THE STEREOCHEMISTRY OF TRANSITION METAL CYCLOOCTATETRAENYL COMPLEXES: DI-h^3,$h^{3'}$ CYCLOOCTATETRAENEDINICKEL, A SANDWICH COMPOUND WITH TWO ENVELOPED NICKEL ATOMS

DAVID J. BRAUER * and CARL KRÜGER **

*Max-Planck-Institut für Kohlenforschung, 4330 Mülheim a.d. Ruhr, Lembkestr. 5
(B.R.D.)*

(Received June 7th, 1976)

Summary

The crystal structure of dicyclooctatetraenedinickel, [(COT)Ni]$_2$, has been determined from three-dimensional, single crystal X-ray data collected by counter methods. Crystals of [(COT)Ni]$_2$, belong to the monoclinic system with $a = 8.2906(3)$, $b = 11.4185(5)$, $c = 7.2340(3)$ Å, $\beta = 115.978(2)°$, d(calc) = 1.757 gcm^{-3}, $Z = 2$. The space group is C_{2h}^5-$P2_1/a$. The structure was refined aniso-tropically (hydrogen atoms and a nickel atom fragment isotropically) by full-matrix least-squares techniques. Final values of R and R_w were 0.046 and 0.079, respectively, for the 1055 unique, absorption and extinction corrected reflections with $I > 2\sigma(I)$. Crystals of [(COT)Ni]$_2$ consists of discrete molecules with crystallographic C_i ($\bar{1}$) symmetry. The compound possesses a sandwich structure with both metal atoms between the COT rings. Each nickel atom forms π-allyl type bonds to three carbon atoms of each COT ring. The nickel atoms are disordered over three sites. The effect of this disorder on the interpretation of the derived structural parameters is discussed.

Introduction

Two binary complexes of 1,3,5,7-cyclooctatetraene (COT) and nickel have been reported. One compound has the empirical composition [(COT)Ni]$_x$ (I) [1], while the other is (COT)$_2$Ni (II) [1]. (COT)$_2$Ni, which is stable only at low temperatures, decomposes at room temperature to yield I and COT. Because both of these nickel compounds are air sensitive and I is particularly insoluble

---

* Present address: Gesamthochschule Wuppertal, Fachbereich Anorganische Chemie, 5600 Wuppertal 2, Gewerbeschulstr. 34 (B.R.D.).
** To whom correspondence should be addressed.

in most common solvents, little detailed structural information is available for them.

Reactions of COT with numerous nickel compounds have been found to yield I [2,3]. In addition I may be prepared by electrochemical reduction of nickel salts in presence of COT [4]. Whether the ease of isolation of I is due to its thermodynamic stability or rather to its insolubility (kinetic stability) is not clear. In order to clarify the bonding in I, we have investigated this compound by single crystal X-ray diffraction methods.

Experimental

Black crystals of I, prepared by the electrochemical technique [4], were kindly supplied by Dr. Leuchte of this Institute. One of these crystals was placed in a glass capillary under argon. The space group and preliminary unit cell constants were obtained from precession and Weissenberg photographs. The crystal was transferred to an automated diffractometer (Siemens + PDP-8/s) and aligned so that c^* and the ϕ-axis were coincident. Nickel filtered CuK_α radiation was used. The θ values for the $CuK_{\alpha 1}$ ($\lambda = 1.54051$ Å) and $CuK_{\alpha 2}$ ($\lambda = 1.54433$ Å) doublets of 29 reflections with $114° < 2\theta < 138°$ were recorded at room temperature. Accurate unit cell constants were derived from these 2θ values by a least-squares technique. Crystals of I belong to the monoclinic system with $a = 8.2906(3)$ *, $b = 11.4185(5)$, $c = 7.2340(3)$ Å and $\beta = 115.978(3)°$. The crystals have a calculated density of 1.757 gcm^{-3} with for four formula units per unit cell. The systematic absences $h0l$, $h = 2n + 1$, and $0k0$, $k = 2n + 1$, are unique for the space group $P2_1/a$. The absorption coefficient for $CuK_{\bar\alpha}$ radiation is 33.7 cm^{-1}.

