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A new type of tetranuclear cyclopentadienylnickel cluster: synthesis and structural characterisation

Stanisław Pasynkiewicz [a,*], Antoni Pietrzykowski [a], Barbara Kryza-Niemiec [a], Romana Anulewicz-Ostrowska [b]

[a] *Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw, Poland*
[b] *University of Warsaw, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland*

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Abstract

A novel, 65-electron tetranuclear nickel cluster of the formula $Cp_3Ni_4(CH_3C{\equiv}CCH_3)_3$ (**6**) was isolated and identified as the product of the reaction of nickelocene with methyllithium in the presence of 2-butyne at the molar ratio of reactants 1:1:1. The compound was fully characterised by spectroscopic and X-ray measurements. It crystallises from hexane in an orthorhombic crystal system and space group *Pbcn*. Corresponding unit cell parameters were determined as $a = 26.438(5)$, $b = 11.219(2)$, $c = 16.328(3)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 4843(2)$ Å^3; $Z = 8$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nickel; Lithium; Nickel clusters; Cyclopentadienyl; Crystal structure

1. Introduction

Tetranuclear cyclopentadienylnickel clusters have been studied only to a small extent. Only a few examples of such compounds are known up to now. One of them is tetrakis(η^5-cyclopentadienyl)tetranickeltrihydride $Ni_4Cp_4H_3$, a crystalline, paramagnetic compound, the structure of which has been determined by single-crystal neutron diffraction [1–3]. The other example is tetrakis(η^5-cyclopentadienyl)tetranickeldihydride $Ni_4Cp_4H_2$, also crystalline but a diamagnetic compound [4].

On the other hand, the tetrakis(η^5-cyclopentadienyl)tetranickel cluster Ni_4Cp_4 of a closed-shell and 60-electron configuration is unknown, although it should be stable, as 60 valence electrons is a 'magic number' for such a structure of tetranuclear clusters. It seems that this number of valence electrons is insufficient for tetranuclear cyclopentadienylnickel clusters and additional electrons from two or three hydride ligands are necessary to make the compounds stable. The only known stable cyclopentadienylnickel cluster without additional ligands is hexakis(η^5-cyclopentadienyl)hexanickel Ni_6Cp_6 [5,6]. This octahedral compound has 90 valence electrons, the number exceeding the required number (84). Other known tetranuclear cyclopentadienylnickel clusters also contain more valence electrons than expected. In the clusters $Ni_4Cp_4Se_2$ [7] and $Ni_4Cp_3(CO)BrSe_2$ [8] additional electrons are donated by selenium ligands forming 68 and 66 valence electron clusters respectively.

The number of examples of tetranuclear nickel clusters with other than cyclopentadienyl ligands is also very limited. In contrast to cyclopentadienylnickel clusters, all these clusters, i.e. $Ni_4(CNR)_4(PhC_2Ph)_3$ [9], $Ni_4(CO)_4(CF_3C_2CF_3)_3$ [10] and $Ni_4(CpGa)_4(CO)_6$ [11], have 60 valence electrons and fulfil the 18 valence electron rule.

Reaction of nickelocene with methyllithium in the presence of 2-butyne at the molar ratio of reactants 1:1:1 leads to the formation of several organonickel compounds. Five of these products were isolated and characterised by us previously [12]. In this paper we describe the isolation and characterisation of a novel, 65-electron tetranuclear nickel cluster of the formula $Cp_3Ni_4(CH_3C{\equiv}CCH_3)_3$.

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* Corresponding author. Tel.: +48-22-660-7971; fax: +48-22-660-5462.
E-mail address: pasyn@ch.pw.edu.pl (S. Pasynkiewicz).

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2. Results and discussion

The reaction of nickelocene with methyllithium in the presence of 2-butyne (molar ratio 1:1.1:1) was carried out in THF at the temperature range from −40°C to room temperature. The products were hydrolysed with deoxygenated water and separated by column chromatography on neutral alumina. The last chromatographic band eluted from the column with toluene afforded after concentration dark crystals. These crystals were recrystallised from hexane with a small amount of methylene chloride to give crystals suitable for X-ray measurements.

The compound was identified as a tetranuclear nickel cluster of the formula $Cp_3Ni_4(CH_3C{\equiv}CCH_3)_3$ (**6**) based on elemental analysis, EPR and mass spectra and single crystal X-ray structure determination.

