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Crystal and molecular structure of 2-3- η^2 - (butyne-1,4-diol)bis(triisopropylphosphane)nickel(0): ($^i\text{Pr}_3\text{P}$) $_2\text{Ni}(\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})$ —some peculiarities of the complexation of 2-butyne-1,4-diol with nickel(0) complexes

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Abstract

The crystal and molecular structure of 2-3- η^2 -(butyne-1,4-diol)bis(triisopropylphosphane)nickel(0) has been determined by an X-ray diffraction study. The complex crystallizes in the monoclinic space group $C2/c$: a 31.918(5), b 21.067(4), c 20.738(4) Å, β 130.48(1)°, Z = 16. The structure was solved by the heavy-atom method and refined to R = 0.038. Three symmetrically independent molecules have very similar geometrical characteristics. The nickel atom has a trigonal-planar coordination. The structure of ($^i\text{Pr}_3\text{P}$) $_2\text{Ni}(\text{HOCH}_2\text{-C}_2\text{-CH}_2\text{OH})$ is compared with those of other complexes of the $L_n\text{Ni}(\text{HOCH}_2\text{-C}_2\text{-CH}_2\text{OH})$ type to elucidate some peculiarities of the complexation of 2-butyne-1,4-diol with nickel(0) complexes.

Introduction

Recently we investigated the influence of ligands with different electron-donor properties on the process of acetylene complexation with nickel(0) complexes using infrared spectroscopic measurements [1,2] and in the case of (Ph_3P) $_2\text{Ni}(\text{MeOCH}_2\text{-C}_2\text{-CH}_2\text{OMe})$ and (C_yP) $_2\text{Ni}(\text{MeOCH}_2\text{-C}_2\text{-CH}_2\text{OMe})$ with the help of X-ray diffraction studies [3].

For most nickel(0) complexes of acetylenes $L_2\text{Ni}(\text{Y-C}_2\text{-Y})$ there exists a correlation between reactivity parameter, infrared frequencies and structural details of the bonding [4].

Complexes of π -acidic acetylenes are stabilized by phosphane ligands with marked electron-donor properties, indicating a considerable back-donation ($d \rightarrow \pi^*$) from the metal to the acetylene causing the decrease of acetylenic bond order.

One of the most frequently used experimental criteria of acetylene-metal bond strength is the difference in the $C\equiv C$ stretching frequency between the nonordinated and the coordinated ligand [5].

However, there are some arguments in favour of being careful in using $C\equiv C$ -stretching frequencies for the direct calculation of the bond order in special cases [6].

One example is the complex $(Ph_3P)_2Ni(HOCH_2-C_2-CH_2OH)$ [7,5] in which the complexed disubstituted acetylene is probably distorted by the existence of intra- and intermolecular $OH \cdots O$ hydrogen bonds. Therefore it seemed quite interesting to elucidate the structural peculiarities of the complexation of 2-butyne-1,4-diol in connection with the existence of $OH \cdots O$ hydrogen bonds and the influence of ligands.

Experimental

The complex $(^iPr_3P)_2Ni(HOCH_2-C_2-CH_2OH)$ (I) was prepared as published [1,2]: A suspension of 2.75 g (10 mmol) $Ni(cod)_2$, 3.2 g (20 mmol) iPr_3P and 0.86 g (10 mmol) $HOCH_2-C_2-CH_2OH$ in 50 ml of tetrahydrofuran (THF) at $-78^\circ C$ was stirred for 1 h at -78 to $20^\circ C$ and 30 min at 30 to $40^\circ C$. Addition of 50 ml of hexane followed by filtration and cooling resulted in a crude crystalline precipitate. Golden yellow crystals were obtained by recrystallization from a THF/hexane mixture. Yield: $C_{22}H_{48}Ni_2O_2P_2$, 0.90 g (20%).

