

**(2-3- $\eta$ -2-Butyne-1,4-diol)[ $N,N'$ -ethanediylidenebis(2,6-diisopropylaniline)]nickel(0),  
[Ni(C<sub>26</sub>H<sub>36</sub>N<sub>2</sub>)(C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>)]**

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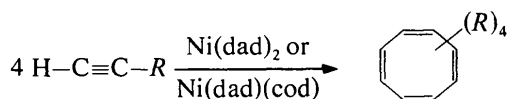
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(Received 15 June 1983; accepted 21 October 1983)

**Abstract.**  $M_r = 521.39$ , tetragonal,  $I4_1/a$ ,  $a = 18.655$  (18),  $c = 17.591$  (16) Å,  $V = 6122$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.131$  (2) g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.70926$  Å,  $\mu = 6.15$  cm<sup>-1</sup>,  $T = 293$  K,  $F(000) = 2240$ ,  $R = 0.0525$  for 2066 reflections. In the title compound the Ni atom has coordination number three if 2-3- $\eta$ -2-butyne-1,4-diol is regarded as a monodentate ligand, and the inner coordination sphere is essentially planar.

**Introduction.** Since the early work of Reppe (Reppe, Schlichting, Klager & Toepel, 1948) it is well known that Ni compounds can act as catalysts for the cyclooligomerization of alkynes. Besides the well established tetramerization of acetylene itself, for which an attractive alternative mechanism was recently proposed (Wilke, 1978), there are only very few literature reports on selective tetramerization catalysts for functionalized alkynes; in general, cyclic trimers, dimers, and polymers are formed together with substituted cyclooctatetraenes (Jolly & Wilke, 1975; Jolly, 1982).

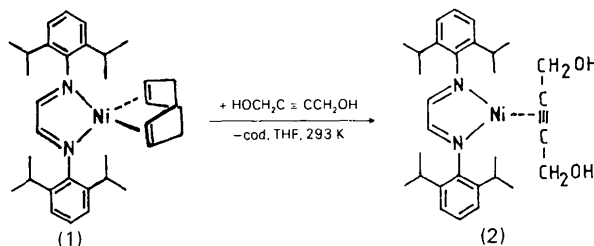
We have now found that 1,4-diaza-1,3-dienes (dad) in complexes of composition (dad)<sub>2</sub>Ni or (dad)Ni(cod) (cod = 1,5-cyclooctadiene) (tom Dieck, Svoboda & Kopf, 1978; tom Dieck, Svoboda & Greiser, 1981) act as controlling ligands for the very selective cyclo-tetramerization of functionalized alkynes like HC≡C-CH<sub>2</sub>OH (tom Dieck, Lauer & Diercks, 1983) and HC≡C-C(=O)-OR (Diercks & tom Dieck, 1983).



In all these catalytic reactions, which are performed at room temperature, a blue intermediate is visible. With 2-butyne-1,4-diol, which does not oligomerize under these mild conditions, we could isolate a blue compound of composition (dad)Ni(2-butyne-1,4-diol), which gave suitable crystals for an X-ray structural investigation.

Complex (2) is characterized by an intense electronic charge-transfer transition in the visible [wavelength of

maximum absorption in tetrahydrofuran (THF) 618 nm]. The infrared spectrum shows a strong band at 1811 cm<sup>-1</sup> for the coordinated triple bond. The free ligand does not exhibit an infrared-active C≡C vibration.



To discriminate between the possible complex structures and to gain information about types of intermediates in the catalytic oligomerization of alkynes a structural investigation seemed necessary.

