found to exhibit discotic mesomorphism.[7,8] As the only difference between these three complexes concerns the type of 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} and those of the mesogenic Pd-C_8H_{17} and Cu-C_8H_{17}. Very interestingly, the crystal structure analyses showed Ni-C_8H_{17} to be structurally isomorphous with Pd-C_8H_{17} and consequently with the P-form of Cu-C_8H_{17}.

2 EXPERIMENTAL

The two complexes 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) were prepared as

shown in Figure 1. The ligand was prepared following a known procedure.[9] The complexes were purified by several recrystallizations and their physical data are given below:
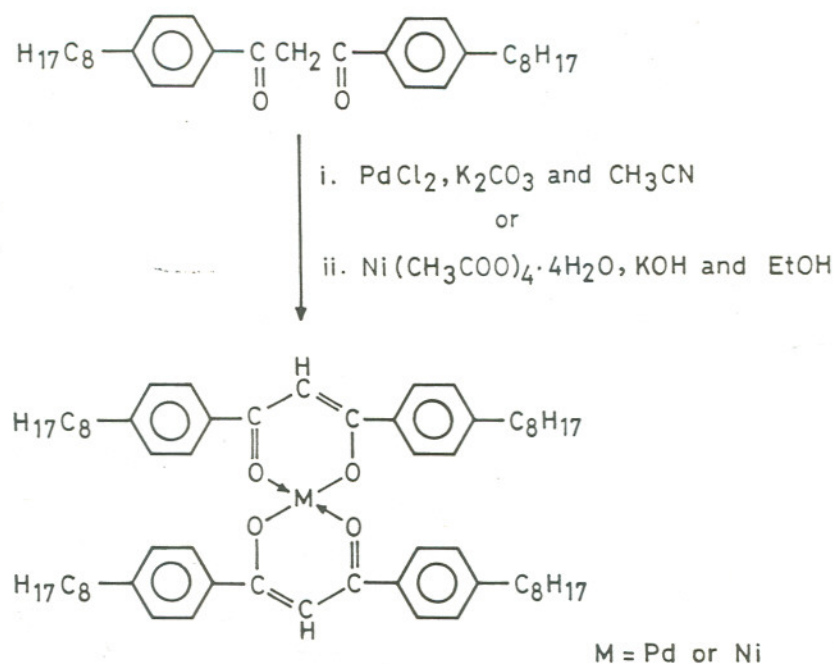

FIGURE 1 Synthetic route.

TABLE I

Crystal data of Pd-C_8H_{17}, Ni-C_8H_{17} and unit cell parameters of the P-form of Cu-C_8H_{17}

	Pd-C_8H_{17}	Ni-C_8H_{17}	Cu-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)	10.341(3)
b (Å)	11.537(1)	11.320(8)	11.621(2)
c (Å)	13.089(2)	13.242(2)	12.817(2)
α (°)	104.119(9)	101.919(8)	107.35(1)
β (°)	94.73(1)	92.796(9)	98.86(2)
γ (°)	108.88(1)	108.520(7)	93.58(3)
V(Å³)	1407	1399	1394
Z	1	1	
Space group	P$\bar{1}$	P$\bar{1}$	
ρ_{calc} (gm/cc)	1.174	1.125	
$\mu_{C_uK_a}$ (cm⁻¹)	30.556	8.1136	
$F_{(000)}$	536	518	

Bis[1,3-di(*p-n*-octylphenyl)propane-1,3-dionato] palladium(II):

Transition temperature: $C \xrightarrow{99} D_1 \xrightarrow{121.5} D \xrightarrow{138.5°C} I$

IR ν_{max}(Nujol) 1610 and 1580 cm^{-1}; UV-Vis $\lambda_{max}^{CH_2Cl_2}(\varepsilon)$ 404(17,900), 376.5(30,750), 304.5(56,200) and 273.5(40,650). Elemental analysis: found C, 74.00% and H, 8.67%; $C_{62}H_{86}O_4Pd$ requires C, 74.37% and H, 8.59%.