Precession photographs indicated either that the crystal possessed a small twinned component or that a crystallite was also scattering. It was possible to index these extra reflections $h'k'l'$, which were related to the major set of reflections hkl by a noncrystallographic mirror plane perpendicular to c^*. On the diffractometer the ratio of $I(h'k'l')/I(hkl)$ was found to be 0.012 for hkl planes of moderate intensity. The ratio was somewhat larger for several very intense $I(hkl)$'s, possibly indicating the presence of extinction effects. Since the $h'k'l'$ reflections were much weaker than their hkl counterparts and since these reflections only overlapped when $h = 4n$, it was decided that they would not seriously effect the data. Therefore no correction for the crystallite scattering was applied.

Intensity data (hkl, $\bar{h}kl$, $2\theta \leqslant 134°$) were measured with nickel filtered $CuK_{\bar\alpha}$ radiation by the $\theta - 2\theta$ scan technique. Variable scanning speeds (2.5, 5.0, 10.0 and 20.0°/min in 2θ) and five Ni attenuators were used to optimize the counting rate and to prevent coincident losses. The widths of the symmetrical scans (1.04 — 1.92° in 2θ) were chosen from a function of Bragg angle. Stationary-crystal-stationary-counter background measurements, BR and BL, were made at the beginning and ending positions of the scan. The counting time of each background measurement was one-half of the time used to make

---

one scan of the reflection. The intensity of the left-half *PL*, right-half *PR* and full peak *P* were also recorded. After the collection of 40 reflections, one reflection (800) was remeasured both with and without an occulator inserted in the lower half of the counter window. Thus the crystal alignment, instrument stability and crystal decay was monitored. The fluctuations of the monitor reflection were not larger than ±3%. A total of 1306 reflections were recorded. Finally the dimensions of the crystal were measured and the faces were indexed.

The data were corrected for background, monitor fluctuation and absorption *. The transmittance ranged from 0.224 to 0.396 and the intensities were converted to structure factor amplitudes by taking these factors in account. Of the unique 1087 reflections measured, 1055 had intensities $I > 2\sigma(I)$, where $I = 0.5(PL + PR + P) - BL - BR$ and $\sigma^2(I) = 0.25(PL + PR + P) + BL + BR$. These "observed" reflections were assigned weights w equal to $\sigma^{-2}(|F_o|)$,

$$\sigma(|F_o|) = \frac{K}{2F_o}[\sigma^2(I) + 0.03^2 I^2]$$

where K is a scaling factor. "Unobserved" reflections were assigned zero weights.

Solution and refinement of the structure

The structure was solved by a combination of direct methods and heavy atom techniques. The distribution of E's was consistent with a centric structure. The coordinates of a nickel atom and eight carbon atoms obtained from an E-map were the same as those derived by the heavy atom technique. Inspection of a difference Fourier map revealed that the Ni atoms were approximately 50 : 50% disordered. Refinement proceeded using nickel atoms with occupancy 0.5 separated by 1 Å.

The structure was refined by full-matrix least-squares techniques. The function minimized was $\Sigma w\Delta^2$, where $\Delta = ||F_o| - |F_c||$. Relativistic scattering factors [5] were used for all atoms except H [6]. The real and imaginary values for the anomalous scattering of Ni [7] were used in the calculation of F_c. In the latter stages of refinement, a secondary extinction parameter, similar to that described by Larson [8] except that all path lengths were assumed to be 1 cm, was also refined.

After anisotropic refinement, the positions of the hydrogen atoms were located in a difference Fourier map. A subsequent difference Fourier synthesis has a peak ($1.6e/Å^3$) about 1 Å from Ni(1). This peak height may be compared with that of a typical carbon atom in this structure, $7.4e/Å^3$. A twentieth of a nickel atom was entered at this position and assigned an isotropic temperature factor.