X-Ray diffraction study of $(^iPr_3P)_2Ni(C_4H_6O_2)$ (I)

An X-ray diffraction study of I was carried out with an automatic Enraf-Nonius CAD4 diffractometer ($\lambda(Mo-K_\alpha)$, graphite monochromator, $\omega : \theta = 1.2 : 1$ scan

Table 1

Crystal data

Crystal colour	golden-yellow
Chemical formula	$C_{22}H_{48}O_2P_2Ni$
Molecular weight	$465.28 \text{ g mol}^{-1}$
Crystal system	monoclinic
Space group	$C2/c$
Cell constants	$a = 31.918(4) \text{ \AA}$ $b = 21.067(5) \text{ \AA}$ $c = 20.738(4) \text{ \AA}$ $\beta = 130.48(1)^\circ$
Volume	10606.2 \AA^3
Z	16
Density (calculated) D_c	1.17 g cm^{-3}
Absorption coefficient $\mu(Mo-K_\alpha)$	8.7 cm^{-1}
Unique data measured	9682
Observed data with $I \geq 3\sigma(I)$	6348
R	0.038
R_w	0.052
Rest electron density	$0.51(6) \text{ e \AA}^{-3}$

Table 2

Atomic coordinates (esd's in parentheses)

Atom	x	y	z
<i>Molecule A</i>			
NiA	-0.20787(1)	0.24999(2)	-0.20787(2)
P1A	-0.25576(3)	0.20674(5)	-0.17788(4)
P2A	-0.25583(3)	0.29319(5)	-0.33363(4)
O1A	-0.0398(1)	0.2161(2)	0.0186(2)
O2A	-0.04012(9)	0.2842(2)	-0.0984(4)
C1A	-0.1344(1)	0.2293(2)	-0.1118(2)
C2A	-0.1343(1)	0.2703(2)	-0.1569(2)
C3A	-0.0945(2)	0.1916(2)	-0.0328(2)
C4A	-0.0947(1)	0.3090(2)	-0.1564(2)
C5A	-0.1908(1)	0.2629(3)	-0.0165(2)
C6A	-0.2499(1)	0.2562(2)	-0.0978(2)
C7A	-0.2746(2)	0.3210(2)	-0.1335(2)
C8A	-0.3484(1)	0.1452(3)	-0.3225(3)
C9A	-0.3323(1)	0.1977(2)	-0.2597(2)
C10A	-0.3660(2)	0.1915(3)	-0.2309(2)
C11A	-0.2152(2)	0.0856(3)	-0.1676(3)
C12A	-0.2250(2)	0.1299(2)	-0.1210(2)
C13A	-0.2519(2)	0.0960(3)	-0.0915(3)
C14A	-0.2744(2)	0.1784(2)	-0.4151(2)
C15A	-0.2497(1)	0.2437(2)	-0.4018(2)
C16A	-0.1901(1)	0.2360(2)	-0.3642(2)
C17A	-0.3658(2)	0.3088(3)	-0.5004(3)
C18A	-0.3321(1)	0.3025(3)	-0.4044(2)
C19A	-0.3476(2)	0.3555(3)	-0.3727(3)
C20A	-0.2519(2)	0.4041(3)	-0.4129(3)
C21A	-0.2258(2)	0.3704(2)	-0.3296(2)
C22A	-0.2161(2)	0.4146(3)	-0.2632(3)
<i>Molecule B</i>			
NiB	0.0000	0.44086(3)	0.250
P1B	-0.04412(3)	0.49590(4)	0.13260(4)
O1B	-0.0284(1)	0.2480(1)	0.1627(2)
C1B	-0.0188(1)	0.3566(2)	0.2096(2)
C3B	-0.0526(2)	0.3098(2)	0.1403(2)
C5B	-0.0075(1)	0.4200(2)	0.0648(2)
C6B	-0.0094(1)	0.4885(2)	0.0876(2)
C7B	0.0488(1)	0.5141(3)	0.1499(2)
C8B	-0.0642(2)	0.6232(2)	0.0601(2)
C9B	-0.0506(1)	0.5838(2)	0.1339(2)
C10B	-0.0916(2)	0.6014(2)	0.1472(2)
C11B	-0.1473(2)	0.4528(2)	0.0749(2)
C12B	-0.1139(1)	0.4633(2)	-0.0453(2)
C13B	-0.1490(2)	0.4958(3)	-0.0417(2)
<i>Molecule C</i>			
NiC	0.0000	0.5914(3)	0.750
P1C	0.04414(3)	0.00395(5)	0.72086(4)
O1C	0.0284(1)	0.2517(1)	0.7195(2)
C1C	0.0187(1)	0.1434(2)	0.7473(2)
C3C	0.0529(1)	0.1904(2)	0.7456(2)
C5C	-0.0486(2)	-0.0149(3)	0.5526(2)
C6C	0.0093(1)	0.0118(2)	0.6062(2)