**Experimental.** Equimolar amounts of (1) (tom Dieck, Svoboda & Greiser, 1981) and 2-butyne-1,4-diol reacted in THF at room temperature for 24 h. The solid residue, after evaporation, was recrystallized from hot *n*-hexane. Crystal  $\sim 0.4 \times 0.3 \times 0.3$  mm. Syntex P2<sub>1</sub> diffractometer,  $\theta/2\theta$  scan mode,  $2\theta \leq 50.0^\circ$ ,  $h/k/l$  range: 22/22/20. Cell parameters obtained by least-squares refinement from setting angles of 15 automatically centred reflections. 2713 independent, non-systematically absent (in  $I4_1/a$ ) reflections measured. No absorption or secondary-extinction corrections. Structure solved by Patterson and Fourier methods [SHELX77 (Sheldrick, 1977)]. No intensity drop of three standard reflections measured after each block of 97 reflections.  $x$  and  $y$  parameters of Ni fixed in 0 positions, no restrictions on  $z$ . H atoms calculated in ideal positions and refined in last least-squares refinement (on  $F$ ), i.e. no restrictions on any atomic parameter except Ni ( $x$ ,  $y$ ). Scattering factors for all atoms except Ni included in the SHELX77 program; for Ni from *International Tables for X-ray Crystallography* (1974). Final conventional  $R$  factor 0.0525 for 2066 structure factors with  $|F| > 3\sigma(|F|)$ ;  $R_w$

= 0.0388;  $w = 2.1975/\sigma^2(|F|)$ . Final difference map showed no peak  $>0.03 \text{ e } \text{Å}^{-3}$ ; all  $\Delta/\sigma$  values  $<0.08$ . Plots performed with program *SCHAKAL* (E. Keller, Univ. Freiburg, unpublished).

**Discussion.** Table 1 gives the atomic parameters,\* Table 2 the bond distances and corresponding angles. The molecular structure (Fig. 1) shows a mononuclear Ni complex with a chelating dad ligand and a 'side-on' coordinated alkyne. The coordinated alkyne is no longer linear but displays a *cis* geometry. The deviation from linearity [C(2')-C(2)-C(21) = 152.4°] is typical for  $\eta$ -coordinated alkynes. There is also an increase in length of the C≡C bond upon coordination. The value of 1.274 Å is intermediate between that for normal C≡C (1.20 Å) and C=C bonds (1.34 Å). The considerable electron transfer from the metal to the electrophilic alkyne is also reflected in a decrease of backbonding to the dad ligand, if (2) [N(1)-C(1) = 1.304, C(1)-C(1') = 1.434 Å] is compared to (dad)<sub>2</sub>Ni<sup>0</sup> (tom Dieck, Svoboda & Greiser, 1981) [N(1)-C(1) = 1.339, C(1)-C(1') = 1.378 Å]. The much shorter Ni-N(1) distance in (2) (1.886 Å) than in (dad)<sub>2</sub>Ni (1.928 Å, average value) also indicates a partial oxidation of the metal.

Although many monomeric alkyne complexes of the type  $L_2\text{Ni}(\text{alkyne})$  are claimed in the literature, there is only one such structure established by X-ray methods (Dickson & Ibers, 1972) for the complex bis(*tert*-butyl isocyanide)(diphenylacetylene)nickel(0). On the other hand, three alkynediol complexes of Pt have been structurally characterized, one with Pt<sup>0</sup> (Dubey, 1975)

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38975 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\text{eq}}(\text{Å}^2)$
Ni	0	0	0.2582 (1)	0.061 (1)
N(1)	0.0620 (1)	0.0255 (2)	0.1779 (1)	0.063 (3)
C(1)	0.0360 (2)	0.0136 (3)	0.1103 (2)	0.086 (5)
C(11)	0.1338 (2)	0.0518 (2)	0.1895 (2)	0.059 (3)
C(12)	0.1448 (2)	0.1258 (2)	0.1982 (2)	0.070 (3)
C(13)	0.2117 (2)	0.1483 (2)	0.2191 (3)	0.089 (4)
C(14)	0.2673 (2)	0.1017 (3)	0.2304 (3)	0.092 (4)
C(15)	0.2555 (2)	0.0294 (3)	0.2211 (2)	0.084 (4)
C(16)	0.1894 (2)	0.0023 (3)	0.2002 (2)	0.071 (3)
C(121)	0.0858 (2)	0.1795 (3)	0.1861 (3)	0.093 (4)
C(122)	0.0793 (4)	0.2330 (4)	0.2474 (4)	0.202 (8)
C(123)	0.0988 (3)	0.2179 (4)	0.1110 (4)	0.176 (7)
C(161)	0.1791 (2)	-0.0770 (3)	0.1913 (3)	0.089 (4)
C(162)	0.1895 (4)	-0.1172 (3)	0.2654 (3)	0.149 (7)
C(163)	0.2295 (4)	-0.1008 (3)	0.1329 (4)	0.169 (7)
C(2)	0.0306 (2)	0.0151 (2)	0.3564 (2)	0.060 (3)
C(21)	0.0928 (2)	0.0475 (2)	0.3954 (2)	0.068 (3)
O(21)	0.0867 (1)	0.0482 (1)	0.4763 (1)	0.060 (2)