Anisotropic refinement (Ni(3) and the H atoms being refined isotropically) continued with the occupancies of the Ni atoms being varied. In order to investigate the nature of the disorder, two constrained models for the Ni atom occupancies were applied. In model A, the sum of the three occupancies was

---

* In addition to several local programs, modified versions of the following programs were used: Coppens, Leiserowitz and Rabinovich's DATAP absorption program, Ahmed's FOSUM Fourier program, Weizmann Institute's BDLS least-squares program, Davids's DAESD distance and angle program and Johnson's ORTEP thermal ellipsoid plotting program.

constrained to be 1. This constraint was also used in model B in which the occupancy of Ni(1) was held at 0.5. The final values of $R = \Sigma\Delta/\Sigma|F_o|$, the summation excluding "unobserved" reflections, and $R = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2}$ were 0.0452 and 0.0791, respectively for model A and 0.0456 and 0.0795, respectively, for model B. Since model A is not significantly better than model B at the 1% level [9] and since the parameters of the two models are essentially identical, we will refer only to the parameters of model B in the subsequent discussion. In a difference map calculated at the end of refinement, the only peaks greater than $0.2e/\text{Å}^3$ were near the Ni atoms, the largest ($0.5e/\text{Å}^3$) being

TABLE 1

POSITIONAL PARAMETERS FOR [(COT)Ni]$_2$

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$
Ni(1)	0.0810(1)	0.00026(6)	0.7207(1)
Ni(2)	−0.0183(1)	0.05715(6)	0.6724(1)
Ni(3)	0.1472(10)	−0.0573(6)	0.6725(12)
C(1)	0.3204(3)	0.0237(2)	0.6992(3)
C(2)	0.2618(3)	0.1141(2)	0.7892(4)
C(3)	0.1180(3)	0.1911(2)	0.7087(4)
C(4)	−0.0209(3)	0.2090(2)	0.5101(4)
C(5)	−0.0484(3)	0.1823(2)	0.3110(4)
C(6)	0.0460(4)	0.1200(2)	0.2210(4)
C(7)	0.1856(4)	0.0390(2)	0.3000(5)
C(8)	0.2875(3)	−0.0089(2)	0.4981(5)
H(1)	0.418(5)	−0.019(3)	0.804(6)
H(2)	0.333(6)	0.131(3)	0.940(7)
H(3)	0.113(5)	0.235(3)	0.824(5)
H(4)	−0.099(5)	0.254(3)	0.528(5)
H(5)	−0.165(5)	0.216(3)	0.213(6)
H(6)	−0.000(5)	0.135(4)	0.069(8)
H(7)	0.210(5)	0.002(3)	0.191(7)
H(8)	0.365(5)	−0.073(4)	0.512(6)

THERMAL PARAMETERS FOR [(COT)Ni]$_2$

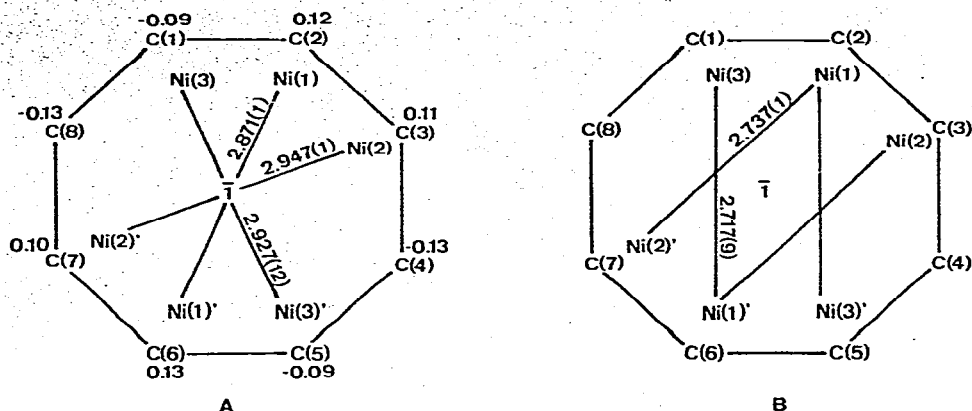| Atom	$U_{11}(U_{iso})$	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ni(1)	0.0482(6)	0.0398(6)	0.0431(6)	−0.0107(4)	−0.0019(3)	0.0223(4)
Ni(2)	0.0433(7)	0.0345(6)	0.0466(6)	−0.0084(4)	−0.0046(3)	0.0262(5)
Ni(3)	0.037(3)					
C(1)	0.0362(11)	0.0484(12)	0.0706(17)	0.0007(10)	0.0097(12)	0.0151(11)
C(2)	0.0524(12)	0.0532(13)	0.0440(12)	−0.0141(10)	−0.0026(9)	0.0132(10)
C(3)	0.0639(13)	0.0449(12)	0.0553(13)	−0.0064(11)	−0.0098(10)	0.0353(11)
C(4)	0.0533(13)	0.0278(10)	0.0721(16)	0.0025(8)	0.0027(8)	0.0322(12)
C(5)	0.0576(13)	0.0375(11)	0.0558(13)	−0.0009(11)	0.0126(10)	0.0170(11)
C(6)	0.0717(16)	0.0573(13)	0.0454(13)	−0.0229(13)	0.0009(10)	0.0263(11)
C(7)	0.0731(16)	0.0593(14)	0.0677(17)	−0.0203(14)	−0.0215(13)	0.0479(14)
C(8)	0.0409(12)	0.0439(12)	0.0950(12)	−0.0044(8)	−0.0101(11)	0.0411(14)
H(1)	0.067(9)					
H(2)	0.092(11)					
H(3)	0.079(10)					
H(4)	0.080(10)					
H(5)	0.075(9)					
H(6)	0.095(12)					
H(7)	0.074(11)					
H(8)	0.088(12)					

Fig. 1. Projections of the disordered nickel atoms on one C₈ ring. In A the Ni—Ni contacts of the centro-symmetric model are shown, and in B the Ni—Ni contacts of the asymmetric model are indicated. In A, the deviations of the carbon atoms from the best plane through the carbocyclic ring are shown. The nickel atoms are —1.70 Å from this plane.

1.3 Å from Ni(2) and Ni(3)'. While this peak conceivably could indicate further disorder of the nickel atoms, no attempt was made to include it in the refinement since the peak itself was asymmetric and the peak height indicated that not more than 1—2% of a nickel atom was present at that site.

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN [(COT)Ni]₂

Atoms	Bond length (Å)	Atoms	Bond length (Å)	Atoms	Angle (°)
Ni(1)—Ni(1)' ^{a}	2.871(1)	C(1)—C(2)	1.417(4)	C(8)—C(1)—C(2)	135.9(3)
Ni(2)—Ni(2)'	2.947(1)	C(1)—C(8)	1.409(5)	C(1)—C(2)—C(3)	132.4(3)
Ni(3)—Ni(3)'	2.927(12)	C(2)—C(3)	1.387(4)	C(2)—C(3)—C(4)	133.6(2)
Ni(1)—Ni(2)'	2.737(1)	C(3)—C(4)	1.409(4)	C(3)—C(4)—C(5)	135.6(2)
Ni(1)—Ni(3)'	2.719(9)	C(4)—C(5)	1.390(4)	C(4)—C(5)—C(6)	135.8(2)
Ni(1)—C(1)	2.076(3)	C(5)—C(6)	1.411(4)	C(5)—C(6)—C(7)	132.4(3)
Ni(1)—C(2)	1.880(2)	C(6)—C(7)	1.395(4)	C(6)—C(7)—C(8)	133.7(3)
Ni(1)—C(3)	2.208(2)	C(7)—C(8)	1.417(5)	C(7)—C(8)—C(1)	134.7(2)
Ni(1)—C(5)'	2.102(2)	C(1)—H(1)	0.96(4)	C(2)—C(1)—H(1)	110(2)
Ni(1)—C(6)'	1.888(3)	C(2)—H(2)	1.01(5)	C(8)—C(1)—H(1)	114(2)
Ni(1)—C(7)'	2.196(3)	C(3)—H(3)	0.99(4)	C(1)—C(2)—H(2)	119(2)
Ni(2)—C(2)	2.193(3)	C(4)—H(4)	0.88(4)	C(3)—C(2)—H(2)	109(2)
Ni(2)—C(3)	2.851(3)	C(5)—H(5)	1.00(4)	C(2)—C(3)—H(3)	108(2)
Ni(2)—C(4)	2.089(2)	C(6)—H(6)	1.01(6)	C(4)—C(3)—H(3)	118(2)
Ni(2)—C(6)'	2.213(3)	C(7)—H(7)	0.99(4)	C(3)—C(4)—H(4)	105(2)
Ni(2)—C(7)'	1.848(4)	C(8)—H(8)	0.96(4)	C(5)—C(4)—H(4)	119(2)
Ni(2)—C(8)'	2.097(3)			C(4)—C(5)—H(5)	109(2)
Ni(3)—C(8)	2.130(9)			C(6)—C(5)—H(5)	115(2)
Ni(3)—C(1)	1.647(8)			C(5)—C(6)—H(6)	113(3)
Ni(3)—C(2)	2.179(8)			C(7)—C(6)—H(6)	114(3)
Ni(3)—C(4)'	2.152(8)			C(6)—C(7)—H(7)	112(3)
Ni(3)—C(5)'	1.676(8)			C(8)—C(7)—H(7)	114(2)
Ni(3)—C(6)'	2.181(9)			C(7)—C(8)—H(8)	119(3)
				C(1)—C(8)—H(8)	106(3)