Table 2 (continued)

Atom	x	y	z
<i>Molecule C</i>			
C7C	0.0079(2)	0.0798(2)	0.5805(2)
C8C	0.1469(2)	0.0461(2)	0.8685(3)
C9C	0.1136(1)	0.0369(2)	0.7730(2)
C10C	0.1487(1)	0.0045(3)	0.7560(2)
C11C	0.0640(1)	-0.1233(2)	0.6883(2)
C12C	0.0513(1)	-0.0835(2)	0.7359(2)
C13C	0.0912(2)	-0.1015(2)	0.8311(2)

mode, $20 \leq 52^\circ$). The crystals are monoclinic, space group $C2/c$: a 31.918(5), b 21.067(4), c 20.738(4) Å, β 130.48(1)°.

10422 reflections were collected at +20°C (room temperature), of which 9682 were unique. No absorption correction was applied. After averaging, 6348 reflections with $I \geq 3.0 \sigma(I)$ were used in the calculations. The crystallographic data are listed in Table 1.

The structure was solved using the heavy-atom method which revealed the positions of the three Ni-atoms. The remaining atoms were located in subsequent Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined by least-squares techniques with all non-hydrogen atoms anisotropic to $R = 0.038$, $R_w = 0.052$. The highest peak in the final difference Fourier synthesis was 0.51 e Å⁻³.

The final atomic parameters are listed in Table 2. Tables of atomic coordinates of H-atoms, anisotropic thermal parameters for other atoms and interatomic distances and bond angles for the complex I are available from the authors.

All calculations were performed with a PDP-11/23 PLUS Computer using the SDP-PLUS program package.

Discussion

The molecular structure of the compound named in the title is shown in Fig. 1 together with the numbering scheme. In the unit cell there are three symmetrically independent molecules **A**, **B** and **C**. Molecules **B** and **C** occupy special positions in the two-fold axes whereas molecule **A** is in a general position. Nevertheless the geometrical parameters of all three molecules are quite similar. Therefore the bond distances and angles in the following discussion are averaged over all molecules. Main bond distances and bond angles for all three molecules **A**, **B** and **C** are listed in Table 3.

The coordination about the nickel atom is trigonal-planar. The dihedral angle (the angle between the normals to the planes through P1, Ni, P2 and C1, Ni, C2) is 11.3(3)°. The Ni-P distances are 2.191(1) Å. The P1-Ni-P2 angle is 115.94(4)°. The average values of the phosphorus-carbon and the carbon-carbon bond lengths in the isopropyl chain are 1.864(4) and 1.528(8) Å respectively. The alkyne ligand is coordinated "side-on" at the carbon-carbon triple bond. The nickel-alkyne C distances in the three molecules vary slightly within the range 1.885(4)-1.896(2) Å.

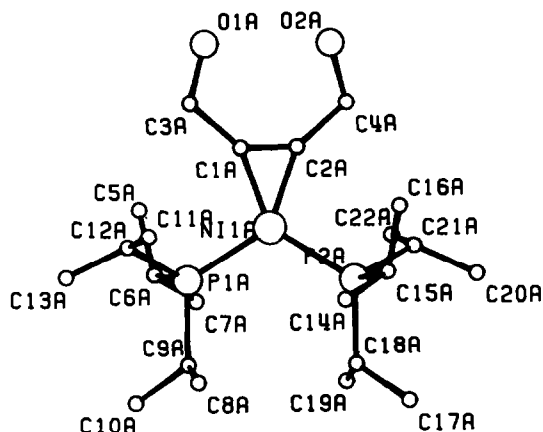


Fig. 1. Molecular structure of molecule A in I.

