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CARBON COMPOUNDS OF THE TRANSITION METALS
XI*. THE STRUCTURE OF (DIPHENYLACETYLENE)BIS(CYCLOPENTADIENYLNICKEL)

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The reaction of bis(cyclopentadienylcarbonylnickel), (I), with various acetylenes results in the replacement of the two bridging carbon monoxide groups by one molecule of acetylene[1,2]. From the formal analogy between the reactions of (I) and of cobalt octacarbonyl[3,4] with acetylenes, a bridging acetylene structure was proposed similar to that found in (diphenylacetylene)bis(tricarbonylcobalt)[5]. Of a number of complexes whose unit cell dimensions and spacegroups were determined[6] the diphenylacetylene complex was chosen for a three-dimensional X-ray analysis. In this particular determination our interest lay more in the elucidation of the overall molecular geometry rather than in a precise evaluation of interatomic distances. Few polynuclear complexes of nickel have been analysed. At the time of the analysis, in 1962, this was probably the first binuclear structure to be solved.

EXPERIMENTAL

Crystal data

(Diphenylacetylene)bis(cyclopentadienylnickel), $C_{24}H_{20}Ni_2$, mol. wt. 425.8, orthorhombic, $a = 17.73 \pm 0.05$, $b = 9.49 \pm 0.03$, $c = 11.62 \pm 0.04$ Å, $U = 1955$ Å^3, $D_m = 1.45 \pm 0.02$ g·cm^{-3}, $D_c = 1.45 \pm 0.01$ g·cm^{-3}, $Z = 4$, systematic absences $0kl$ when $k+l$ odd, $h0l$ when h odd, spacegroup either $Pna2_1$ (C^9_{2v}, No. 33) or $Pnam$ (D^{16}_{2h}, No. 62), $\mu = 38.4$ cm^{-1} for Co-K_α radiation.

Unit cell dimensions were estimated from Weissenberg photographs taken with Co radiation and precession photographs taken with Mo radiation. Intensity data were collected on equi-inclination photographs taken with Co radiation. The crystal used was approximately cube-shaped with edge 0.20 mm, $\mu t \sim 0.8$. Seven levels were recorded, hnl ($n = 0$–5) and $hk0$. After Lorentz and polarisation corrections had been applied the data were combined onto an arbitrary relative scale by comparison of common reflexions. No absorption correction was made.

SOLUTION OF THE STRUCTURE AND REFINEMENT

The systematic absences do not determine the spacegroup uniquely. With four molecules in the unit cell the more symmetrical spacegroup, *Pnam*, requires that the molecule possess an accurate centre of symmetry or a mirror plane of symmetry whilst these restrictions do not apply with the spacegroup $Pna2_1$. Since the molecular

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* For part X see ref. 13.

configuration of $PhC_2Ph(CO)_6Co_2$ is without symmetry we presumed that the space-group $Pna2_1$ would be more likely and the supposition was justified by the analysis.

The analysis proceeded by the normal heavy-atom method. The nickel atom positions were deduced from an unsharpened three-dimensional Patterson synthesis and successive Fourier syntheses of electron density revealed the twenty four carbon atoms.

The structure was then refined by full-matrix least-squares methods with the weighting scheme $w^{-1} = 1 + F_0^2/8\ F_{min}^2$. For the unobserved reflexions a contribution was made to the least-square totals only if $|F_c| > |F_{min}|$ in which case ΔF was put equal to $|F_{min}| - |F_c|$ and a weight of 0.9 applied. The final R factor, $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, was 10.1 % for 1079 reflexions (six strong low-ordered planes were removed from the calculation after their F_c values persistently calculated much higher than the observed value) or 9.6 % for 1032 non-zero intensities*. Of the 47 reflexions which were too weak to be measured 22 calculated less than F_{min}. The refinement was restricted to isotropic thermal vibrations and no attempt was made to include any of the hydrogen atoms in the model.

TABLE 1

ATOMIC PARAMETERS

The quantities in parentheses are the estimated standard deviations estimated from the diagonal elements of the last cycle of least-squares.