^{a} Primed atoms are related to their counterpart in Table 1 as follows: $x'y'z' = -x, -y, 1-z$.

A plot of $\langle w\Delta^2 \rangle$ versus $|F_o|$ indicated that the weights for the weaker reflections were chosen too high. A plot of $\langle w\Delta^2 \rangle$ versus $\sin\theta/\lambda$ was reasonably flat. The error of fit was 4.87. The final value of the extinction parameter settled at 0.00048(8), the largest correction being applied to the $|F_c|$ of the 110 reflection, 60% *. The positional and thermal parameters are given in Table 1. The numbering scheme for the Ni and C atoms is shown in Fig. 1, the H atoms being numbered after the C atoms to which they are attached. Bond distances and angles are listed in Table 2. Error estimates were made using the diagonal elements of the inverse least-squares matrix.

Results and discussion

Crystals of $[(COT)Ni]_x$ consist of discrete, dimeric molecules, $x = 2$. All intermolecular contacts are normal, the shortest being H(1)...H(2) $(1 - x, -y, 2 - z)$, 2.44(6) Å. The asymmetric unit contains COT ligand and three partially occupied sites for the nickel atoms, the sum of their site occupation factors being 1. The second half of the dimer is generated by an inversion symmetry element at 0, 0, 1/2. This dimer is the first example of a sandwich compound with two metal atoms between two monocyclic (CH) rings.

Each nickel atom forms "sandwich-type" bonds with π-allyl fragments in each COT ring (Fig. 2 and 3). Therefore the compound may be classified as a
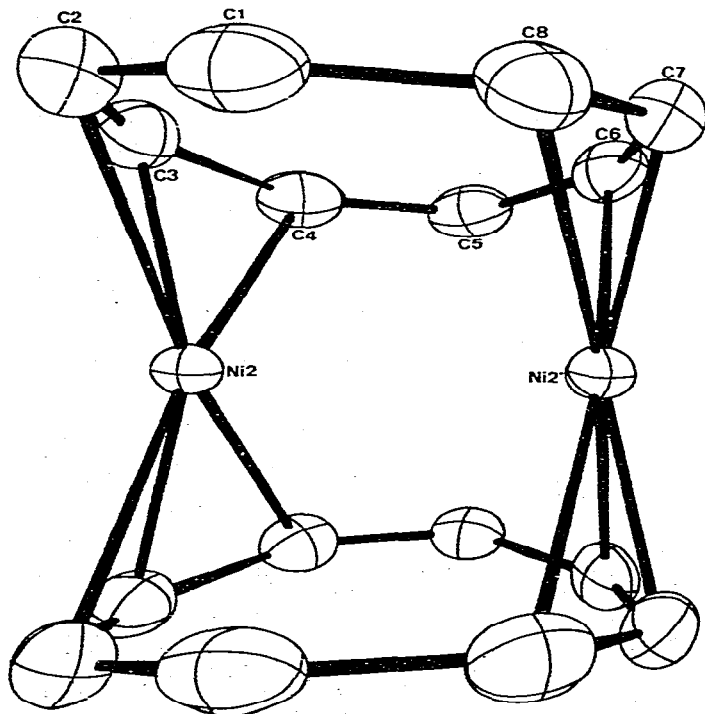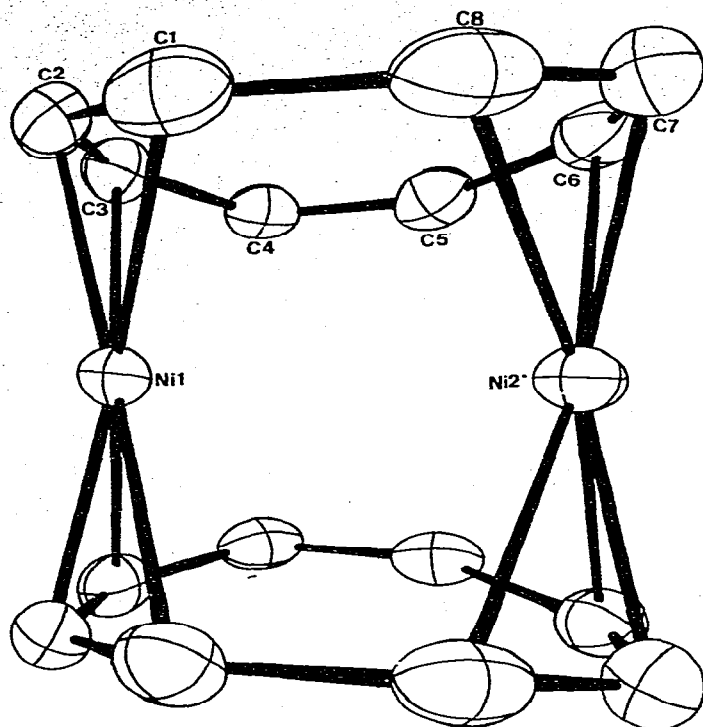