The average C1–Ni–C2 angle is $39.4(2)^\circ$. The coordinated alkyne is no longer linear but displays a *cis* geometry. The deviations from linearity (bond angles C1–C2–C4 = $138.8(3)^\circ$, and C2–C1–C3 = $138.5(3)^\circ$), are typical of η^2 -coordinated alkynes [9]. The C1–C2 distance of $1.275(6)$ Å is intermediate between that for normal C≡C (1.20 Å) and C=C bonds (1.34 Å).

Some peculiarities of complexation of 2-butyne-1,4-diol

The comparison of geometrical parameters of complexes $L_2Ni(HOCH_2-C_2-CH_2OH)$ (see Table 4) with $L = Ph_3P$ and 1Pr_3P indicates that the alkyne is more distorted in the case of a ligand with higher σ -donor activity, which is in good agreement with our earlier results [3].

Thus in the complex $(^1Pr_3P)_2Ni(HOCH_2-C_2-CH_2OH)$ (I) the acetylenic triple bond length is longer, the bend-back angle is larger and all Ni–P bond distances are longer in comparison with its phenyl analogue $(Ph_3P)_2Ni(HOCH_2-C_2-CH_2OH)$ (II).

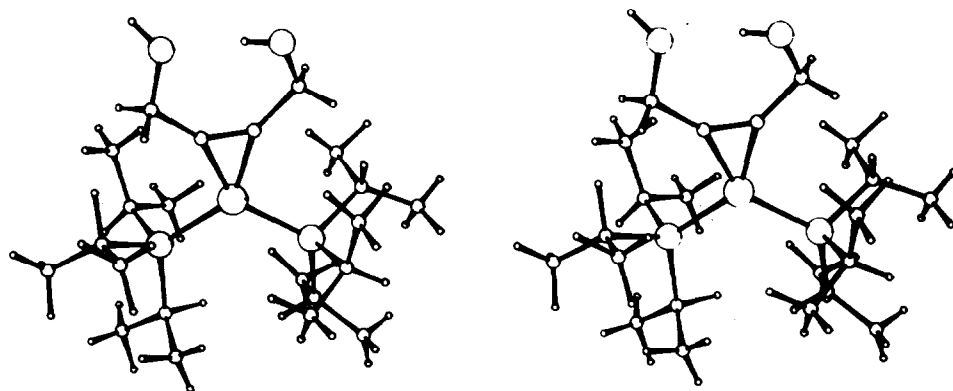


Fig. 2. Stereo plot of molecule A in I.

Table 3

Relevant bond distances (Å) and angles (°) of I

	Molecule		
	A	B	C
Ni1–P1	2.188(1)	2.1917(9)	2.193(1)
Ni1–P2	2.1885(9)	2.1917(9)	2.193(1)
Ni1–C1	1.896(2)	1.887(3)	1.885(4)
Ni1–C2	1.896(3)	1.887(3)	1.885(4)
P1–C6	1.863(4)	1.863(6)	1.867(3)
P1–C9	1.872(3)	1.866(5)	1.857(4)
P1–C12	1.862(4)	1.864(4)	1.857(4)
P2–C15	1.866(5)		
P2–C18	1.864(4)		
P2–C21	1.864(6)		
O1–C3	1.426(5)	1.429(5)	1.423(5)
O2–C4	1.426(4)		
C1–C2	1.275(6)	1.280(4)	1.270(7)
C1–C3	1.492(5)	1.481(5)	1.490(6)
C2–C4	1.499(7)		
C5–C6	1.514(4)	1.530(7)	1.517(5)
C6–C7	1.509(7)	1.514(5)	1.519(7)
C8–C9	1.522(8)	1.534(6)	1.535(6)
C9–C10	1.538(8)	1.548(8)	1.536(7)
C11–C12	1.517(8)	1.553(9)	1.538(7)
C12–C13	1.517(9)	1.534(5)	1.550(5)
C14–C15	1.519(6)		
C15–C16	1.526(6)		
C17–C18	1.535(6)		
C18–C19	1.533(9)		
C20–C21	1.520(7)		
C21–C22	1.521(8)		
P1–Ni1–P2	115.75(4)	116.12(4)	115.95(5)
P1–Ni1–C1	102.8(1)	102.38(9)	102.6(1)
P1–Ni1–C2	141.0(1)	141.4(2)	141.3(1)
P2–Ni1–C1	141.2(1)	141.4(2)	
P2–Ni1–C2	103.0(1)	102.38(9)	102.6(1)
C1–Ni1–C2	39.3(2)	39.7(1)	39.4(2)
Ni1–P1–C6	109.6(1)	110.5(2)	
Ni1–P1–C9	121.8(2)	120.4(1)	
Ni1–P1–C12	111.3(2)	112.6(1)	
C6–P1–C9	100.5(2)	101.5(2)	
C6–P1–C12	102.4(2)	102.0(2)	
C9–P1–C12	109.1(4)	107.9(2)	
Ni1–P2–C15	109.6(2)		
Ni1–P2–C18	121.8(2)		
Ni1–P2–C21	111.6(2)		
C15–P2–C18	100.8(2)		
C15–P2–C21	102.5(2)		
C18–P2–C21	108.3(2)		
Ni1–C1–C2	70.4(2)	70.2(3)	
Ni1–C1–C3	150.3(3)	151.6(2)	
O2–C4–C2	111.6(4)		
P1–C6–C5	112.1(3)		
P1–C6–C7	110.5(3)		