The mass spectrum (EIMS 70 eV) reveals the intensive (100%) parent ion at *m/e* 589 (calculated for ^{58}Ni) with isotopic pattern characteristic for four nickel atoms. The remaining fragments present in the spectrum are as follows: 535 $(M-CH_3C_2CH_3)^+$, 469 $(M-CpH)^+$, 427 $(Ni_4Cp_3)^+$, 304 $(Ni_3Cp_2)^+$, 246$(Ni_2Cp_2)^+$, 188 $(NiCp_2)^+$, 123 $(NiCp)^+$.

The molecular structure of **6** is shown in Fig. 1 and selected bond lengths and angles are presented in Tables 2 and 3 respectively. The core of the compound forms a triangle of three nickel atoms (Ni(2); Ni(3) and Ni(4)) with the fourth nickel atom (Ni(1)) bonded to Ni(2). Ni–Ni distances are within the range of nickel–nickel single bonds from 2.384 Å (Ni(3)–Ni(4)) to 2.449 Å (Ni(2)–Ni(3)). Two of the 2-butyne ligands have undergone carbon–carbon bond formation to produce an organic ligand containing four carbon atoms. This ligand is bonded via two σ-bonds to Ni(1) forming a nickelacyclopentadienyl ring consisting of Ni(1), C(2), C(3), C(7) and C(6) atoms. This ring is nearly planar with maximum deviation from the mean plane defined by all five atoms of 0.098(8) Å for C(6). The third 2-butyne ligand is bonded to the triangle of nickel atoms in $\mu_3(\eta^2)$ mode as observed for several homo- and heterometallic alkyne clusters [13]. We have observed this type of bonding for $[(NiCp)_3(H_3CC{\equiv}CCH_3)]$ [12]. The corresponding bond lengths in these two compounds are very similar (the values for $[(NiCp)_3(H_3CC{\equiv}CCH_3)]$ are in brackets): C(15)–C(16) 1.35(2) [1.366(5)]; C(15)–Ni(3) 1.858(13) and C(16)–Ni(4) 1.882(13) [1.868(3) and 1.871(3)]; C(15)–Ni(2) 2.01(2) and C(16)–Ni(2) 1.975(14) [1.961(3) and 1.960(3)].

The compound **6** is paramagnetic. Its EPR spectrum indicates an axial symmetry with $g_x = g_y = 2.095$ and $g_z = 2.050$. A hyperfine coupling into two lines is observed along the *z*-axis with coupling constant 29 G.

The formation of the tetra(cyclopentadienylnickel) cluster **6** was surprising. This is a 65 valence electron cluster and formally counting only three nickel atoms fulfills the 18 valence electron rule; the fourth one has 19 valence electrons. One could expect that it would be much less stable than the trinickel cluster **5** also formed in this reaction which is an open chain 50 valence electron cluster where all three nickel atoms fulfil the 18 valence electron rule. Moreover, it is a new type of tetranuclear cyclopentadienylnickel cluster, where three nickel atoms form a three-membered ring and the fourth nickel atom is engaged in a nickelacyclopentadienyl ring.

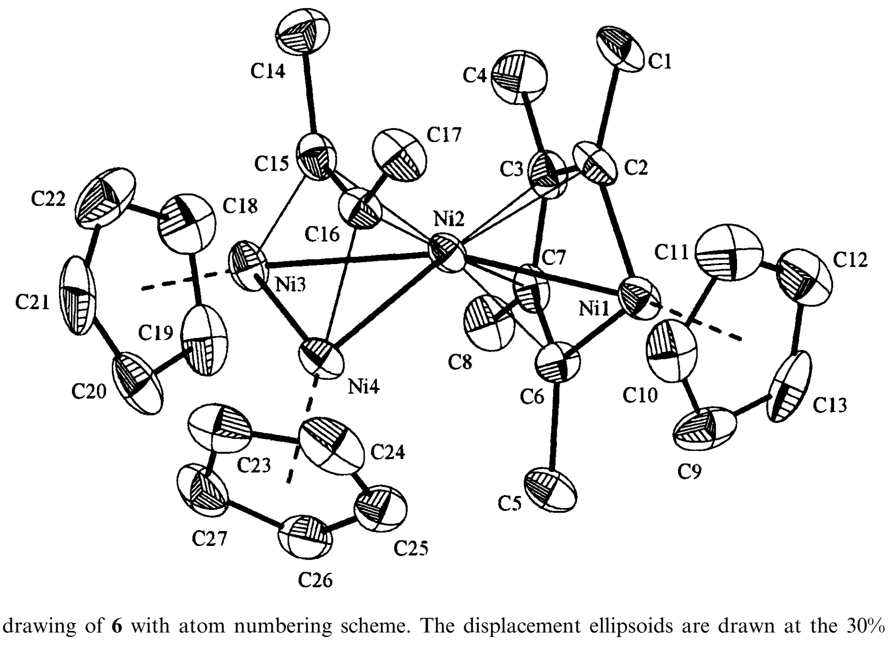
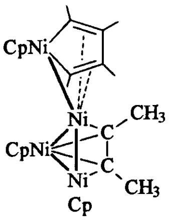


