

Solvo-Thermal Application for the Synthesis of [Et₄N][(μ -H)Mo₂(CO)₁₀] and its Bidentate Phosphine Derivatives and the X-ray Structure of (μ -Ph₂P(CH₂)₂PPh₂)[Mo(CO)₄(NCCH₃)₂]

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Abstract

The compounds [Et₄N][(μ -H)(μ -Ph₂P(CH₂)_nPPh₂)Mo₂(CO)₈] (n = 1 and 2) and their parent compound [Et₄N][(μ -H)Mo₂(CO)₁₀] were synthesized using solvo-thermal method. The IR spectra are identical with those prepared by conventional methods. Protonation of [Et₄N][(μ -H)(μ -Ph₂P(CH₂)_nPPh₂)Mo₂(CO)₈] using CF₃CO₂H at -70° in CH₃CN led to the capture of the intermediate [(CO)₄MoDPPEMo(CO)₄], which was isolated as a solid material and identified by elemental analysis, FT-IR and X-ray structure as (μ -Ph₂P(CH₂)₂PPh₂)[Mo(CO)₄(NCCH₃)₂]. The X-ray analysis show the following parameters, P_{2/n} (No. 14), Z=2, a = 11.957 (2) Å, b = 10.403(1) Å, c = 16.987(7) Å, α = 90°, β = 108.4(2)°, γ = 90°. The structure shows a center of inversion at the middle of the hydrocarbon chain which connects the two phosphorus donor sites.

Keywords: Crystal structure; Molybdenum; Carbonyl; Phosphine.

Introduction

Since the discovery of the non-substituted binuclear metal carbonyl hydrides of group 6 by Hayter ^[1], a rapid development began after the discovery of HM(C₅H₅)(CO)₃ where M = (Cr, Mo) by Fisher, Hafner and Stahl ^[2]. Studies of hydride complexes play a prominent role in the industrial process used for the production of a wide range of organic chemicals ^[3]. Also, these compounds are used for selective reduction of α & β -unsaturated carbonyl compounds ^[4]. In recent years many organometallic compounds were synthesized using Teflon lined autoclave instead of the conventional reflux method ^[5-7]. In this paper, we report the synthesis of binuclear molybdenum carbonyl hydrides and their phosphine substituted compounds employing solvo-thermal method.

Experimental

All manipulations were carried out using dry nitrogen. Most solvents used were purified by standard methods as indicated below. Tetrahydrofuran (THF) was refluxed under nitrogen and distilled immediately prior to use from 0.1M sodium benzophenone blue solution. Acetonitrile and dichloromethane were predried over CaCl₂ and distilled from P₂O₅. Hexane was stirred with H₂SO₄ to remove any of olefins, washed with water

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and then refluxed and distilled under nitrogen from CaSO₄. Infrared spectra were recorded in THF at room temperature with Bruker IFS-25 OPUS/IR spectrometer over wave number range from 400 to 4000 cm⁻¹.

Synthesis of [Et₄N] [(μ-H)Mo₂(CO)₁₀]

The parent compound Et₄N⁺ salt of [(μ-H)Mo₂(CO)₁₀]⁻ was prepared by solvo-thermal method. Teflon-lined 250ml laboratory autoclave was charged with 1.0 mmol Mo(CO)₆ and 0.5 mmol of KBH₄ dissolved in 25 ml dry THF. The autoclave was flushed with nitrogen, closed tightly and left for one day in oven at 80 °C. Red solution was formed and 0.5 mmol Et₄NBr in 10 ml ethanol was added. The solution was cooled to room temperature and filtered. About 100 ml of hexane was added and upon cooling to +10 °C, yellow solid was isolated. Samples suitable for chemical analysis were crystallized from THF-hexane at +10 °C. The yellow solid was identified by FT-IR (ν_{CO} 2043(w), 1943(s), 1881(m); (ν_{CN} 2255 cm⁻¹) and was similar to that prepared by Hayter^[1].

Synthesis of [Et₄N][(μ-H)(μ-Ph₂P(CH₂)_nPPh₂)Mo₂(CO)₈] (n = 1 and 2)

A 250 ml-Teflon autoclave was charged with 1.4 mmol of [Et₄N][(μ-H)Mo₂(CO)₁₀] and 1.4 mmol of Ph₂P(CH₂)_nPPh₂ (n = 1 and 2) in 50 ml dry THF. The autoclave was flushed with nitrogen, closed tightly and left in an oven for about one day at 70 °C. The final product was cooled to room temperature and about 50 ml of hexane was added, and left in fridge over night. Yellow solid were isolated by filtration and recrystallized from a 1:1 mixture of toluene and methanol. The IR data are similar to that obtained by the published method^[8].

Synthesis of (μ-Ph₂P(CH₂)₂PPh₂)[Mo(CO)₄(NCCH₃)₂]

Protonation of [(μ-H)(μ-Ph₂P(CH₂)₂PPh₂)Mo₂(CO)₈]⁻ in CH₃CN as solvent using CF₃CO₂H at low temperature (-70 °C) using Schlenk flask. The reaction was completed within 10 minutes. Solvent was removed in vacuo, and the remaining solids were recrystallized from CH₂Cl₂/hexane at +10 °C gave a pale yellow product in moderate yield. The yellow solid was characterized by elemental analysis, Anal. Calc. for Mo₂P₂O₈N₂C₃₈H₃₀: C, 45.55; H, 3.35; N, 3.13; P, 6.92; Found C, 45.89; H, 3.34; N, 3.24; P, 7.01, FT-IR spectroscopy ν_{CO} (cm⁻¹) in THF solution (2021m, 1916s,br, 1857m,br) (ν_{CN} 2255 cm⁻¹) and by X-ray analysis as (μ-Ph₂P(CH₂)₂PPh₂)[Mo(CO)₄(NCCH₃)₂].

X-ray structure analysis

A single crystal of the neutral compound was obtained by crystallization from CH₂Cl₂/hexane. Yellow crystals of the (μ-Ph₂P(CH₂)₂PPh₂)[Mo(CO)₄(NCCH₃)₂] compound were mounted in a sealed capillary tube to prevent loss of crystallinity from exposes to air. Data collected at 23 °C on Enraf Nonius CAD-4 diffractometer using

graphite monochromated Mo k_{α} irradiation ($\lambda = 0.71073 \text{ \AA}$) and the $w/2\theta$ scanning technique with a 3.8° take off angle. Twenty six atoms were refined using 2496 reflections used in the refinement process to define a monoclinic unit cell all with lattice constants are given in (table 1). Successful structure refinement identified the space group as $P2_1/n$.

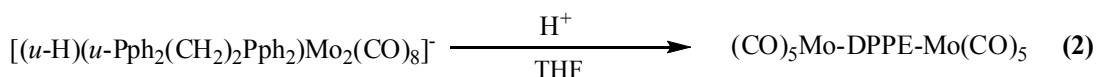
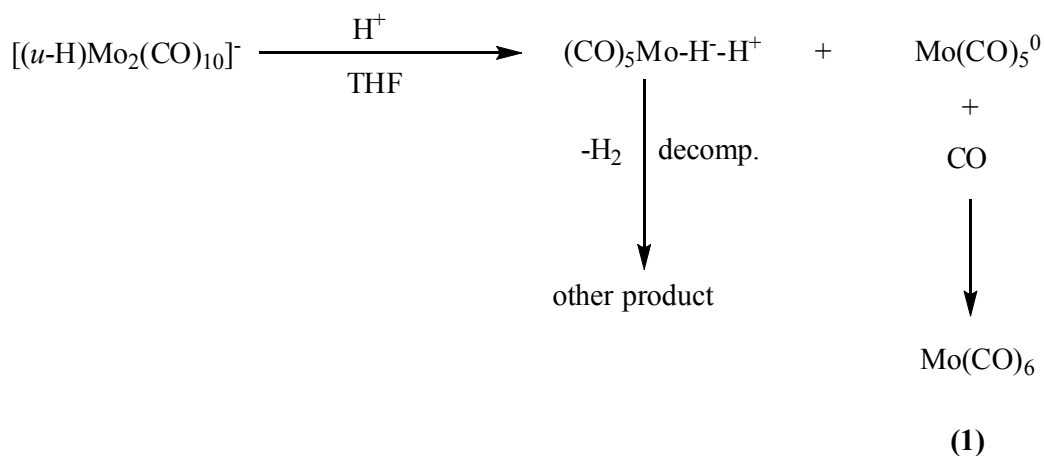
Table 1: Crystal data and structure refinement

Empirical formula	$\text{Mo}_2\text{P}_2\text{O}_8\text{N}_2\text{C}_{38}\text{H}_{30}$
Formula weight	888
Space group	$P2_1/n$ (No. 14)
Crystal system Monoclinic	$Z = 2$
Unit cell dimension	
$a = 11.957(2) \text{ \AA}$	$\alpha = 90^{\circ}$
$b = 10.403(1) \text{ \AA}$	$\beta = 108.4(2)^{\circ}$
$c = 16.987(7) \text{ \AA}$	$\gamma = 90^{\circ}$
Volume	$1999(2) \text{ \AA}^3$
Density (calculated)	2.30 mg/m^3
Absorption coefficient	14.5 cm^{-1}
Crystal size	$0.30 \times 0.25 \times 0.15 \text{ mm}^3$
Radiation Mo K_{α}	($\lambda = 0.71073 \text{ \AA}$)
Reflection collected	3516
Reflections used in analysis	2496
Factors	
R	0.043
R_w	0.064

Results and Discussion

Synthesis of $[\text{Et}_4\text{N}][(\mu\text{-H})\text{Mo}_2(\text{CO})_{10}]$ and its bidentate phosphine derivatives are achieved by using 250 ml-Teflon autoclave according to the IR spectrum which is identical to those prepared by reflux method [1,9]. The simplicity and time saving give this method an advantage over the conventional one. Protonation of $[(\mu\text{-H}) (\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)\text{Mo}_2(\text{CO})_8]$ with $\text{CF}_3\text{CO}_2\text{H}$ in THF or CH_3CN in absence of added ligand led to creation of two open coordination sites on adjacent metal atoms which were easily captured by the solvent to stabilize the generated $16e^-$ intermediate. In case of using THF as solvent in the absence of added ligand, the time for the completion of the reaction was longer than that in the presence of added ligand and the yields were less. The reaction is believed to proceed by decomposition of part of the metal carbonyl complex in solution, which may provide free CO required for the capturing of the vacant coordination sites, producing (in low yield) the dimer

(CO)₅Mo-DPPE-Mo(CO)₅ ^[9]. Protonation of the parent compound [Et₄N][(μ -H)Mo₂(CO)₁₀] in THF solution in absence of added ligand led to the formation of Mo(CO)₆. A possible explanation is presented in equations 1 and 2.



By using CH₃CN as solvent in the absence of added ligand we successfully captured the intermediate and was isolated as yellow solid material which is comparable to the nonisolable complex (μ -Ph₂P(CH₂)₂PPh₂)[Mo(CO)₄(THF)]₂. The final product was identified by FT-IR and X-ray structure as (μ -Ph₂P(CH₂)₂PPh₂)[Mo(CO)₄(NCCH₃)]₂. The ν_{CO} (cm⁻¹) IR spectrum shows three bands at 2021(m), 1916(s,br) and 1857(m). The infra red pattern predicted for local pseudo C_{2v} symmetry should exhibit four ν_{CO} stretching bands, 2A₁+B₁+B₂. However, only three bands were resolved in THF solvent. Nevertheless, the band at 1916cm⁻¹ was broad and probably composed of two unresolved bands, which is similar to the pattern of (CO)₄Mo(dPPE) ^[10,11], but different in intensity from (μ -Ph₂P(CH₂)₂PPh₂)Mo(CO)₈ (L) (L= bidentate ligands of G5A) in intensity bands ^[8]. The stretching frequencies at 2021 (m), 1916 (s, br) and 1857 (m) cm⁻¹ are lower in energy than those assigned for (CO)₄Mo(dPPE), and suggests the incorporation of CH₃CN in the compound.

Protonation of [(μ -H)(μ -Ph₂PCH₂PPh₂)Mo₂(CO)₈]⁻ with CF₃COOH in CH₃CN with the same conditions ends up with the formation of different products.

