Accepted Manuscript

Synthesis, physicochemical analysis of two new hemilabile ether-phosphine ligands and their first stable *bis*-ether-phosphine/Cobalt(II) tetrahedral complexes

Ismail Warad, Assem Barakat

PII: S0022-2860(16)31313-8

DOI: 10.1016/j.molstruc.2016.12.023

Reference: MOLSTR 23221

To appear in: Journal of Molecular Structure

Received Date: 8 September 2016

Revised Date: 6 December 2016

Accepted Date: 7 December 2016

Please cite this article as: I. Warad, A. Barakat, Synthesis, physicochemical analysis of two new hemilabile ether-phosphine ligands and their first stable *bis*-ether-phosphine/Cobalt(II) tetrahedral complexes, *Journal of Molecular Structure* (2017), doi: 10.1016/j.molstruc.2016.12.023.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Synthesis, physicochemical analysis of two new hemilabile ether-phosphine ligands and their first stable *bis*-ether-phosphine/Cobalt(II) tetrahedral complexes

Ismail Warad^{1,*} and Assem Barakat^{2,3}

 ¹Department of Chemistry, AN-Najah National University P.O. Box 7, Nablus, Palestine.
 ²Department of Chemistry, College of Science, King Saud University, P. O. Box 2455, Riyadh 11451, Saudi Arabia.
 ³Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426, Ibrahimia, Alexandria 21321, Egypt.

Abstract

New tridentate ether-phosphine {P, 2O} and ether-phosphine oxide {OP, 2O} ligands with P and O donor-atoms have been synthesized starting from ClCH₂CH(OCH₃)₂. The oxidation process of Ph₂PCH₂CH(OCH₃)₂ to its oxide derivative Ph₂P(=O)CH₂CH(OCH₃)₂ was monitored by ³¹P-NMR for the first time. The desired ligands and their Co(II) complexes structures were deduced from IR, EA, MS, NMR, UV-Vis., TG/DTG and XRD physical measurements. The tridentate chelating coordination behavior of the ether-phosphine wasn't detected leading only to the mono-dentate coordination mode through the phosphorous atoms to set up a X₂Co[η¹-Ph₂PCH₂CH(OCH₃)₂]₂ as final isomer formula (X = Cl or Br). The Cl₂Co[η¹-Ph₂PCH₂CH(OCH₃)₂]₂ isomer belongs to complex **1** was supported by single crystal measurement. Polar/non-polar intermolecular short contacts were detected by XRD and Hirshfeld surface theoretical analysis.

Keywords: Cobalt(II) complexes; P~O Hemilabile ligands; XRD; Hirshfeld surface analysis.

*Corresponding author. Tel. +00970923410003. E-mail address: warad@najah.edu

Introduction

The hemilability concept in chelate ligands possessing hard and soft donor atoms combination, P-and O or N donor atoms composed a very famous families of such ligands [1-6]. Particularly, ether-phosphine hemilabile as hybrid ligand (P-O) can stabilize varieties of metal ions complexes, including the geometries and their oxidation states through bidentate or multidentate coordination modes [3-8]. Indeed, the phosphorus donor π -acceptor stabilizes metal ions center in a low oxidation state, while the oxygen σ -donor atom makes the center more susceptible to higher oxidation state reactions. Such features played a critical role in controlling geometries and oxidation state of metal ions center [4-7]. Due to the hemilabile of P~O(N) ligands, the O or N σ -donor is generated like a unique intramolecular solvent behavior preventing degeneration of the desired complexes through vacant coordination sites preservation [5-12]. Furthermore, the steric and electronic variety of such hemilabile ligands allow to possess potentially multi-dentate mode of coordination. Mononuclear or homo-/ hetero-, bi- or polymetallic complexes were also isolated [4-11].

As a part of our outstanding studies on preparation of ether-phosphine ligands and their ruthenium(II) complexes for carbonyl compounds hydrogenation process [9-12], we here like to presence the synthesis, spectral characterization, thermal and solid state analysis of the (2,2-dimethoxyethyl)diphenylphosphine, (2,2-dimethoxyethyl)diphenylphosphine oxide and their tetrahedral $X_2Co[\eta^1-Ph_2PCH_2CH(OCH_3)_2]_2$ complexes structures.

Experimental

Materials, instrumentations and procedure

The reactions were performed in Argon inert-atmosphere by using Schlenk-line system. