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THE MOLECULAR AND CRYSTAL STRUCTURE OF (TRICYCLOHEXYLPHOSPHINE)METHYLNICKEL(II) 2,4-PENTANEDIONATE*; A SQUARE-PLANAR COMPLEX CONTAINING A σ-NICKEL–CARBON BOND

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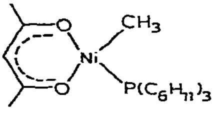
SUMMARY

The molecular and crystal structure of (tricyclohexylphosphine)methylnickel(II) 2,4-pentanedionate has been determined by conventional Patterson and Fourier synthesis and refined anisotropically to a final *R* value of 0.08, including hydrogen atoms. Coordination about the nickel atom is square-planar with the angles subtended at the nickel being: O(1)–Ni–O(2) = 93°; O(1)–Ni–C(19) = 84°; C(19)–Ni–P = 93°; P–Ni–O(2) = 90°. The Ni–C(19) σ-bond length is 1.94(1) Å. The cyclohexyl rings are all in the chair conformation having an average C–C distance of 1.53 Å and are bonded equatorially to the phosphorus in a tetrahedral arrangement with the average P–C distance being 1.861 Å. The pentanedione ligand is planar within experimental error. Molecules of the title compound pack as discrete units in the crystal with no non-hydrogen intermolecular distance being less than 3.6 Å.

INTRODUCTION

As part of our research on the molecular geometries of intermediates and products obtained during the investigation of possible catalyst systems, we have examined the structure of (I)[1]. Compound (I) is of interest in connection with the mechanism of the reduction of nickel 2,4-pentanedionate by aluminum trialkyls[1]. Furthermore the structure provides the first Ni–C(σ) distance for a simple alkyl derivative[2,3].



(I)

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[*] Acetylacetonate.

EXPERIMENTAL

The title compound was prepared by the treatment of a 1/1 adduct of tricyclohexylphosphine and nickel 2,4-pentanedionate with trimethylaluminum[1]. A light-yellow, plate-like crystal, suitable for X-ray studies, obtained by recrystallization in ether, was sealed under argon in a glass capillary and mounted with the (001) direction parallel to the φ axis. Preliminary investigations of Weissenberg and precession photographs indicated the crystal symmetry to be orthorhombic and the systematic absences consistent with the unique space group *Pbcn* (No. 60). Cell constants, given along with other crystal data in Table 1, were derived from a least-squares refinement using 32 independent 2 θ diffractometer measurements. The molecular formula was determined by mass spectroscopic methods.

TABLE 1

CRYSTAL DATA

$C_{24}H_{43}NiO_2P$: mol. wt. 453.29
$a=18.57(1)$, $b=17.97(1)$, $c=14.85(2)$ Å
Systematic absences: $0kl$, $k=2n+1$; $h0l$, $l=2n+1$
$hk0$, $h+k=2n+1$; $h00$, $h=2n+1$
$0k0$, $k=2n+1$; $00l$, $l=2n+1$
Space group: *Pbcn* (No. 60)
$Z=8$; $F(000)=1975$; $V=4959.3$ Å^3
$D_{calc}=1.214$ g/cm^3; λ[Cu-$K\alpha$(mean) 1.54178 Å]

Three-dimensional single-crystal intensity data were collected as described previously[4] to the limit 2 $\theta=50°$ [Mo-$K\alpha$(mean)]. Of the 4270 reflections collected 2376 (56%) were considered sufficiently above background ($I_0 > 2\sigma(I_0)$) to be observed. The intensity of the monitored reflection, measured after every twenty reflections, varied only randomly, indicating the crystal did not suffer from any radiation damage. Data reduction was carried out in the usual manner[4] without any absorption correction being applied. Standard deviations of the observed structure factor amplitudes were based solely on counting statistics.

STRUCTURE ANALYSIS AND REFINEMENT

The solution of the structure was accomplished by obtaining the Ni and P atom positions from a sharpened Patterson map. A subsequent Fourier map calculated using phases based on these two heavy atoms and the observed amplitudes revealed all non-hydrogen atoms of the structure.

Full-matrix least-squares isotropic refinement for these 30 atoms reduced the residual index R from 0.35 to 0.15 in five cycles. Converting the isotropic temperature factors to anisotropic factors, the refinement continued to $R=0.096$ in 4 cycles. A difference density Fourier map revealed peaks corresponding to chemically reasonable hydrogen atom positions on the methyl and acetylacetonate groups and indicated positive electron density corresponding to the calculated hydrogen positions for the cyclohexyl rings. Holding hydrogen positions fixed and temperature factors constant

TABLE 2

Atom	*x*	*y*	*z*
Ni	0.2337 (1)	0.1570 (1)	0.0424 (1)
P	0.3321 (1)	0.1968 (1)	−0.0179 (1)
O(1)	0.1483 (3)	0.1281 (3)	0.1009 (4)
O(2)	0.1915 (2)	0.1491 (3)	−0.0733 (3)
C(1)	0.4159 (3)	0.1721 (4)	0.0415 (5)
C(2)	0.4256 (4)	0.0883 (4)	0.0555 (6)
C(3)	0.4844 (4)	0.0747 (4)	0.1238 (6)
C(4)	0.5550 (5)	0.1082 (5)	0.0926 (6)
C(5)	0.5483 (4)	0.1920 (5)	0.0703 (6)
C(6)	0.4868 (4)	0.2032 (4)	0.0026 (6)
C(7)	0.3335 (4)	0.3011 (4)	−0.0223 (5)
C(8)	0.3361 (4)	0.3376 (4)	0.0695 (5)
C(9)	0.3393 (5)	0.4216 (4)	0.0605 (5)
C(10)	0.2748 (4)	0.4506 (4)	0.0122 (6)
C(11)	0.2711 (5)	0.4141 (4)	−0.0819 (5)
C(12)	0.2667 (4)	0.3292 (4)	−0.0743 (5)
C(13)	0.3383 (4)	0.1715 (4)	−0.1392 (4)
C(14)	0.3926 (4)	0.2136 (5)	−0.1976 (5)
C(15)	0.3814 (4)	0.1935 (5)	−0.2960 (5)
C(16)	0.3896 (4)	0.1086 (5)	−0.3106 (5)
C(17)	0.3371 (5)	0.0655 (4)	−0.2509 (6)
C(18)	0.3479 (5)	0.0871 (4)	−0.1512 (5)
C(19)	0.2723 (4)	0.1645 (4)	0.1635 (5)
C(20)	0.0879 (4)	0.1073 (4)	0.0646 (5)
C(21)	0.0758 (4)	0.1044 (4)	−0.0255 (5)
C(22)	0.1276 (4)	0.1256 (5)	−0.0888 (5)
C(23)	0.0286 (5)	0.0844 (5)	0.1305 (7)
C(24)	0.1115 (5)	0.1133 (7)	−0.1893 (6)

($U = 0.06$ Å^2), all remaining positional parameters, anisotropic temperature factors and the overall scale factor were refined using statistical weights and the block-diagonal approximation to the least-squares method until all shifts were less than 0.5 σ for all parameters. Weights equal to $1.0/\sigma^2(|F_0|)$ were used in the least-squares calculations and atomic scattering factors used are those of Stewart, Davidson and Simpson[5] for hydrogen and of Cromer and Waber[6] for the remaining atoms. Anomalous dispersion corrections for Ni and P[7] were included in the least-squares calculations.

Final atomic parameters are given in Tables 2, 3 and 4. The estimated standard deviations were calculated from the inverse matrices of the final least-squares cycle. The final *R* value for these parameters is 0.080 (0.047 for weighted *R*) for observed reflections only*.

DISCUSSION

The structure of (I) is illustrated in Fig. 1. Gross features of the structure are

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* A list of the calculated and observed structure factor amplitudes may be obtained from the authors (C.K.).

TABLE 3

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.030 (1)	0.026 (1)	0.027 (1)	−0.000 (1)	0.007 (1)	0.003 (1)
P	0.057 (1)	0.041 (1)	0.050 (1)	0.005 (1)	0.000 (1)	−0.002 (1)
O(1)	0.075 (4)	0.079 (5)	0.079 (4)	0.004 (4)	0.003 (4)	−0.002 (4)
O(2)	0.058 (3)	0.075 (4)	0.074 (4)	−0.007 (4)	0.000 (3)	0.002 (4)
C(1)	0.044 (5)	0.050 (6)	0.059 (5)	−0.001 (4)	−0.010 (5)	0.000 (5)
C(2)	0.064 (6)	0.045 (5)	0.079 (7)	0.002 (5)	−0.002 (6)	0.013 (6)
C(3)	0.057 (6)	0.062 (6)	0.091 (7)	−0.003 (5)	−0.009 (6)	0.017 (6)
C(4)	0.077 (7)	0.103 (9)	0.092 (6)	−0.022 (6)	−0.023 (6)	0.017 (7)
C(5)	0.051 (6)	0.087 (8)	0.140 (10)	−0.006 (6)	−0.031 (7)	0.031 (7)
C(6)	0.059 (6)	0.056 (6)	0.133 (9)	0.001 (5)	−0.010 (6)	0.036 (7)
C(7)	0.049 (5)	0.033 (4)	0.065 (6)	−0.003 (4)	−0.000 (5)	0.009 (5)
C(8)	0.098 (7)	0.045 (5)	0.058 (6)	−0.002 (6)	0.001 (5)	−0.007 (5)
C(9)	0.113 (8)	0.039 (5)	0.057 (6)	0.002 (5)	0.003 (6)	−0.007 (5)
C(10)	0.097 (7)	0.044 (5)	0.085 (7)	0.015 (6)	0.005 (6)	−0.000 (5)
C(11)	0.083 (7)	0.051 (6)	0.087 (7)	0.017 (7)	−0.012 (6)	0.017 (5)
C(12)	0.061 (5)	0.039 (5)	0.087 (7)	0.009 (5)	−0.002 (6)	0.002 (5)
C(13)	0.062 (6)	0.038 (6)	0.042 (5)	0.005 (5)	0.004 (5)	−0.002 (4)
C(14)	0.086 (7)	0.057 (6)	0.046 (5)	−0.007 (6)	0.019 (5)	−0.002 (5)
C(15)	0.092 (7)	0.078 (7)	0.058 (6)	−0.011 (6)	0.019 (6)	0.005 (6)
C(16)	0.075 (7)	0.122 (9)	0.045 (6)	−0.011 (7)	0.007 (5)	−0.013 (6)
C(17)	0.110 (8)	0.057 (7)	0.081 (7)	−0.011 (6)	0.007 (7)	−0.020 (6)
C(18)	0.106 (8)	0.043 (6)	0.051 (6)	−0.009 (6)	−0.002 (6)	−0.004 (5)
C(19)	0.085 (6)	0.053 (6)	0.065 (6)	0.000 (6)	0.032 (6)	0.010 (5)
C(20)	0.062 (6)	0.060 (7)	0.076 (7)	0.009 (5)	0.013 (6)	0.006 (6)
C(21)	0.049 (6)	0.076 (6)	0.062 (6)	−0.000 (5)	0.014 (5)	−0.000 (6)
C(22)	0.076 (7)	0.076 (7)	0.060 (6)	0.009 (6)	0.006 (5)	0.005 (5)
C(23)	0.067 (8)	0.090 (8)	0.190 (11)	0.030 (6)	0.071 (8)	0.045 (9)
C(24)	0.061 (7)	0.204 (14)	0.077 (7)	−0.027 (8)	−0.033 (6)	0.012 (8)

the square-planar configuration about the Ni and the presence of discrete molecular units in the crystal. The chair conformation of the cyclohexyl rings as well as their tetrahedral arrangement around the phosphorus are seen in Fig. 1 and the stereoscopic drawing[8] in Fig. 2, which shows 50% probability ellipsoids. Intramolecular distances and angles are given in Fig. 1; angles within the cyclohexyl rings are given separately in Table 5. Estimated standard deviations for these interatomic distances and angles are obtained from the previously calculated estimated standard deviations in positional coordinates.

Bonding characteristics of nickel(II) systems, containing chelated pentanedionates, have been well established[9,10]. Ni–O (chelate) distances (1.89 Å average) are shorter by approximately 0.1 Å in square-planar Ni^{II} complexes than in corresponding octahedral complexes[10]. This is probably due to the presence of *d*-electrons in the Ni–O antibonding orbitals in the latter steric arrangement[10].

The Ni–O distance *trans* to the Ni–C(σ) bond shows an insignificant lengthening (0.015 Å), but is consistent with a *trans* effect. Other distances in the pentanedionate fragment are in good agreement with the previous results mentioned above. The difference between the C(20)–C(21) distance (1.36 Å) and the related C(21)–C(22) distance (1.40 Å) is worth noting. A statistical test[11], which is often used to decide

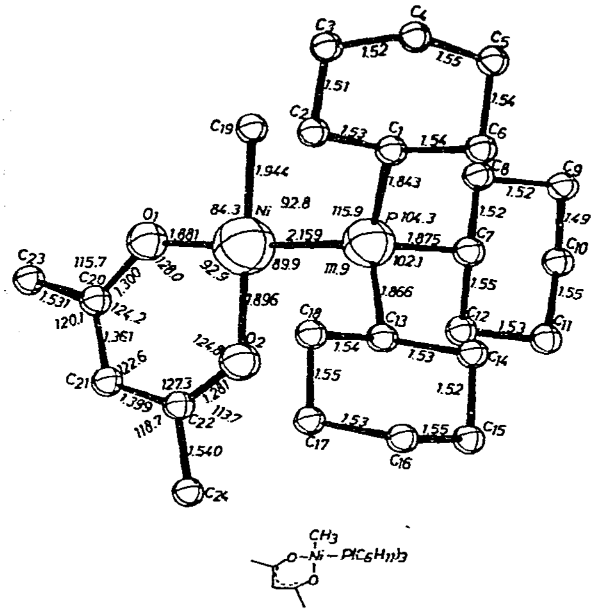


Fig. 1.

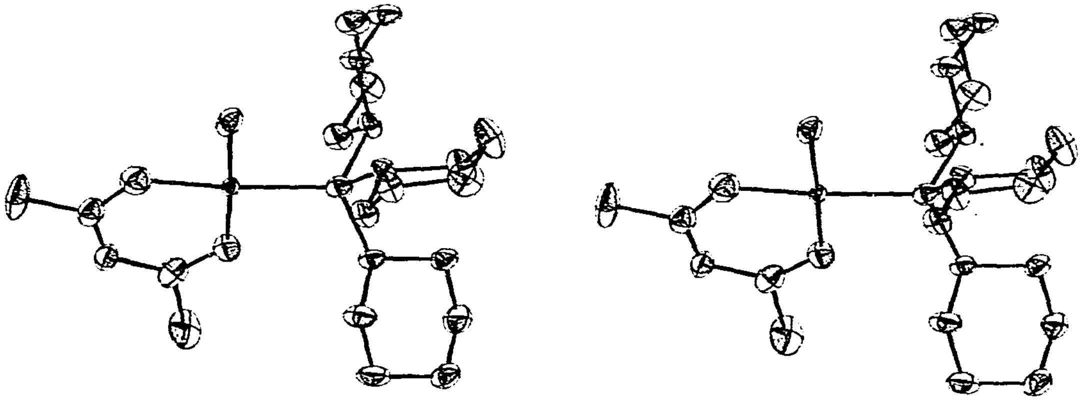


Fig. 2. Stereoscopic drawing of the molecule, showing 50% probability ellipsoids.