Fig. 2.

Fig. 3.

bis-π-allyl complex of Ni(II). The dimeric nature of the molecule requires the bis-π-allylnickel fragments to have a *cis* geometry rather than the *trans* geometry found in bis-π-methallylnickel [10]. While the *cis* orientation of the π-allyl fragments in the nickel coordination plane is unusual, an equilibrium in solution between the *cis* and *trans* isomers of bis-π-allylnickel has been postulated [11] and *cis* oriented π-allyl fragments have been found only in compounds that have constrained organic ligands (for example, 1,1,2,4,4-pentamethylene(tri-cyclohexylphosphine)nickel [12]).

Unfortunately, several features of the structure are obscured by the disorder of the nickel atoms. After eliminating all other Ni—Ni contact patterns by the reasonable requirements of these contact being greater than 2.0 Å and of a unique structure for [(COT)Ni]$_2$, we were left with two patterns (Fig. 1). Pattern A is that which obeys the crystallographic inversion symmetry. The contacts of pattern B do not obey the space group symmetry, which seems assured not only by the systematic absences but also by the successful solution and refinement of the structure. For the latter pattern, the occupancy of Ni(1) is required to be 1/2, a value in good agreement with the diffraction data vide supra. Since model A places no restrictions on the site occupation factor of Ni(1), we have not been able to resolve this structural dilemma crystallographically.

The Ni—Ni contacts of pattern A are about 0.2 Å longer than those of pattern B. For compounds of nickel(II) in which Ni—Ni bonds have been proposed, the

Ni—Ni distances are as short as 2.38 Å in $[(C_6H_5)_2N_3]_4Ni_2$ [13] and as long as 2.76 Å in di-π-ethylthiolatobis(ethyltrithiocarbonato)dinickel [14]. Regardless of the pattern exhibited by the Ni atoms in $[(COT)Ni]_2$, the Ni—Ni distances seem too long for strong Ni—Ni bonds.

Another unresolved feature is the stereochemistry of the COT, Ni interaction. Three possibilities are to be discussed. If the molecules have pattern A Ni—Ni contacts, then two π-allyl fragments of each COT ring are positioned as shown in Fig. 2. The molecular symmetry would be approximately D_{2h} (mmm). The bridging COT rings in dinuclear compounds such as $(COT)Fe_2(CO)_5$ [15] and $(COT)_3Cr_2$ [16] show similar geometries. If the individual molecules have Ni—Ni contacts of type B, however, then each COT ring will have adjacent π-allyl fragments and an isolated carbon—carbon double bond (Fig. 3). Depending on whether or not in the individual molecules the positions of the double bond in the COT rings obey the crystallographic symmetry, two structures are possible. Such obedience implies a structure of C_{2h} ($2/m$) symmetry, the molecules being translationally disoriented in the crystal, an unlikely situation. The other structure would have C_{2v} ($2mm$) symmetry (Fig. 3).