Fig. 1. The ORTEP drawing of **6** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level.



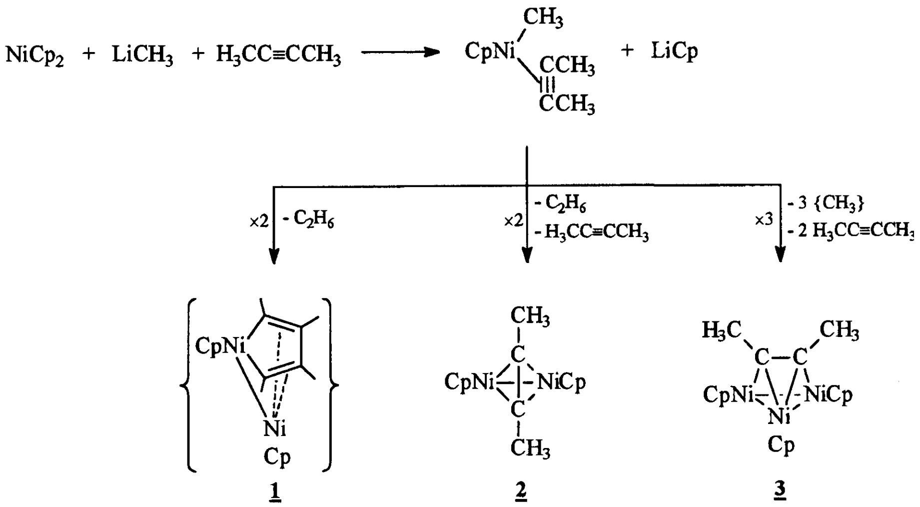
Its formation can be explained by kinetic reasons. Nickelocene reacts with methyl lithium and 2-butyne (Scheme 1) forming the unstable nickelocene analogue **1** and compounds **2** and **3** [12]. The compound **1** reacts with **2** and **3** and as the result of nickelocene elimination two other compounds are formed: the cluster **5** previously described by us [12], and the new cluster **6** (Scheme 2).

3. Experimental

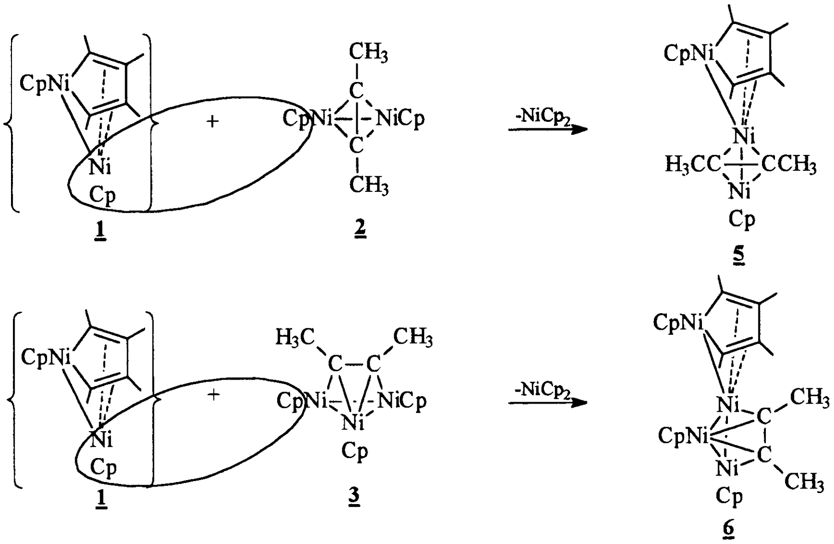
All reactions were carried out in an atmosphere of dry argon or nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods. Elemental analyses were performed on a Perkin–Elmer 2400 analyser. ^{1}H and ^{13}C-NMR spectra were measured on Varian Gemini-200 and VXR-300 instruments. Mass spectra were recorded on AMD-604 and AMD M-40 mass spectrometers. EPR spectra were recorded on a Bruker ESP300e spectrometer.