X-ray structure of (μ -Ph₂P(CH₂)₂PPh₂)[Mo(CO)₄(NCCH₃)]₂

Lists of the pertinent interatomic distances and angles in the compound are given in tables 2 and 3 respectively and referenced to the numbering schemes of the molecular diagram and its packing as shown in figures 1 and 2. In this structure the six coordinate Mo atoms reside in an octahedral environment, the structure also shows that the acetonitrile group is cis to the phosphine. The Mo-C-O linkage deviate from linearity by no more than 3° as is usual for metal carbonyl structures. The Mo-C bonds

of carbonyl groups trans to each other are in the 2.06-2.035Å range, and the one trans to the P-donor site is in the 2.001Å range, and the last type is one trans to the acetonitrile group and slightly shorter than the first two types, 1.941Å. Similar behavior have been noticed in $\text{Mo}(\text{CO})_5(\text{R}_2\text{PX})$ where $\text{R} = \text{Ph}$ and $\text{X} = \text{NHC}_6\text{H}_4\text{-4-Me}$ [12]. The structure shows a center of inversion at the middle of the hydrocarbon chain which connects the two phosphorous donor sites.

Conclusion

The results of this research confirm that the hydrocarbon chain which connects the two phosphine donor sites plays a major role in the shaping of the final product resulted from the protonation of $[(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{Mo}_2(\text{CO})_8]^-$ ($n = 1$ and 2)

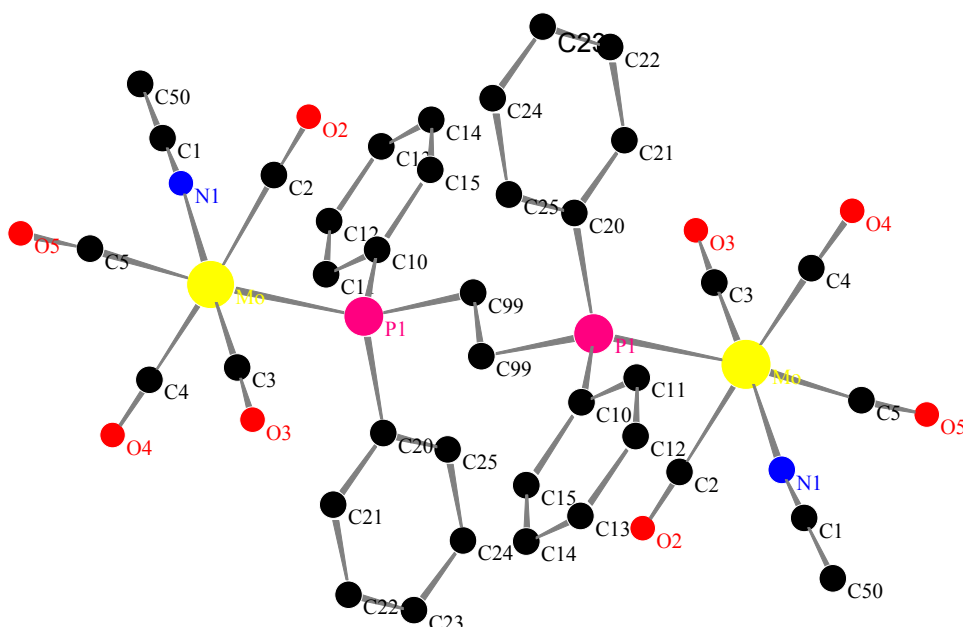


Figure 1: Molecular structure of the $(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)[\text{Mo}(\text{CO})_4(\text{NCCH}_3)]_2$ compound with colored numbering atoms