Bis[1,3-di(*p-n*-octylphenyl)propane-1,3-dionato] nickel(II):

IR ν_{max}(Nujol) 1610 and 1580 cm^{-1}; UV-Vis $\lambda_{max}^{CH_2Cl_2}(\varepsilon)$ 426(3,630), 375.5(30,950), 347.5(47,800), 286.5(26,800), 263(27,500) and 225(22,850). Elemental analysis: found C, 78.29% and H, 9.27%; $C_{62}H_{86}O_4Ni$ requires C, 78.09% and H, 9.02%.

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 the crystals to be triclinic.

TABLE II

Details of data collection and refinement

	Pd-C_8H_{17}	Ni-C_8H_{17}
Radiation used	CuK$_\alpha$	CuK$_\alpha$
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°	50°
Unique reflections	4895	4105
Ranges of h	0 to 12	0 to 11
k	-13 to 13	-12 to 12
l	-15 to 15	-14 to 14
Corrections applied	Lp and absorption[10]	Lp
Program used for refinement	SHELX-76	SHELX-76[11]
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
Residual electron density:		
ρ_{min} (el/Å^3)	-0.48	-0.29
ρ_{max} (el/Å^3)	0.59	0.19

TABLE III

Final fractional atomic coordinates and $U_{eq}(\text{Å})^2$

Atom	Pd-C_8H_{17}				Ni-C_8H_{17}			
	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)	0.1359(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)	0.0613(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)	-0.1116(6)	-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)	-0.4381(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 IV

Average $U_{eq}(\text{Å}^2)$ values of different groups of atoms

	Pd-C_8H_{17}	Ni-C_8H_{17}	P-form of Cu-C_8H_{17}	Pd-$C_{10}H_{21}$
Core	0.065(5)	0.075(3)	0.061(6)	0.048(5)
Phenyl ring A	0.069(7)	0.082(7)	0.062(7)	0.059(9)
Phenyl ring B	0.077(9)	0.081(8)	0.069(7)	0.053(4)
Chain A	0.09(2)	0.09(3)	0.08(2)	0.07(2)
Chain B	0.09(2)	0.10(2)	0.09(2)	0.07(2)

The unit cell dimensions determined and refined on a diffractometer are listed in Table I. The closeness of the unit cell constants suggest isomorphism between the two crystal structures. Comparison with the unit cell constants of the P-form of Cu-C_8H_{17} (Table I) further suggests that both 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 the structural isomorphism. The crystal data of Pd-C_8H_{17} and Ni-C_8H_{17} are presented in Table I.

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 II.
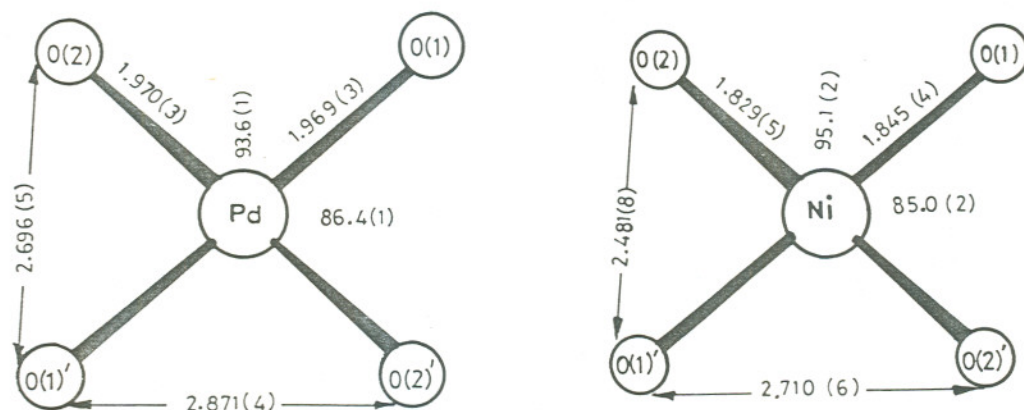
FIGURE 2 Coordination polyhedron around the metal atom.

TABLE V(a)

Bond lengths (Å)

	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)

3 STRUCTURE SOLUTION

Although evidence from the unit cell dimensions and the 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 the 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.

With Z = 1, Pd-C_8H_{17} has to be centric. Placing the palladium atom at (0, 0, 0), a difference Fourier map was computed and positions of all the 33 nonhydrogen atoms could be easily obtained from this map. Details of the subsequent refinement procedures are given in Table II. 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 II depicts the details concerning the weighting functions, R-factors, residual electron density for both the analyses. Hydrogen atoms were geometrically fixed using a C-H distance[12] of 1.08 Å.

TABLE V(b)

Bond angles(°)

	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)			

4 RESULTS AND DISCUSSION

Table III records the positional and the equivalent temperature factors (U_{eq}).

4.1 Thermal Parameters

As could be expected, thermal parameters of the terminal atoms in the chains are the highest. In Table IV, average U_{eq} values of the core, the phenyl rings and the chains of both the crystal structures are compared. The corresponding values observed for the P-form of $Cu\text{-}C_8H_{17}$ have also been included in Table IV to enable comparison.

It is observed that although the U_{eq} values characterizing the nickel complex are marginally higher than those of $Pd\text{-}C_8H_{17}$, the observed differences are not statistically significant. In contrast, the average U_{eq} values of the core of the nickel and copper complexes exhibit significant differences. However, 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 $Pd\text{-}C_8H_{17}$ and $Pd\text{-}C_{10}H_{21}$ (Table IV) shows that despite the increase in the chain length, the thermal parameters of the latter are lower than those of the former.

4.2 Molecular Dimensions

The dimensions of the square planar coordination polyhedra around the metal atoms are presented in Figure 2. As the oxygen atoms O(1) and O(2) are part of the diketone ring system, the coordination polyhedra have rectangular character-
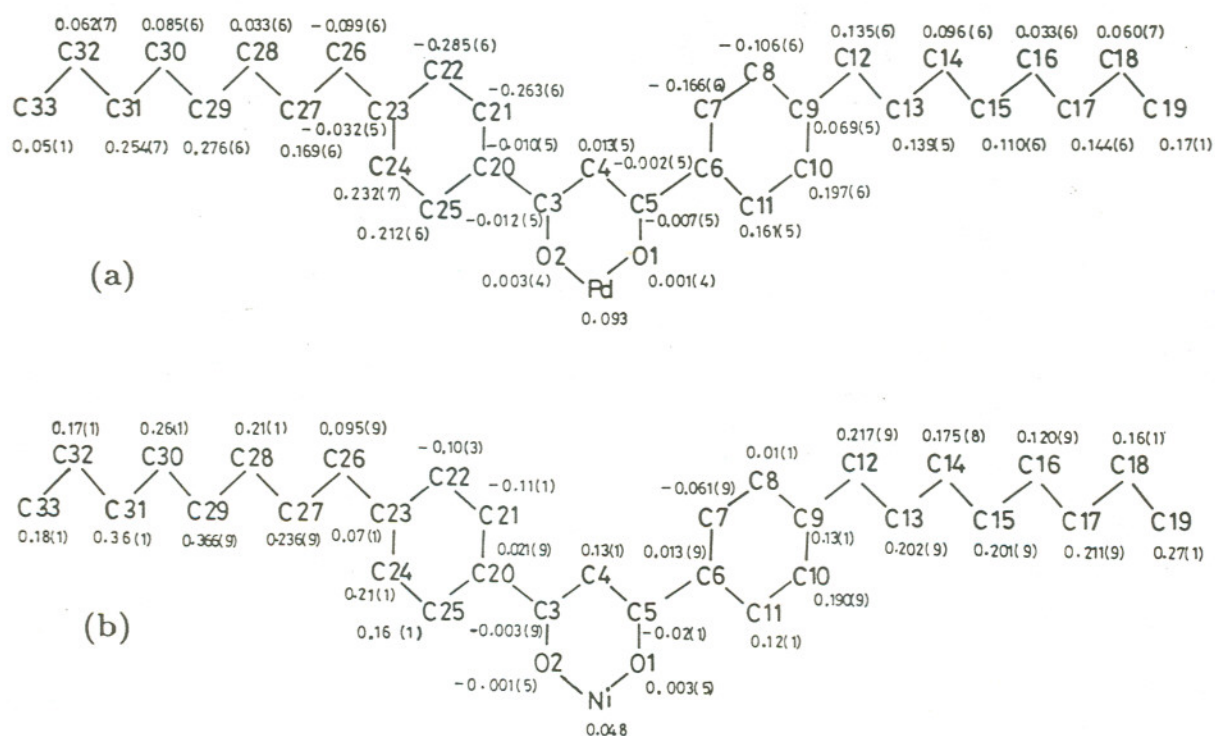

