

Fig. 2. A view of the crystal structure along the c axis.

ring is almost coplanar with (001). In Fig. 2 is shown the superposition of the formyl groups. The shortest intermolecular contacts were observed between methyl C and formyl O atoms: $\text{C}(41)\cdots\text{O}(4)^* = 3.25(1) \text{ \AA}$. Other intermolecular contacts, involving C(6) with C(4), C(5), C(6) and O(4); or O(4) with C(4) and C(5); or methyl groups with other methyl groups or with O(1), are not remarkable, being in the range 3.44–3.79 Å.

* In the equivalent position $y - x, -x, \frac{1}{2} + z$.

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Structure of (Cycloocta-1,5-diene)(tolan)nickel*

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Abstract. $[\text{Ni}(\text{C}_{14}\text{H}_{10})(\text{C}_8\text{H}_{12})]$, $M_r = 345.13$, monoclinic, $P2_1/c$, $a = 11.429(2)$, $b = 8.648(1)$, $c = 17.724(3) \text{ \AA}$, $\beta = 89.26(1)^\circ$, $V = 1751.6 \text{ \AA}^3$, $Z = 4$, $D_x = 1.31 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$, $\mu(\text{Mo K}\alpha) = 11.08 \text{ cm}^{-1}$, $F(000) = 728$, $T = 291 \text{ K}$. Final $R = 0.044$ ($wR = 0.051$) for 2490 unique observed reflections. The Ni atom has an approximately trigonal planar coordination geometry, with the C=C bonds of the coordinated cycloocta-1,5-diene and the C≡C triple

All the molecules overlapping in the same spiral must have the formyl group disordered in the same position to avoid steric hindrance.

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bond of the tolan ligand occupying the three coordination sites. The central C–C bond of the coordinated tolan molecule lies approximately parallel to the coordination plane of the metal.

Introduction. In tris(ligand) complexes of the d^{10} transition metals, single-faced π -acceptor ligands adopt a conformation in which the π -acceptor orbital of the ligand aligns itself parallel to the coordination plane of the metal (Hartley, 1972). Tris(ethylene)platinum (Howard, Mason & Spencer, 1983) and tris(ethylene)-

* Tolan is diphenylethyne.

nickel (Fischer, Jonas & Wilke, 1973) are two such examples. An explanation is to be found in the ability of the empty p orbitals on the metal to mix selectively into the filled d orbitals in the trigonal plane and enhance the backbonding in that plane (Hoffmann & Röscher, 1974). The structure of the title compound was determined because we were interested in establishing what would happen to the orientation of one π -acceptor group (in this case the tolan ligand) when the other two groups were forced to adopt a configuration in which the π -acceptor orbitals are perpendicular to the coordination plane of the metal, such as is the case with the ligand cycloocta-1,5-diene.

The preparation of the title compound was first described by Muetterties in 1978 (Anderson, Beier, Day, Muetterties, Pretzer, Thomas & Thorn, 1978), but the authors were unable to isolate the compound because of an unfavourable equilibrium that exists between the complex and the dinuclear species $(\text{cod})_2\text{Ni}_2(\text{C}_2\text{Ph}_2)$ [cod = cycloocta-1,5-diene, (C_2Ph_2) = tolan]. The compound was, however, successfully isolated while attempting to prepare $(\text{tmeda})\text{Ni}(\text{C}_2\text{Ph}_2)$ (tmeda = tetramethylethylenediamine) from $(\text{cod})_2\text{Ni}$, tolan and tmeda (Apotecher, 1983).

Experimental. The title compound was prepared by slowly adding 2.76 g $(\text{cod})_2\text{Ni}$ over 4 h to a cooled (253 K) solution of 1.15 g tmeda and 1.74 g tolan dissolved in 150 ml pentane. The yellow suspension was stirred for 3 days at 253 K, after which time the solution turned red and a yellow solid was formed. The precipitate was filtered off at 253 K, washed with pentane and dried in a vacuum. Crystals of the title compound were grown as yellow prisms from dimethylformamide solution. The crystal chosen for data collection measured $0.14 \times 0.10 \times 0.08$ mm. The unit-cell parameters were obtained by a least-squares fit to the θ values of 74 automatically centred reflections ($8.6 \leq \theta \leq 22.3^\circ$). Intensity data were measured within the range $1.1 \leq \theta \leq 26.9^\circ$ on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated $\text{Mo K}\alpha$ X-radiation by a θ - 2θ scan technique in 48 steps, where the time spent measuring the background was half that taken to measure the peak. The intensity of a reflection and its e.s.d. were calculated from $I = \text{INT} - 2(\text{BGL} + \text{BGR})$ and $\sigma(I) = [\text{INT} + 4(\text{BGL} + \text{BGR})]^{0.5}$, where INT, BGL and BGR are the peak intensity, left and right background counts, respectively. The horizontal detector aperture and the (ω) -scan range varied as $3.2 + 1.25\tan\theta$ mm and $0.8 + 0.35\tan\theta^\circ$. The intensities of three standard reflections, remeasured every 100 reflections, showed no significant variation during data collection. Data were corrected for Lorentz and polarization effects, but not for absorption. $\sigma(F)$ was calculated from $\sigma(F) = [\sigma(I)^2 + (Ik)^2]^{0.5}/2F$, where $k=0.02$. Of a total of 3765 ($\pm h$, $+k$, $+l$) independent measured intensities,

2490 satisfied the criterion $I \geq 2.0\sigma(I)$, and only these were used in the solution and refinement of the structure. Computer programs used in this investigation include modified versions of the *DATAP* data reduction program (Coppens, Leiserowitz & Rabino- vich, 1965), *TRACER* (Jacobson & Lawton, 1965) for cell reduction, *SHELX* (Sheldrick, 1974) for crystal structure solution and refinement, a modified version of the *ORFLS* least-squares program for blocked-diagonal refinement (Busing, Martin & Levy, 1962), *DAESD* for distances and angles (Davis & Harris, 1970), the *XANADU* molecular geometry program (Roberts & Sheldrick, 1976), and the *ORTEP* thermal-ellipsoid plotting program (Johnson, 1976).

The structure was solved by the heavy-atom method. Refinement was by blocked least-squares methods, where the function minimized was $\sum w(\Delta F)^2$ with $w = 1/\sigma(F)^2$ and $\Delta F = |F_o| - |F_c|$. The positions of the H atoms were calculated [$d(\text{C}-\text{H}) = 1.08 \text{ \AA}$] and included in the refinement with fixed isotropic thermal parameters ($U_{\text{H}} = 0.1 \text{ \AA}^2$). Refinement converged at $R = 0.044$ ($wR = 0.051$) for 208 variables (n) and 2490 reflections (m), and the value of the 'error of fit', $S = [\sum w(\Delta F)^2/(m-n)]^{0.5}$, was 2.7, indicating a slight underestimation of the error of an observation of unit weight. In the final refinement cycle the maximum shift-to-e.s.d. ratio was 0.008. A correction for the effects of anomalous dispersion for Ni ($f' 0.285$, $f'' 1.113$) was included in the structure-factor calculations. Atomic scattering curves were taken from *International Tables for X-ray Crystallography* (1974). In the final difference Fourier synthesis, peaks of $\pm 0.35 \text{ e \AA}^{-3}$ were observed in the vicinity of the Ni atom. Positional parameters are in Table 1 and bond lengths and angles and selected torsion angles in Table 2.*

Discussion. Fig. 1 shows the molecular structure, and Fig. 2 the packing of molecules in the unit cell.

As can be seen from Fig. 1, the acetylenic bond of the tolan ligand is found to lie in the coordination plane of the Ni atom. The coordination geometry around the Ni atom is approximately trigonal planar with the two olefinic groups of the cycloocta-1,5-diene and the acetylene occupying the three coordination sites; the midpoints of the three C–C bonds and the Ni atom are coplanar to within 0.01 Å. The C=C bonds of the cyclooctadiene ligand lie approximately perpendicular to the plane of the metal and are twisted by 82.1° (C19, C20) and 93.9° (C15, C16) about the axis joining the midpoint of the respective bond to the nickel atom

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and a table of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43857 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Table 2) relative to the coordination plane of the metal. The corresponding angle for the acetylenic bond (C7—C8) is 2.4°.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Ni	0.3240 (1)	0.1873 (1)	0.3480 (1)	0.052
C1	0.2399 (3)	0.4639 (4)	0.4494 (2)	0.052
C2	0.3268 (4)	0.4625 (5)	0.5041 (2)	0.065
C3	0.3142 (5)	0.5503 (6)	0.5697 (2)	0.078
C4	0.2149 (5)	0.6349 (6)	0.5825 (2)	0.081
C5	0.1287 (4)	0.6362 (6)	0.5299 (3)	0.083
C6	0.1411 (4)	0.5535 (5)	0.4631 (2)	0.067
C7	0.2512 (3)	0.3702 (4)	0.3810 (2)	0.047
C8	0.2235 (3)	0.3423 (4)	0.3124 (2)	0.048
C9	0.1589 (3)	0.3882 (4)	0.2455 (2)	0.048
C10	0.0870 (4)	0.5170 (5)	0.2451 (2)	0.064
C11	0.0260 (4)	0.5575 (6)	0.1812 (3)	0.081
C12	0.0353 (4)	0.4688 (6)	0.1171 (2)	0.077
C13	0.1067 (4)	0.3410 (5)	0.1153 (2)	0.069
C14	0.1678 (3)	0.3000 (5)	0.1793 (2)	0.062
C15	0.4031 (4)	0.0546 (5)	0.2625 (2)	0.071
C16	0.3068 (4)	-0.0200 (5)	0.2890 (2)	0.073
C17	0.3081 (5)	-0.1521 (5)	0.3459 (3)	0.096
C18	0.3284 (7)	-0.1082 (7)	0.4239 (4)	0.149
C19	0.3679 (5)	0.0514 (6)	0.4406 (3)	0.084
C20	0.4679 (4)	0.1175 (5)	0.4137 (2)	0.072
C21	0.5561 (5)	0.0401 (8)	0.3639 (4)	0.134
C22	0.5291 (5)	0.0243 (7)	0.2855 (3)	0.106

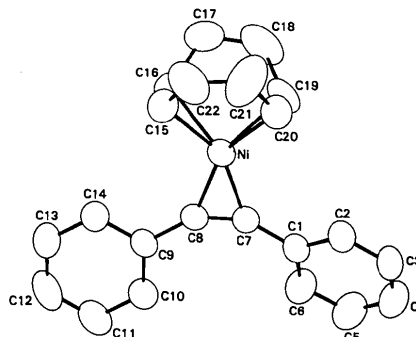


Fig. 1. The molecular structure of the title compound, with atom numbering.

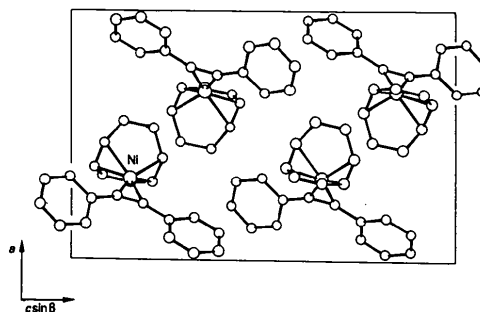


Fig. 2. The packing of the title compound in the unit cell, viewed down *b* looking towards the origin.

Table 2. Selected interatomic distances (Å), angles (°) and torsion angles (°), with e.s.d.'s in parentheses

Ni—C7	1.878 (3)	C10—C11	1.383 (6)
Ni—C16	2.086 (4)	C13—C14	1.386 (5)
C1—C2	1.398 (5)	C16—C17	1.524 (6)
C4—C5	1.366 (7)	C19—C20	1.358 (7)
C1—C7	1.462 (5)	C22—C15	1.524 (7)
C9—C10	1.385 (5)	Ni—C15	2.097 (4)
C12—C13	1.374 (7)	Ni—C20	2.116 (4)
C15—C16	1.355 (6)	C3—C4	1.368 (7)
C18—C19	1.484 (8)	C1—C6	1.390 (6)
C21—C22	1.436 (8)	C8—C9	1.461 (5)
Ni—C8	1.881 (3)	C11—C12	1.375 (6)
Ni—C19	2.085 (5)	C14—C9	1.403 (5)
C2—C3	1.394 (6)	C17—C18	1.456 (9)
C5—C6	1.389 (6)	C20—C21	1.491 (7)
C7—C8	1.284 (5)		
C7,8—Ni—C15,16*	134.6 (2)	C7,8—Ni—C19,20	133.4 (2)
C15,16—Ni—C19,20	91.7 (2)	C2—C1—C6	117.9 (3)
C2—C1—C7	120.9 (3)	C6—C1—C7	121.2 (3)
C1—C7—C8	150.3 (3)	C7—C8—C9	148.5 (3)
C8—C9—C10	121.9 (3)	C8—C9—C14	120.0 (3)
C10—C9—C14	118.1 (3)	C16—C15—C22	126.3 (4)
C15—C16—C17	124.9 (3)	C16—C17—C18	115.9 (4)
C17—C18—C19	119.0 (5)	C18—C19—C20	125.4 (5)
C19—C20—C21	125.3 (5)	C20—C21—C22	117.7 (5)
C21—C22—C15	117.3 (4)		
C1—C7—C8—C9	3.7	C6—C1—C7—C8	23.2
C7—C8—C9—C10	-2.5	C2—C1—C7—C8	-158.8
C7—C8—C9—C14	178.2	C15—C15,16—Ni—C7,8	93.9
C19—C19,20—Ni—C7,8	82.1	C8—C7,8—Ni—C19,20	-177.6
C7—C7,8—Ni—C15,16	175.9		

* C_x,y is the midpoint between the atoms C_x and C_y.

Coordination of the tolan ligand to the Ni atom results in lengthening of the C—C bond [1.284 (5) Å, *cf.* 1.198 (4) Å in free tolan (Mavris & Moustakali-Mavridis, 1977)] and the phenyl groups are bent away from the metal [C(phenyl)—C—C 146°], as has been observed for other nickel complexes [(*t*-BuNC)₂Ni(C₂Ph₂): 1.285 (20) Å, C(phenyl)—C—C 149° (Dickson & Ibers, 1972); (codNi)₂(C₂Ph₂): 1.386 (11) Å, 140.6 (4)° (Abdel-Meguid, Dabestani, Day, Muettterties, Pretzer & Thomas, 1976); {P(Me)₂-C₂H₄P(Me)₂}Ni(C₂Ph₂): 1.290 (3) Å, 146.0 (2)° (Angermund, Krüger, Mynott & Pörschke, 1985)].

The planes of the phenyl groups are not coplanar with the acetylene carbon atoms, but are twisted by different amounts around the C—Ph bonds, presumably as a result of crystal packing effects. There are, however, no intermolecular contacts between non-hydrogen atoms less than 3.2 Å.

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Struktur von Bis[di(1,5-di-*p*-tolyl-1,4-pentazadienido)nickel(II)]

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Abstract. $[\text{Ni}_2(\text{C}_{14}\text{H}_{14}\text{N}_5)_4]$, $M_r = 1126.62$, tetragonal, $I4_1/a$, $a = 19.147(1)$, $c = 31.312(9)$ Å, $V = 11480.0$ Å³, $Z = 8$, $D_x = 1.303$ g cm⁻³, $\text{Cu K}\alpha$, $\lambda = 1.54184$ Å, $\mu = 12.248$ cm⁻¹, $F(000) = 4704$, $T = 293$ K, final $R = 0.053$ for 2780 significant [$I > 3\sigma(I)$] reflections. The crystal structure consists of dinuclear complexes. The two molecules in the asymmetric unit are closely similar and differ only by the orientation of the tolyl rings. Four N₅ zigzag chains of the pentazadienido ligands coordinate two Ni²⁺ ions in a distorted octahedral arrangement. The complexes are aligned parallel to the c axis and centered on $\bar{4}$, resulting in S_4 point symmetry for each complex.

Einleitung. Im Rahmen unserer Untersuchungen über Metallkomplexe mit Triazenido- und Pentazadienidoliganden (Beck & Strähle 1985, 1986*a,b,c*) berichten wir im folgenden über die Struktur von tetragonalem Bis[di(1,5-di-*p*-tolyl-1,4-pentazadienidonickel(II))].

Experimentelles. Beim Umkristallisieren von $[\text{Ni}(\text{ToI}(\text{NNNNNTol})_2)_2]$ aus Tetrahydrofuran/*n*-Hexan entstehen neben einer triklinen und einer solvathaltigen monoklinen Form auch braune solvatreie tetragonale Kristalle. Diese bilden quadratische Säulen, deren Enden pyramidenförmig zulaufen. Abmessungen des verwendeten Kristalls $1 \times 0,2 \times 0,2$ mm; Buerger-Präzessionsaufnahmen, Laue-Symmetrie $4/m$, beo-

bachtete Auslöschungsregeln: hkl nur vorhanden für $h + k + l = 2n$, $hk0$ nur vorhanden für $h, k = 2n$, $00l$ nur vorhanden für $l = 4n$, tetragonale Raumgruppe $I4_1/a$; Vierkreisdiffraktometer CAD-4 (Enraf-Nonius, Delft), $\text{Cu K}\alpha$, Graphitmonochromator, Verfeinerung der Gitterparameter anhand von 25 genau zentrierten Reflexen ($10 < \theta < 22^\circ$); Registrierung der Reflexintensitäten mit ω/θ -scan im Beugungswinkelbereich von $3 < \theta < 60^\circ$; $h + 21$, $k + 21$, $l \pm 35$; jede Stunde drei Intensitätskontrollreflexe, ohne signifikanten Intensitätsverlust; 8730 Reflexe erfasst, LP-Korrektur, empirische Absorptionskorrektur (Azimutscan), Transmissionsfaktoren 0,952–0,997 (North, Phillips & Mathews, 1968); 4356 symmetrieunabhängige Reflexe ($R_{\text{int}} = 0,021$), davon 2780 mit $I > 3\sigma(I)$ für die Verfeinerungsrechnungen, Lage beider Nickelatome aus den Direkten Methoden, N- und C-Atome aus nachfolgenden Differenzfouriersynthesen, Lagen der H-Atome berechnet und bei der Strukturfaktorrechnung berücksichtigt. Ni-, N- und C-Atome mit anisotropen Temperaturfaktoren basierend auf F -Werten verfeinert, Extinktionskoeffizient mit in die Verfeinerung einbezogen, $3,601 \times 10^{-7}$ (Zachariasen, 1963), $R = 0,053$, $wR = 0,060$, 362 Parameter, $S = 5,610$, $1/w = \sigma^2 F$, $(\Delta/\sigma) < 0,001$, $\Delta\rho < |0,521| \text{ e Å}^{-3}$. Die Atomformfaktoren wurden den *International Tables for X-ray Crystallography* (1974) entnommen; Computer DEC-PDP 11/60; *Structure Determination Package* (Frenz, 1978).