whether two bond lengths are different, indicated the difference is highly significant on the basis of 1 σ, but is not significant using 2 σ. As usual standard deviations are underestimates, so that the difference is not considered significant. Out-of-plane distances from the least-squares plane of the chelating ring, given by $-6.280\,X + 16.902\,Y + 0.461\,Z = 1.282$, are: O(1) = −0.003; O(2) = 0.002; C(20) = 0.009; C(21) = 0.005; C(22) = −0.002 Å; and are all within experimental error. Other important out-of-plane distances are: Ni = −0.077; P = −0.049 and C(19) = −0.136 Å. These deviations will be discussed in connection with the coordination about the nickel.

In the tricyclohexylphosphine portion of the molecule the geometry is similar to that found for tricyclohexylphosphine fragments of other structures determined

TABLE 4

Atom	*x*	*y*	*z*	*Atom*	*x*	*y*	*z*
H(1)	0.410	0.198	0.107	H(13)	0.287	0.187	−0.166
H(2A)	0.377	0.063	0.082	H(14A)	0.445	0.196	−0.176
H(2B)	0.438	0.060	0.000	H(14B)	0.388	0.271	−0.187
H(3A)	0.471	0.098	0.185	H(15A)	0.327	0.205	−0.317
H(3B)	0.493	0.015	0.131	H(15B)	0.418	0.219	−0.340
H(4A)	0.596	0.100	0.143	H(16A)	0.442	0.095	−0.289
H(4B)	0.574	0.080	0.033	H(16B)	0.382	0.095	−0.378
H(5A)	0.534	0.220	0.131	H(17A)	0.344	0.007	−0.264
H(5B)	0.597	0.214	0.046	H(17B)	0.283	0.080	−0.271
H(6A)	0.483	0.261	0.000	H(18A)	0.312	0.055	−0.100
H(6B)	0.502	0.174	0.000	H(18B)	0.402	0.069	−0.132
H(7)	0.381	0.318	0.000	H(19A)	0.234	0.165	0.214
H(8A)	0.291	0.320	0.107	H(19B)	0.330	0.195	0.155
H(8B)	0.384	0.317	0.104	H(19C)	0.270	0.100	0.175
H(9A)	0.341	0.447	0.126	H(21)	0.015	0.800	0.000
H(9B)	0.387	0.438	0.025	H(23A)	0.000	0.100	0.140
H(10A)	0.228	0.439	0.047	H(23B)	0.050	0.045	0.155
H(10B)	0.280	0.511	0.003	H(23C)	0.010	0.145	0.145
H(11A)	0.224	0.434	−0.118	H(24A)	0.145	0.175	−0.195
H(11B)	0.317	0.431	−0.122	H(24B)	0.070	0.165	−0.210
H(12A)	0.221	0.312	0.000	H(24C)	0.065	0.105	−0.200
H(12B)	0.271	0.305	−0.143				

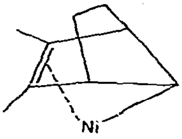
TABLE 5

Atoms	*Angle*	*Atoms*	*Angle*	*Atoms*	*Angle*
P–C(1)–C(2)	113.7	P–C(7)–C(8)	113.7	P–C(13)–C(14)	117.9
P–C(1)–C(6)	117.0	P–C(7)–C(12)	109.5	P–C(13)–C(18)	111.1
C(2)–C(1)–C(6)	107.8	C(8)–C(7)–C(12)	109.5	C(14)–C(13)–C(18)	110.3
C(1)–C(2)–C(3)	109.6	C(7)–C(8)–C(9)	110.7	C(13)–C(14)–C(15)	109.7
C(2)–C(3)–C(4)	110.8	C(8)–C(9)–C(10)	111.0	C(14)–C(15)–C(16)	110.8
C(3)–C(4)–C(5)	112.5	C(9)–C(10)–C(11)	108.9	C(15)–C(16)–C(17)	110.8
C(4)–C(5)–C(6)	109.1	C(10)–C(11)–C(12)	110.9	C(16)–C(17)–C(18)	110.2
C(6)–C(6)–C(1)	110.0	C(11)–C(12)–C(7)	108.7	C(17)–C(18)–C(12)	110.1