FIGURE 3 Displacements, δ's, of the nonhydrogen atoms from the plane through the crystallographically independent half of the core. (a) $Pd\text{-}C_8H_{17}$ (b) $Ni\text{-}C_8H_{17}$.

istics. The Pd-O lengths average to 1.970(3) Å and the Ni-O lengths average to 1.837(8) Å. The observed reduction in the latter value is commensurate with the reduction in the single bond metallic radii (single bond metallic radii for palladium and nickel are 1.283 and 1.154 Å respectively).[13]

The bond lengths and valence angles are listed in Table V(a) and V(b) respectively. Within the limits of experimental errors, the dimensions could be considered normal.

As in the case of the other metallo-organic discogens studied by us earlier,[1-5] the crystallographically independent half of the core constituted by the atoms Pd, O(1) to C(5), is not strictly planar. The angle, η, between the M-O-C-C groups in each half of the molecular core is 2.8° in Pd-C_8H_{17} and 3.1° in Ni-C_8H_{17}. Figure 3 shows the displacements, δ's, of atoms from the planes through the crystallographically independent half of the respective cores.

4.3 Molecular Conformation

The phenyl rings in both the molecules are tilted with respect to the core. The angles of tilt are 8 and 12° in the palladium complex and 5 and 7° in the nickel complex. The corresponding tilts for the octyl chains are 3 and 12° in the palladium complex and 3 and 7° in the nickel complex. The octyl chains are fully extended in an all-*trans* conformation. In this conformation, the end-to-end dimensions of the molecules (Table VI) resemble model B of Ohta *et al.*[14] Table VI includes the

TABLE VI

Comparison of the end-to-end molecular
dimensions

	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
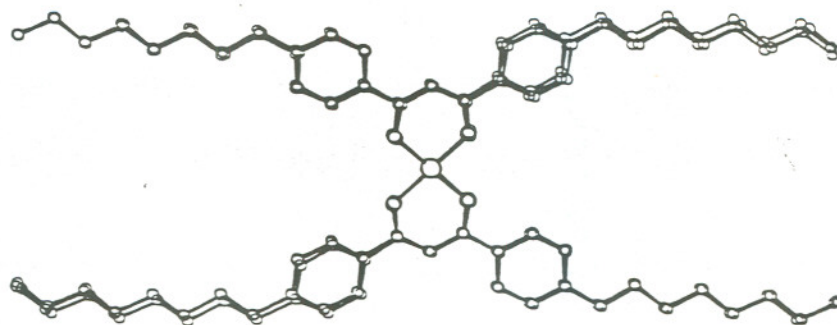
FIGURE 4 Superposition of molecules in the isomorphous structures, Pd-C_8H_{17}, Ni-C_8H_{17} and the P-form of Cu-C_8H_{17}.

dimensions of the isomorphous P-form of Cu-C_8H_{17} also. A superposition of the molecular conformations of the 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 4.