3.1. Reaction of nickelocene with methyllithium in the presence of 2-butyne

A solution of 1.9 g of $NiCp_2$ (10.1 mmol) and 0.8 cm^3



Scheme 1.



Scheme 2.

of 2-butyne (10.1 mmol) in 70 cm^3 THF was cooled to −55°C. A solution of methyllithium in Et_2O (7.1 cm^3, 11.1 mmol) was then added over 1 h (temperature was maintained at −55 to −50°C). The mixture was stirred at this temperature for the next hour, then it was allowed to warm up slowly to room temperature. Stirring was continued overnight. The volatile substances were removed under reduced pressure, 20 cm^3 of THF and 60 cm^3 of hexane were added and the products were hydrolysed with 40 cm^3 of the deoxygenated water. The organic layer was separated and dried, then solvents were evaporated, the residue was re-dissolved in hexane and chromatographed on Al_2O_3 (deactivated with 5.5% of water) using hexane–toluene mixture as an eluent. The first five coloured bands were separated and the results were previously described by us [12]. The last violet–brown sixth band was eluted with toluene. It was evaporated to dryness and re-dissolved in a mixture of hexane with a few drops of CH_2Cl_2. From this mixture we were able to obtain violet–brown crystals suitable for X-ray measurements. It was identified as a tetranuclear nickel cluster of the formula $Cp_3Ni_4(CH_3C{\equiv}CCH_3)_3$ (**6**). The compound was characterised by elemental analysis. Anal. Found: C, 54.56; H,

Table 1
Crystal data and structure refinement for **6**

Empirical formula	$C_{27}H_{33}Ni_4$
Crystal size (mm)	0.4 × 0.4 × 0.25
Crystal system	Orthorhombic
Space group	*Pbcn*
Unit cell dimensions	
a (Å)	26.438(5)
b (Å)	11.219(2)
c (Å)	6.328(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	4843(2)
Z	8
Formula weight	592.32
Density (calculated) (Mg m^{-3})	1.625
Temperature (K)	293(2)
Absorption coefficient (mm^{-1})	3.074
F(000)	2456
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å, graphite monochromator)
θ range for data collection (°)	1.54–0.12
Scan type	ω–2θ
Index ranges	$0 \le h \le 26$, $0 \le k \le 12$, $0 \le l \le 17$
Reflections collected/unique	5241/5241 ($R_{int} = 0.0000$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5220/0/314
Goodness-of-fit on F^2	1.033
Final R indices [$I > 2\sigma(I)$]	
$R_1 = \Sigma(F_o - F_c)/\Sigma F_o$	$R_1 = 0.0682$
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$	wR_2 (refined) = 0.1895
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (0.1435P)^2$ where $P = (F_o^2 + 2F_c^2)/3$
R indices (all data)	$R_1 = 0.2239$; $wR_2 = 0.3399$
Extinction coefficient	0.00009(14)
Largest difference peak and hole (e Å^{-3})	1.406 and −1.285

Table 2
Bond lengths (Å) between non-hydrogen atoms in **6** [a]