Atom	*x/a*	*y/b*	*z/c*	*B* ($Å^2$)
Ni1	0.1317 (1)	0.1398 (3)	0.1000	3.2 (1)
Ni2	0.2441 (1)	0.1323 (3)	−0.0036 (3)	3.4 (1)
C1	0.0438 (9)	0.2657 (24)	−0.1652 (15)	3.4 (3)
C2	0.0111 (10)	0.3114 (25)	−0.2659 (17)	3.8 (3)
C3	0.0384 (10)	0.2536 (27)	−0.3752 (17)	4.2 (4)
C4	0.1010 (13)	0.1723 (31)	−0.3744 (22)	5.1 (5)
C5	0.1298 (12)	0.1189 (28)	−0.2743 (22)	4.4 (5)
C6	0.1078 (8)	0.1660 (21)	−0.1658 (15)	2.4 (3)
C7	0.1439 (12)	0.1246 (25)	−0.0607 (21)	3.8 (4)
C8	0.1639 (8)	0.0036 (20)	−0.0074 (14)	2.7 (3)
C9	0.1591 (9)	−0.1508 (20)	−0.0187 (16)	2.7 (3)
C10	0.1082 (8)	−0.2170 (22)	−0.0989 (15)	2.9 (3)
C11	0.1033 (12)	−0.3626 (23)	−0.1078 (32)	4.2 (4)
C12	0.1483 (12)	−0.4402 (32)	−0.0339 (20)	4.6 (4)
C13	0.1992 (14)	−0.3863 (28)	0.0344 (25)	5.4 (5)
C14	0.2002 (10)	−0.2269 (26)	0.0523 (18)	4.1 (4)
C15	0.0293 (14)	0.1492 (32)	0.1825 (25)	5.1 (5)
C16	0.0734 (12)	0.0757 (32)	0.2445 (21)	5.4 (5)
C17	0.1439 (14)	0.1734 (34)	0.2780 (26)	5.7 (6)
C18	0.1247 (12)	0.2987 (35)	0.2285 (26)	5.7 (5)
C19	0.0539 (14)	0.2910 (39)	0.1720 (27)	6.7 (6)
C20	0.3240 (15)	0.2913 (40)	−0.0267 (27)	7.0 (6)
C21	0.3298 (15)	0.2585 (36)	0.0766 (26)	6.9 (7)
C22	0.3527 (12)	0.1110 (26)	0.0673 (19)	3.9 (4)
C23	0.3561 (11)	0.0569 (32)	−0.0335 (20)	4.6 (4)
C24	0.3359 (11)	0.1839 (29)	−0.1139 (19)	4.6 (4)

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* Atomic scattering factors were taken from ref. 7a for carbon and from ref. 7b for nickel.

The atomic coordinates obtained from this treatment are listed in Table 1 together with estimated standard deviations obtained from the diagonal elements of the matrix. Details of the molecular geometry are given in Table 2.

TABLE 2

MOLECULAR GEOMETRY

Interatomic distances and estimated standard deviations[12] *(Å)*

Ni1–Ni2	2.329 (4)	Ni1–C7	1.89 (2)
C7–C8	1.35 (3)	Ni1–C8	1.89 (2)
C7–C6	1.43 (3)	Ni2–C7	1.90 (2)
C8–C9	1.47 (3)	Ni2–C8	1.87 (2)
Ni1–C15	2.05 (3)	C15–C16	1.27 (4)
Ni1–C16	2.06 (3)	C16–C17	1.60 (4)
Ni1–C17	2.10 (3)	C17–C18	1.36 (4)
Ni1–C18	2.13 (3)	C18–C19	1.42 (4)
Ni1–C19	2.16 (3)	C19–C15	1.42 (4)
Ni2–C20	2.09 (3)	C20–C21	1.24 (4)
Ni2–C21	2.15 (3)	C21–C22	1.46 (4)
Ni2–C22	2.11 (3)	C22–C23	1.28 (4)
Ni2–C23	2.14 (3)	C23–C24	1.57 (4)
Ni2–C24	2.13 (3)	C24–C20	1.45 (4)
C1–C2	1.38 (3)	C9–C10	1.44 (3)
C2–C3	1.47 (3)	C10–C11	1.39 (3)
C3–C4	1.35 (3)	C11–C12	1.38 (3)
C4–C5	1.37 (3)	C12–C13	1.31 (3)
C5–C6	1.39 (3)	C13–C14	1.54 (3)
C6–C1	1.48 (3)	C14–C9	1.31 (3)