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Ni-N(1)	1.886 (3)	N(1)-Ni-N(1')	83.0 (4)
Ni-C(2)	1.840 (3)	N(1)-Ni-C(2)	118.3 (1)
N(1)-C(1)	1.304 (4)	C(2)-Ni-C(2')	40.5 (2)
N(1)-C(11)	1.440 (4)	Ni-N(1)-C(11)	123.3 (2)
C(1)-C(1')	1.434 (8)	Ni-N(1)-C(1)	114.3 (2)
C(11)-C(12)	1.403 (6)	C(1)-N(1)-C(11)	122.2 (3)
C(11)-C(16)	1.401 (6)	C(1')-C(1)-N(1)	114.1 (3)
C(12)-C(13)	1.367 (6)	N(1)-C(11)-C(12)	119.1 (3)
C(13)-C(14)	1.367 (7)	N(1)-C(11)-C(16)	118.9 (4)
C(14)-C(15)	1.376 (7)	C(12)-C(11)-C(16)	121.6 (3)
C(15)-C(16)	1.383 (6)	C(11)-C(12)-C(13)	117.8 (4)
C(12)-C(121)	1.505 (6)	C(11)-C(12)-C(121)	122.2 (4)
C(121)-C(122)	1.474 (9)	C(121)-C(12)-C(13)	120.0 (4)
C(121)-C(123)	1.522 (9)	C(12)-C(13)-C(14)	122.4 (4)
C(16)-C(161)	1.500 (7)	C(13)-C(14)-C(15)	115.9 (4)
C(161)-C(162)	1.516 (8)	C(14)-C(15)-C(16)	122.2 (4)
C(161)-C(163)	1.514 (8)	C(11)-C(16)-C(15)	117.1 (4)
C(2)-C(2')	1.273 (7)	C(11)-C(16)-C(161)	122.8 (4)
C(2)-C(21)	1.478 (5)	C(15)-C(16)-C(161)	120.2 (4)
C(21)-O(21)	1.428 (4)	C(12)-C(121)-C(122)	114.2 (5)
		C(12)-C(121)-C(123)	108.6 (4)
		C(122)-C(121)-C(123)	109.2 (5)
		C(16)-C(161)-C(162)	112.5 (4)
		C(16)-C(161)-C(16)	112.2 (4)
		C(162)-C(161)-C(163)	108.0 (5)
		C(2')-C(2)-C(21)	152.4 (3)
		C(2)-C(21)-O(21)	113.8 (3)

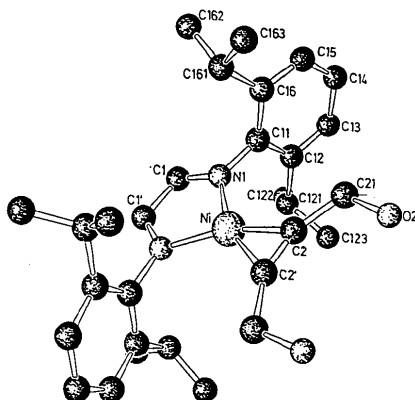


Fig. 1. *SCHAKAL* plot of the molecular structure of (2).