Ni(1)–C(2)	1.86(2)
Ni(1)–C(6)	1.896(12)
Ni(1)–C(12)	2.09(2)
Ni(1)–C(13)	2.09(2)
Ni(1)–C(9)	2.11(2)
Ni(1)–C(11)	2.14(2)
Ni(1)–C(10)	2.17(2)
Ni(1)–Ni(2)	2.430(2)
Ni(2)–C(16)	1.975(14)
Ni(2)–C(15)	2.01(2)
Ni(2)–C(6)	2.044(14)
Ni(2)–C(2)	2.075(13)
Ni(2)–C(3)	2.136(14)
Ni(2)–C(7)	2.159(14)
Ni(2)–Ni(4)	2.415(2)
Ni(2)–Ni(3)	2.449(2)
Ni(3)–C(15)	1.858(13)
Ni(3)–C(21)	2.10(2)
Ni(3)–C(20)	2.14(2)
Ni(3)–C(22)	2.14(2)
Ni(3)–C(18)	2.16(2)
Ni(3)–C(19)	2.19(2)
Ni(3)–Ni(4)	2.384(3)
Ni(4)–C(16)	1.882(13)
Ni(4)–C(23)	2.10(2)
Ni(4)–C(25)	2.12(2)
Ni(4)–C(26)	2.13(2)
Ni(4)–C(27)	2.14(2)
Ni(4)–C(24)	2.16(2)
C(1)–C(2)	1.51(2)
C(2)–C(3)	1.43(2)
C(3)–C(7)	1.43(2)
C(3)–C(4)	1.52(2)
C(5)–C(6)	1.53(2)
C(6)–C(7)	1.39(2)
C(7)–C(8)	1.52(2)
C(9)–C(10)	1.32(2)
C(9)–C(13)	1.41(3)
C(10)–C(11)	1.38(3)
C(11)–C(12)	1.41(3)
C(12)–C(13)	1.37(3)
C(14)–C(15)	1.50(2)
C(15)–C(16)	1.35(2)
C(16)–C(17)	1.51(2)
C(18)–C(19)	1.41(3)
C(18)–C(22)	1.42(3)
C(19)–C(20)	1.40(2)
C(20)–C(21)	1.38(3)
C(21)–C(22)	1.37(3)
C(23)–C(27)	1.41(3)
C(23)–C(24)	1.40(3)
C(24)–C(25)	1.37(3)
C(25)–C(26)	1.38(2)
C(26)–C(27)	1.39(3)

[a] Estimated standard deviations in parentheses.

Table 3
Selected bond angles (°) in 6 [a]

C(2)–Ni(1)–C(6)	84.1(6)
C(16)–Ni(2)–C(15)	39.7(6)
C(6)–Ni(2)–C(2)	75.3(6)
C(6)–Ni(2)–C(7)	38.4(5)
C(3)–Ni(2)–C(7)	38.8(6)
Ni(4)–Ni(2)–Ni(1)	109.47(9)
Ni(4)–Ni(2)–Ni(3)	58.69(7)
Ni(1)–Ni(2)–Ni(3)	163.17(10)
Ni(4)–Ni(3)–Ni(2)	59.95(7)
Ni(3)–Ni(4)–Ni(2)	61.36(7)
C(3)–C(2)–C(1)	121(2)
C(3)–C(2)–Ni(1)	114.2(11)
C(1)–C(2)–Ni(1)	124.2(12)
C(7)–C(3)–C(2)	112.3(13)
C(7)–C(3)–C(4)	123(2)
C(2)–C(3)–C(4)	125(2)
C(7)–C(6)–C(5)	122.7(12)
C(7)–C(6)–Ni(1)	114.0(10)
C(5)–C(6)–Ni(1)	121.4(10)
C(6)–C(7)–C(3)	113.1(13)
C(6)–C(7)–C(8)	124.4(14)
C(3)–C(7)–C(8)	122.5(14)
C(16)–C(15)–C(14)	124.7(14)
C(16)–C(15)–Ni(3)	107.6(10)
C(14)–C(15)–Ni(3)	126.4(12)
C(15)–C(16)–C(17)	128.3(14)
C(17)–C(16)–Ni(4)	124.9(11)
C(15)–C(16)–Ni(4)	104.4(10)

[a] Estimated standard deviations in parentheses.

5.49. Calc. for $C_{27}H_{33}Ni_4$: C, 54.75; H, 5.62%. MS (EI 70 eV) *m/e* (calculated for ^{58}Ni, relative intensities in parentheses) 589 (M^+, 100%), 535 (80%), 469 (92%), 427 (22%), 304 (30%), 246 (24%), 188 (37%), 123 (32%), 58 (10%).

3.2. Crystal structure determination

X-ray measurements were carried out using a KUMA KM-4 diffractometer [14] with graphite monochromated $Mo-K_\alpha$ radiation. The data were collected at room temperature using $\omega-2\theta$ scan technique. The intensity of the control reflections varied by less than 5%, and the linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarisation effects, but no absorption correction was applied. The structure was solved by direct method (SHELXS97) [15] and refined using full-matrix least-squares refinement program (SHELXL97) [16] The non-hydrogen atoms were refined anisotropically, whereas the H-atoms were placed in the calculated positions and their thermal parameters were refined isotropically. The atomic scattering factors were taken from international tables [17]. The details of X-ray measurements and structural computations and crystal data for the compound are given in Table 1. Tables 2 and 3 present the observed bond lengths and bond angles for the compound.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 141945. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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