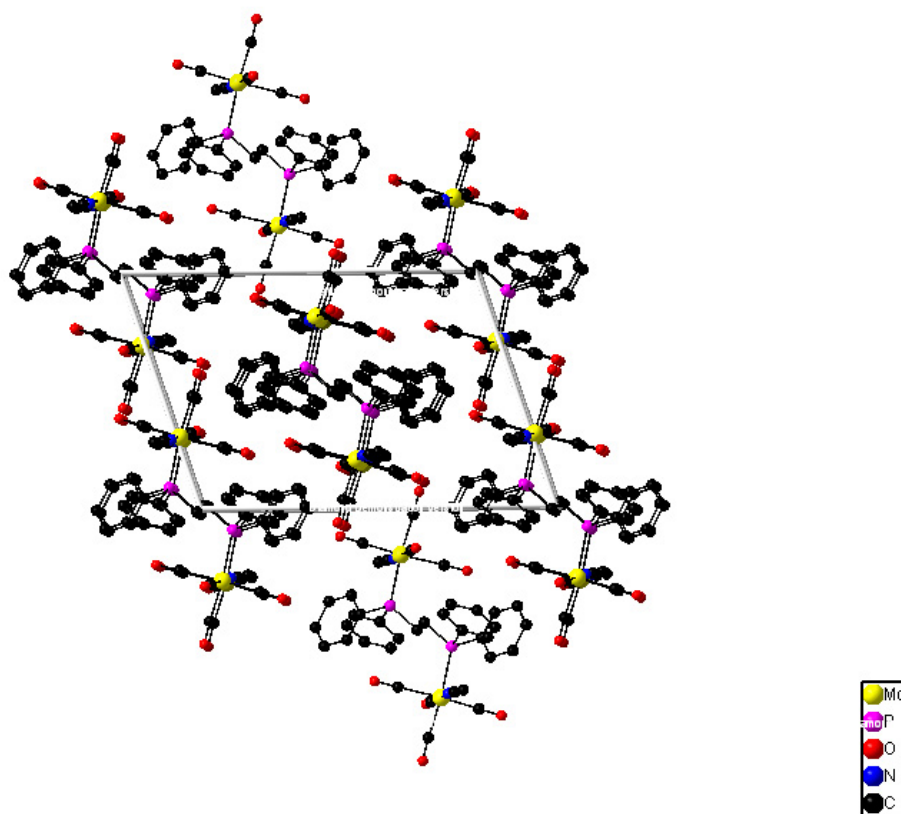


Figure 2: View of the molecular packing diagram showing the 3D structure of the $(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)[\text{Mo}(\text{CO})_4(\text{NCCH}_3)]_2$ compound.

Table 2: Interatomic distance and angles in the $(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)[\text{Mo}(\text{CO})_4(\text{NCCH}_3)]_2$

Atoms	Distances, Å
Mo1-P1	2.542(001)
Mo1-N1	2.201(003)
Mo1-C2	2.026(004)
Mo1-C3	1.941(004)
Mo1-C4	2.035(005)
Mo1-C5	2.001(005)
P1-C99	1.857(004)
P1-C10	1.839(004)
P1-C20	1.829(004)
	Bond Angles (deg.)
P1-Mo1-N1	88.76(10)
C2-Mo1-C3	90.06(17)
C2-Mo1-C4	178.82(16)
C3-Mo1-C5	89.57(18)
C3-Mo1-C5	88.89(17)
C4-Mo1-C5	89.27(18)
C99-P1-C10	103.39(16)

C99-P1-C20	101.37(18)
C10-P1-C20	101.94(17)
Mo1-C2-O2	178.62(40)
Mo1-C3-O3	179.21(36)
Mo1-C4-O4	178.39(40)
P1-C99-C99	110.70(34)
N1-C1-C50	177.78(69)
P1-C10-C11	118.40(29)
P1-C10-C15	122.34(28)
C11-C10-C15	118.90(36)

Table 3: Positional and thermal parameter and their estimated deviation of $(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)[\text{Mo}(\text{CO})_4(\text{NCCH}_3)_2]$.