The C_8 ring has a shallow tub conformation with the carbon atoms deviating ±0.13 Å from planarity (Fig. 1). Bridging COT ligands as in $(COT)_3Cr_2$ are known to exist in a folded conformation the π-allyl fragments being bent away from the metal atoms [16]. If we superimpose two such C_8 rings so that the meso-π-allyl fragment carbon atoms of one ring overlap with terminal π-allyl fragment carbon atoms of the other ring, then the average positions of the overlapping carbon atoms would define a ring in the tub conformation. The disordering of the Ni atoms thus leads to a disordering of the carbon atoms. The extent of the disorder must not be great since both the carbon and hydrogen atoms were revealed as single peaks by the Fourier maps. So unlike the case for nickel atoms, we can resolve the disordered COT atom positions. The hydrogen atom parameters refined surprisingly well considering the disorder problem, to give an average C—H length of 0.98(4) Å *.

The large variation of the Ni—C(allyl) bond lengths, 1.647(8)—2.213(3) Å, is undoubtedly an artefact of disorder in the carbon atom positions. The remaining Ni—C contacts are greater than 2.7 Å and are considered to be nonbonding. At least in this respect, COT bridging in I is different from that found in $(COT)Fe_2(CO)_5$ [15] and $(COT)_3Cr_2$ [16], where the carbon atoms in the positions anti to the π-allyl fragments also are considered to be bonding to the metal atoms **. Interestingly, both bis(π-allyl)nickel [17] and COT^{2-} [18] are yellow while $[(COT)Ni]_2$ is black. Perhaps the color is the result of charge transfer transitions in which the nickel atoms receive charge from those carbon atoms not bound to nickel.

---

* X-ray diffraction studies always yield systematically shortened C—H distances when spherical atom form factors are used.

** A long Fe—Fe single bond was postulated for $(COT)Fe_2(CO)_5$, and the C atoms anti to the π-allyl fragments form long-bridge bonds, Fe—C about 2.50 Å [15]. A short Cr—Cr quadruple bond was found in $(COT)_3Cr_2$, and the C atoms anti to the π-allyl fragments form shorter bridge bonds, Cr—C about 2.30 Å [16]. Apparently metal—metal bonding is a prerequisite for the formation of the electron deficient metal—carbon—metal bridge bond.

References

1 G. Wilke, B. Bogdanović, P. Heimbach, M. Kröner and E.W. Müller, Adv. Chem. Ser. 34 (1962) 137.
2 G. Wilke et al., Angew. Chem. 75 (1963) 10.
3 G. Wilke, Angew. Chem. 72 (1960) 581.
4 H. Lehmkuhl, W. Leuchte and W. Eisenbach, Liebigs Ann., (1973) 692.
5 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104.
6 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
7 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
8 A. Larson, in F.R. Ahmed (Ed.), Crystallographic Computing, Munsksgaard, Copenhagen, 1970, pp. 291—294.
9 W.C. Hamilton, Acta Crystallogr., 18 (1965) 502.
10 P. Uttech and H. Dietrich, Z. Kristallogr., 122 (1965) 60.
11 H. Bönnemann and B. Bogdanović, Angew. Chem., 79 (1967) 817; Angew. Chem. Int. Ed. Engl., 6 (1967) 804.
12 B.L. Barnett, C. Krüger and Y.-H. Tsay, Angew. Chem., 84 (1972) 121.
13 M. Corbett and B.F. Hoskins, Chem. Commun., (1968) 1602.
14 A.C. Villa, A.G. Manfredotti, M. Nardelli and C. Pelizzi, Chem. Commun., (1970) 1322.
15 E.B. Fleischer, A.L. Stone, R.B.K. Dewar, J.D. Wright, C.E. Keller and R. Pettit, J. Amer. Chem. Soc., 88 (1966) 3158.
16 D.J. Brauer and C. Krüger, J. Inorg. Chem., in press.
17 G. Wilke and B. Bogdanović, Angew. Chem., 73 (1961) 756.
18 H.P. Fritz and H. Keller, Z. Naturforsch., 16 b (1961) 231.