Intramolecular angles and estimated standard deviations (°)

Ni1–C7–Ni2	76.0 (7)	Ni1–C8–Ni2	76.6 (7)
Ni1–C7–C6	140.4 (12)	Ni1–C8–C9	136.3 (12)
Ni1–C7–C8	69.0 (12)	Ni1–C8–C7	69.0 (12)
Ni2–C7–C6	134.9 (12)	Ni2–C8–C9	133.9 (12)
Ni2–C7–C8	68.1 (12)	Ni2–C8–C7	69.9 (12)
C6–C7–C8	137.8 (19)	C7–C8–C9	142.0 (19)
C7–Ni1–C8	42.0 (9)	C7–Ni2–C8	42.0 (9)
C7–Ni1–Ni2	52.2 (6)	C7–Ni2–Ni1	51.8 (6)
C8–Ni1–Ni2	51.5 (6)	C8–Ni2–Ni1	51.9 (6)

Best least-squares planes defined by atomic positions

In the following equations X, Y, Z refer to atomic coordinates in Angstrom units.

(*i*) Plane defined by C1, C2, C3, C4, C5 and C6

$$-0.6389X-0.7684Y+0.0373Z+2.4977=0$$

Distances of atoms from this plane (Å)

C1	−0.01	C3	0.05	C5	0.04
C2	−0.01	C4	−0.07	C6	−0.01

(*ii*) Plane defined by C9, C10, C11, C12, C13 and C14

$$-0.7162X-0.0150Y+0.6978Z+2.1341=0$$

Distances of atoms from this plane (Å)

C9	−0.02	C11	0.00	C13	−0.06
C10	−0.01	C12	0.04	C14	0.05

(*iii*) Plane defined by C15, C16, C17, C18 and C19

$-0.4772X+0.2653Y+0.8378Z-1.9304=0$

Distances of atoms from this plane (Å)

C15	−0.03	C17	0.00	C19	0.02
C16	0.02	C18	−0.01	Ni1	−1.72

(*iv*) Plane defined by C20, C21, C22, C23 and C24

$0.9652X+0.2580Y-0.0422Z-6.2582=0$

Distances of atoms from this plane (Å)

C20	0.01	C22	0.02	C24	0.00
C21	−0.02	C23	−0.01	Ni2	−1.76

(*v*) Plane defined by C3, C6, C7, C8, C9 and C12

$0.8840X-0.0153Y-0.4673Z-2.5890=0$

Distances of atoms from this plane (Å)

C3	0.01	C7	−0.02	C9	0.03
C6	−0.02	C8	0.02	C12	−0.02

DISCUSSION

The structure of the crystalline form of (diphenylacetylene)bis(cyclopentadienylnickel) consists of discrete molecules with closest approaches between carbon atoms greater than 3.5 Å which corresponds to the usual van der Waals contacts.