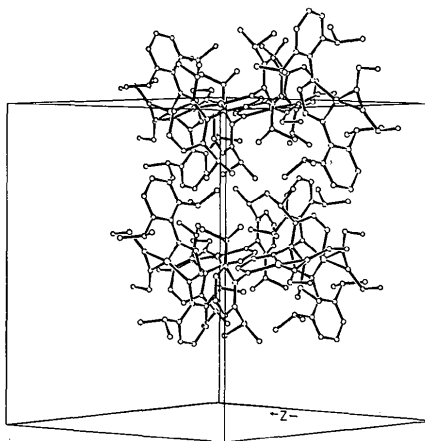


Fig. 2. Unit cell of (2).

and two with Pt<sup>II</sup> (Spagna & Zambonelli, 1973; Dubey, 1976), but there is a considerable discrepancy concerning the important C≡C bond lengths in these latter two, chemically very similar, compounds.

Fig. 2 shows the unit cell of compound (2). There are no close contacts between the individual Ni atoms and/or alkynes which could be interpreted in terms of initial steps of the catalytic reaction discussed above.

One of the authors (RD) wishes to thank the Fonds der Chemischen Industrie, Frankfurt, for a grant.

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*Acta Cryst.* (1984). **C40**, 365–368

## Structure of Octadecacarbonyl-1,2,3:4,5,6-bis- $\mu_3$ [( $\eta$ -toluene)cuprio]-octahedro-hexaruthenium, (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>)<sub>2</sub>Cu<sub>2</sub>Ru<sub>6</sub>(CO)<sub>18</sub>

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(Received 27 June 1983; accepted 25 October 1983)

**Abstract.**  $M_r = 1421.9$ , triclinic,  $P1$ ,  $a = 10.236$  (2),  $b = 10.395$  (3),  $c = 19.267$  (2) Å,  $\alpha = 82.64$  (1),  $\beta = 75.27$  (1),  $\gamma = 82.44$  (2)°,  $V = 1955.9$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.415$  Mg m<sup>-3</sup>,  $D_m$  not measured,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 67.52$  mm<sup>-1</sup>,  $F(000) = 2696$ ,  $T = 293$  K. Final  $R = 0.0377$  for 4357 observed independent reflections. Two essentially similar but independent metal–carbonyl clusters contain Ru<sub>6</sub> octahedra capped by two Cu atoms on opposite trigonal faces. Three terminal carbonyl ligands are bound to each Ru atom, and a toluene molecule is  $\eta$ -bonded to each Cu atom. Cu–Ru distances average 2.66 (6) Å. Ru–Ru distances range from 2.87 to 2.94 Å.

**Introduction.** The title compound has an identical Cu<sub>2</sub>Ru<sub>6</sub> core stoichiometry to that found in (CH<sub>3</sub>CN)<sub>2</sub>Cu<sub>2</sub>Ru<sub>6</sub>C(CO)<sub>16</sub> (Bradley, Pruett, Hill, Ansell, Leonowicz & Modrick, 1982; Ansell, Leonowicz, Modrick & Bradley, 1981), and might be expected to

have a similar structure. We report here that in fact the cluster has a radically different geometry to its carbide-containing analog.

**Experimental.** Material synthesized by reacting [PPh<sub>3</sub>]<sub>2</sub>N]<sub>2</sub>[Ru<sub>6</sub>(CO)<sub>18</sub>] with [Cu(CH<sub>3</sub>CN)<sub>4</sub>][BF<sub>4</sub>] in dry acetone; after extraction from evaporated reaction solution with methylene chloride, crude product recrystallized from warm toluene to give crystals suitable for X-ray examination. Crystal with dimensions 0.20 × 0.19 × 0.23 mm mounted in a thin-walled Lindemann capillary tube, Enraf–Nonius CAD-4 diffractometer, Mo  $K\alpha$  radiation monochromated by a graphite crystal in incident beam. Indexing on 25 centered reflections with intensities ranging from weak to very intense gave lattice parameters. Total of 7092 reflections measured in  $\theta/2\theta$  scan mode,  $0 < \theta < 25^\circ$ , range of  $hkl$ : 0–12, –12–12, –20–22; scan begun 0.75° below calculated  $2\theta$  position for  $K\alpha_1$ , and