Atom	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Mo1	0.3037(3)	0.1556(4)	0.0186(2)	0.0055(3)	0.0066(4)	0.0032(1)	-0.00001(6)	0.0023(3)	0.00057(4)
P1	0.0889(1)	0.1301(1)	-0.0681(7)	0.0056(9)	0.0065(1)	0.0038(4)	-0.0002(2)	0.0027(9)	0.0009(1)
O2	0.2328(4)	0.2074(5)	0.1816(2)	0.0152(4)	0.0197(6)	0.0052(2)	0.0019(9)	0.0009(4)	-0.0032(6)
O3	0.3285(4)	-0.135(4)	0.0622(3)	0.0110(4)	0.0092(4)	0.0082(2)	0.0015(7)	0.0030(5)	0.0044(5)
O4	0.3830(4)	0.1056(5)	-0.1408(2)	0.0172(4)	0.0146(5)	0.0062(2)	0.0007(6)	0.0139(3)	0.0005(5)
O5	0.5702(3)	0.1908(5)	0.1233(3)	0.0073(3)	0.0169(5)	0.0064(2)	-0.0075(7)	0.0006(4)	0.0014(6)
N1	0.2897(4)	0.3613(4)	-0.0137(3)	0.0086(4)	0.0073(4)	0.0053(2)	-0.0030(6)	0.0040(4)	0.0004(5)
C2	0.2579(5)	0.1902(6)	0.1221(3)	0.0079(4)	0.0097(5)	0.0041(2)	-0.0007(8)	0.0026(5)	-0.0016(6)
C3	0.3198(4)	-0.0261(5)	0.0458(3)	0.0068(4)	0.0080(5)	0.0048(2)	0.0000(7)	0.0019(4)	0.0010(5)
C4	0.3553(5)	0.1222(5)	-0.0840(3)	0.0083(4)	0.0092(5)	0.0047(2)	0.0000(8)	0.0054(4)	0.0016(6)
C1	0.2850(5)	0.4672(6)	-0.0338(4)	0.0129(6)	0.0100(6)	0.0078(3)	-0.0042(11)	0.0071(6)	-0.0013(8)
C99	0.4853(6)	0.4313(5)	0.4856(3)	0.0066(3)	0.0082(5)	0.0041(2)	0.0007(7)	0.0045(4)	-0.0025(5)
C10	0.5221(4)	0.2177(5)	0.3866(3)	0.0062(3)	0.0076(4)	0.0033(2)	0.0007(7)	0.0027(4)	-0.0003(5)
C11	0.5524(4)	0.1678(5)	0.3200(3)	0.0122(5)	0.0094(5)	0.0042(2)	-0.0037(9)	0.0066(4)	-0.0037(6)
C12	0.5116(5)	0.0458(6)	0.2888(3)	0.0151(6)	0.0107(6)	0.0045(2)	-0.0004(11)	0.0054(6)	-0.0047(6)
C13	0.4416(6)	-0.0252(6)	0.3217(4)	0.0119(5)	0.0079(5)	0.0054(2)	-0.0041(9)	0.0340(6)	-0.0015(6)
C14	0.4132(5)	0.0232(6)	0.3898(4)	0.0110(5)	0.0099(6)	0.0068(3)	-0.0064(9)	0.0070(6)	-0.0024(7)
C15	0.4527(5)	0.1436(5)	0.4215(4)	0.0093(4)	0.0080(5)	0.0054(2)	-0.0025(8)	0.0958(5)	-0.0009(6)
C20	0.5529(5)	0.4756(5)	0.3408(3)	0.0070(4)	0.0080(4)	0.0029(2)	0.0021(7)	0.0025(4)	0.0000(5)
C21	0.6331(4)	0.5689(5)	0.3353(3)	0.0092(4)	0.0080(5)	0.0043(2)	-0.0015(8)	0.0033(5)	0.0014(5)
C22	0.6067(6)	0.6510(6)	0.2669(4)	0.0121(6)	0.0121(7)	0.0058(3)	-0.0022(11)	0.0017(6)	0.0052(7)
C23	0.4577(7)	0.6395(7)	0.2041(4)	0.0151(8)	0.0147(8)	0.0053(3)	0.0023(13)	0.0032(7)	0.0062(8)
C25	0.4458(5)	0.4646(6)	0.2792(3)	0.0092(5)	0.0135(7)	0.0042(2)	-0.0027(10)	0.0003(5)	0.0026(7)
C50	0.2769(9)	0.5986(7)	-0.0622(7)	0.0279(13)	0.0083(7)	0.0152(7)	-0.0065(16)	0.0117(14)	0.0076(11)
C24	0.4191(6)	0.5501(7)	0.2097(4)	0.0118(7)	0.0166(9)	0.0052(3)	-0.0048(13)	-0.0021(7)	0.0056(8)
C5	0.4734(5)	0.1796(6)	0.0854(3)	0.0083(4)	0.0100(5)	0.0043(2)	-0.0039(8)	0.0034(5)	0.0008(6)

The form of the anisotropic thermal parameter is:

$$\exp[-(\mathbf{B}(1,1)h^2 + \mathbf{B}(2,2)k^2 + \mathbf{B}(3,3)l^2 + \mathbf{B}(1,2)hk + \mathbf{B}(1,3)hl + \mathbf{B}(2,3)kl)]$$

Estimated standard deviation in the least significant digits are shown in parentheses

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