The structure bears resemblance to that of $(PhC_2Ph)[Co(CO)_3]_2$[5] and of $(C_5H_5NiCO)_2$[8]. The two bridging groups in the latter are replaced by the acetylene function. The Ni–Ni vector is almost perpendicular, within 0.8°, to the C–C vector of the original alkyne, the same condition as is found in the cobalt complex. To each nickel atom is attached a π-bonded cyclopentadienyl group. The average Ni–C distances are 2.10 and 2.12 Å, which correspond to Ni–ring-plane separations of 1.72 and 1.76 Å, and can be compared with the previously reported values of 2.107, 2.13 and 2.12 Å for the half-sandwich complexes C_5H_5NiNO[9], $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$[10] and $(C_5H_5Ni)_3(CO)_2$[11] and the previously unreported values 2.10, 2.11, 2.11 and 2.13 Å found in $(C_5H_5NiCO)_2$[8]. The cyclopentadienyl rings are planar, within one standard deviation, with average C–C distances of 1.41 and 1.40 Å for the rings attached respectively to Ni1 and Ni2. The carbon atoms in these rings are the least-well determined and the individual distances thus have the largest standard deviations and greatest variations between themselves. It would have been necessary to determine more intensities and to refine the structure anisotropically in order to obtain greater precision but as mentioned in the introduction we were more interested in the overall geometry. The Ni–C(alkyne) distances, however, fall within the rather narrow range of 1.87–1.90 Å with average of four independent estimates of 1.89 Å. The unsaturated organic function is thus symmetrically bonded to the nickel atoms. Without prejudice to any discussion of the nature of the bonding between these carbon atoms and the metal atoms, we note that this distance is scarcely different from the sum of covalent radii, *viz.* 1.90–1.93 Å obtained from $r_{Ni}=1.16$ Å and a covalent radius of 0.74–0.77 Å for sp^2- and sp^3-hybridised carbon respectively. The value is possibly smaller than that reported for $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$[10], namely 1.96(1) Å.

The nickel atoms are separated by only 2.33 Å and this is the shortest distance yet known to us for this element. A value of 2.39 Å has been recorded for the triangular arrangement in $(C_5H_5Ni)_3(CO)_2$[11] and a value of 2.36 Å for $(C_5H_5NiCO)_2$[8].

The C–C distances in the central portion of the ligand agree rather well with those of Sly for the cobalt compound. Thus the central C–C distance is found to be 1.35 Å and the alkyne–phenyl distance 1.45 Å (average) to be compared with the values of 1.37 and 1.46 Å. However it should be remembered that the standard deviations of these distances are 0.03 Å. The phenyl groups, which are planar to within two standard deviations, are twisted from the symmetrical bridging position but to differing extents (see Fig. 1), so that the angle between the phenyl groups is 60°. This compares with the angle of 62° found in the corresponding analysis of the cobalt complex. The ligand is no longer linear, as in the uncomplexed form, but is bent symmetrically at the central carbon atoms to give angles of 138 and 142°. The corresponding values for the cobalt system are 137 and 139°.

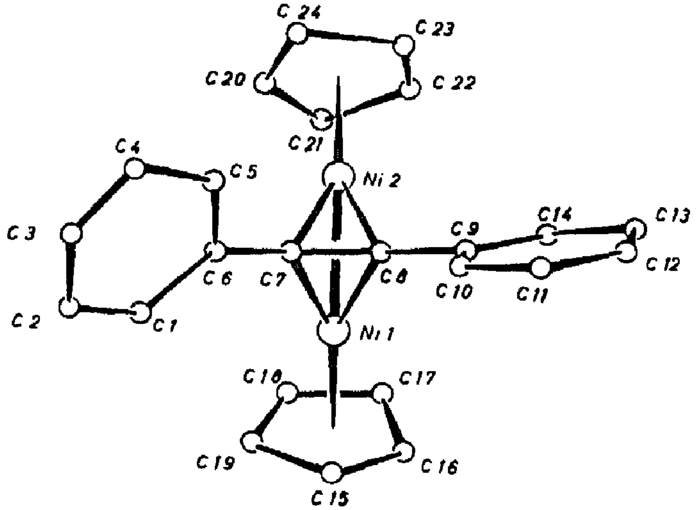

Fig. 1. Projection of molecule showing numbering scheme.

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SUMMARY

The molecular configuration of (diphenylacetylene)bis(cyclopentadienylnickel) has been determined by X-ray analysis. The dull, olive green crystals belong to the orthorhombic system, spacegroup $Pna2_1$, with $a = 17.73$, $b = 9.49$ and $c = 11.62$ Å. The two central carbon atoms of the ligand, which latter is no longer linear in the complex, lie perpendicular to the two nickel atoms so that these four atoms form a symmetrical tetrahedron. The nickel atoms are 2.33 Å apart and the average Ni–C distance is 1.89 Å. The cyclopentadienyl groups are π-bonded to the nickel atoms. The phenyl groups do not appear to participate in the bonding.

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