Table 3 (continued)

	Molecule		
	A	B	C
C5–C6–C7	109.7(3)		
P1–C9–C8	111.5(3)	118.9(3)	
P1–C9–C10	119.1(2)	110.8(3)	
C8–C9–C10	109.7(4)	108.9(3)	
P1–C12–C11	112.0(3)	111.3(3)	
P1–C12–C13	117.5(4)	118.6(3)	
C11–C12–C13	111.9(4)	111.3(3)	
P2–C15–C14	110.3(4)		
P2–C15–C16	112.6(2)		
C14–C15–C16	108.9(4)		

The molecules in I exhibit intra- and intermolecular OH...O hydrogen bonding. The average intramolecular O1...O2 bond length is equal to 2.810(5) Å. There exists only one intermolecular hydrogen bridge between the O1 atom of molecule A and the O1 atom of molecule with a distance of 2.850(5) Å. No other OH...O hydrogen bonds are formed in complex I.

The phenyl analogue (Ph₃P)₂Ni(HOCH₂–C₂–CH₂OH) (II) shows a tetrameric structure with H-bonded eight-membered oxygen rings [7]. Each molecule is bonded to two neighbours with the intermolecular O...O distance of 2.766(6) Å.

The complex (dad)Ni(HOCH₂–C₂–CH₂OH) (III) forms no hydrogen bonds [8].

Table 4

Selected characteristics of complexes L_nNi(HOCH₂–C₂–CH₂OH)

	I	II	III
L _n	2 ¹ Pr ₃ P	2 Ph ₃ P	dad ^a
electronic param. χ (cm ⁻¹)	3.1	12.9	–
steric parameter Θ (°)	160	145	–
Δγ(C≡C (cm ⁻¹))	431	405	399
<i>Distances (Å)</i>			
C–C	1.275(6)	1.228(6)	1.273(7)
Ni–C	1.889(3)	1.839(5)	1.840(3)
	1.889(3)	1.829(5)	
Ni–P	2.191(1)	2.166(1)	–
	2.191(1)	2.161(1)	
<i>Angles (°)</i>			
C–C–CH ₂ OH	138.8(3)	142.1(5)	152.4(3)
	138.5(3)	140.5(4)	152.4(3)
bend back	41.2(3)	37.9(5)	27.6(3)
	41.5(3)	39.5(4)	27.6(3)
C–Ni–C	39.4(2)	39.1(2)	40.5
<i>O–O bond length (Å)</i>			
intramolecular	2.810(5)	2.617(6)	3.70
intermolecular	2.850(5)	2.766(6)	> 7

^a dad = *N,N'*-ethanediyldienebis(2,6-diisopropylaniline).

Inspection of Table 4 may lead to the conclusion that there is a certain correlation between the bend-back angles and the presence of intra- and intermolecular hydrogen bonds. However, there is obviously no direct influence of the hydrogen bonds on the distortion of the alkyne in the NiC_2 moiety. This is indicated by the C–C and Ni–C bond distances being nearly the same in complexes with and without hydrogen bridges.

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