4.4 Molecular Packing

As in the case of P-form of Cu-C_8H_{17}, the molecular arrangement is essentially layer-like (Figure 5). The layer structure is stabilized by nonbonded interactions of the type core . . . chain, phenyl ring . . . phenyl ring, phenyl ring . . . chain and chain . . . chain. Regular stacking of the layers along the crystallographic
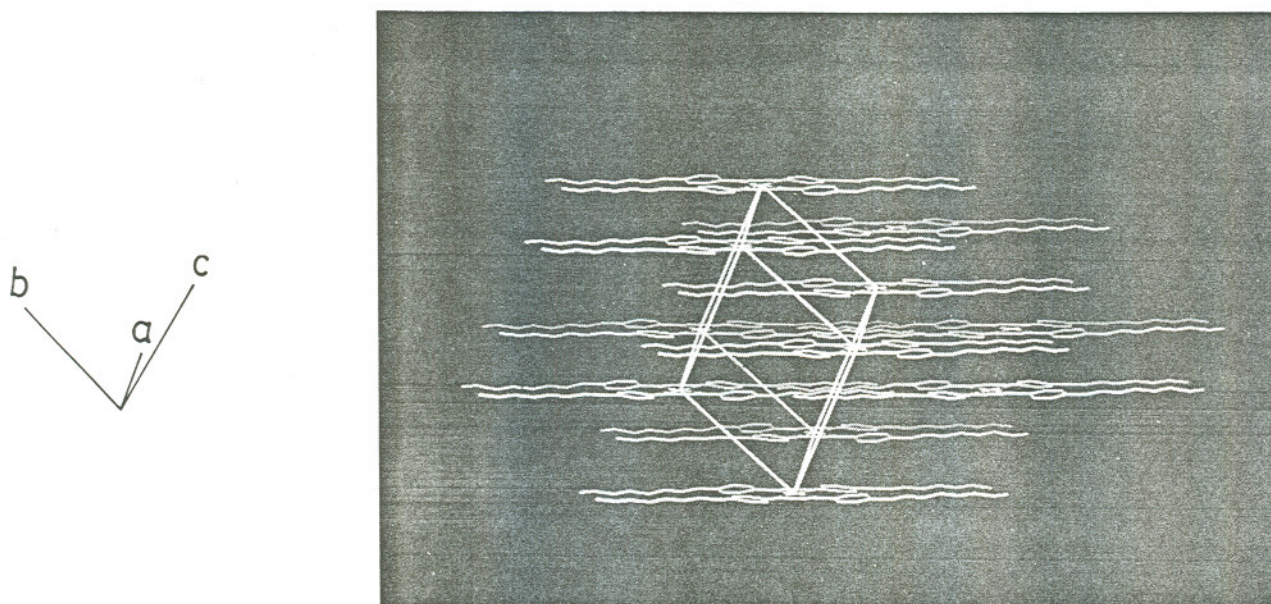
FIGURE 5   Layer structure observed in Ni-C_8H_{17}. See Color Plate I.
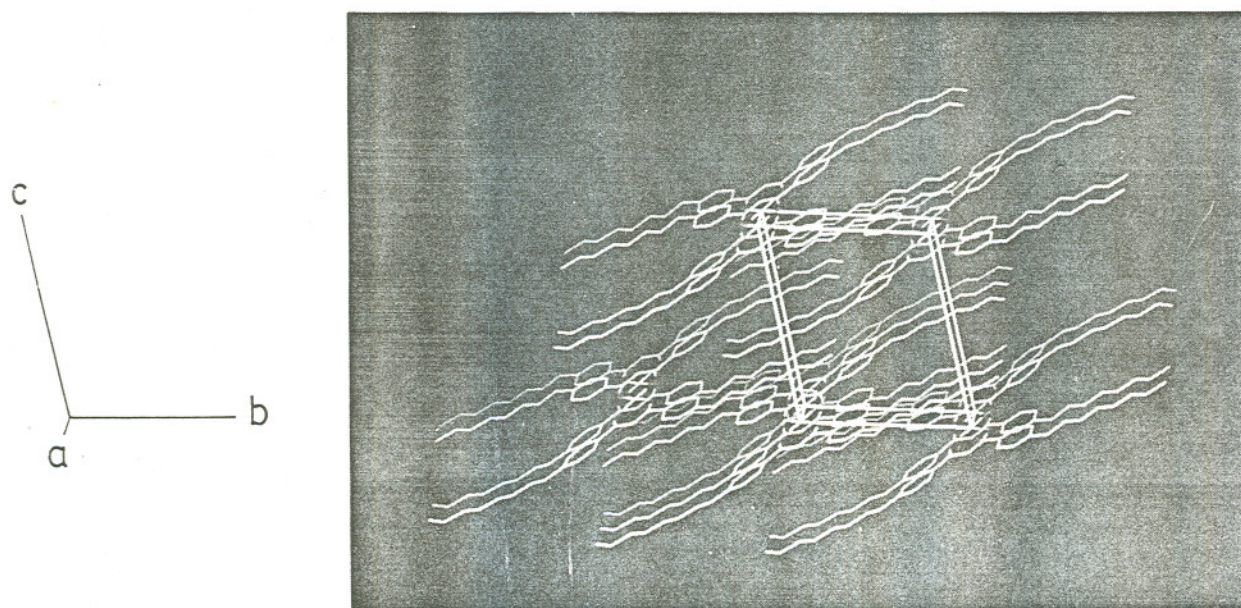
FIGURE 6   Columnar arrangement in Pd-C_8H_{17}. See Color Plate II.
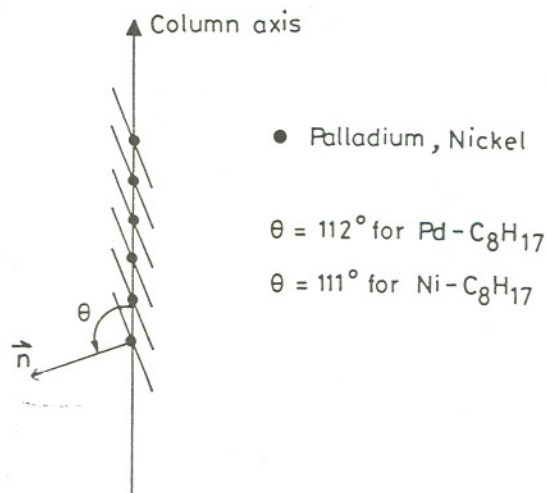
FIGURE 7   Schematic representation of the tilt, θ, of the core with respect to the column axis. Here, ñ is the normal to the least squares plane through the core.

a-axis introduces a columnar structure depicted in Figure 6. In each of the five columns shown in Figure 6, two adjacent molecules have been included. The tilts, θ's of the cores of the palladium and the nickel complexes with respect to the column axis are 112 and 111° respectively (Figure 7). The columnar structure is stabilized by nonbonded interactions which are of the 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 $\pm b$, $\pm (b + c)$ and $\pm (2b + c)$.

The crystal structure analyses of $Pd-C_8H_{17}$ and $Ni-C_8H_{17}$ have conclusively established their isomorphism with the P-form of $Cu-C_8H_{17}$. However, it is quite intriguing that only two of these complexes are mesogenic. It must be pointed out that the absence of mesomorphism in salicylaldimine complex of nickel, has been associated with the tetrahedral coordination of the metal atom.[15] In the case of $Ni-C_8H_{17}$, there is clearly no evidence for such tetrahedral coordination. It is generally observed that the structure and properties are closely correlated. If the isomorphous copper and palladium complexes could be mesogenic, why not the isomorphous nickel complex? To look into this anomaly, thermal studies are being carried out, the details of which will be reported at a later stage.

Acknowledgment

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