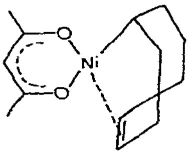
in this laboratory and is not considered different from that of the phosphine in the free state. The average C–C ring distance is 1.53 Å and the average P–C distance is 1.861 Å. Deviations from ideal tetrahedral angles about the phosphorus atom reflect the orientation and steric effects of the cyclohexyl rings. Two of the rings (O(7)–C(12)) and (C(13)–C(18)) are approximately staggered with respect to the pentanedionate plane, while the remaining ring (C(1)–C(6)) is nearly eclipsed to the methyl group and pentanedionate plane. This is the probable cause for the slight angle deformation of the angles C(1)–P–Ni (115.9°) and C(19)–Ni–P (92.8°). Interestingly the cyclohexyl rings of this ligand have always been found bonded to the phosphorus from the equatorial position of the chair conformation.

As mentioned above, the coordination about the nickel is square-planar which is emphasized by the sum of the angles around the nickel being 360°. From the out-of-plane distances of the pentanedionate plane given previously, clearly the principle distortion of the coordination, although small, occurs at the methyl carbon atom. This is probably due to minimization of the steric interaction between the methyl group and the cyclohexyl ring (C(1)–C(6)), where two intramolecular distances (C(19)---C(1) = 3.23 and C(19)---C(2) = 3.54 Å) are of borderline significance.

The important feature of this present study is the Ni–C(methyl) distance of 1.94(1) Å. This is significantly shorter than the value of 2.01–2.01 Å predicted by Churchill[3], but is in excellent agreement with two Ni–C(σ) distances found in structures where the tetrahedral carbon is part of a cyclic ring system. In the nickel complex (II), with norbornadienyl acting as a σ, π bidentate ligand, the Ni–C(σ) distance was found to be 1.96(1) Å[12]. The Ni–C(σ) value of 1.95(2) Å[2] was found in complex (III), containing a cyclooctenyl group also bonded to nickel as a σ, π bidentate ligand. Although there are some angular distortions about the carbon atoms in the quoted structures (II) and (III), as well as in the present study, this is not thought to be a significant factor in influencing the Ni–C(sp^3) distance.



(II)



(III)

REFERENCES

1 P. W. Jolly, K. Jonas, C. Krüger and Y.-H. Tsay, *J. Organometal. Chem.*, 33 (1971) 109.
2 O. S. Mills and E. F. Paulus, *Chem. Commun.*, (1968) 738.
3 M. R. Churchill, in *Perspectives in Structural Chemistry*, Vol III, Wiley, New York, 1970, pp. 147-150.
4 C. Krüger, *J. Organometal. Chem.*, 22 (1970) 697.
5 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, 42 (1965) 3175.
6 D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18 (1965) 104.
7 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53 (1970) 1891.
8 C. K. Johonson, *Program ORTEP, Revised ORNL*-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
9 W. Horrocks Jr., D. H. Tempelton and A. Zalkin, *Inorg. Chem.*, 7 (1968) 1552, and references therein.
10 F. A. Cotton and J. J. Wise, *Inorg. Chem.*, 5 (1966) 1200, and references therein.
11 D. W. J. Cruickshank and A. P. Robertson, *Acta Crystallogr.*, 6 (1953) 698.
12 L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2 (1962) 713.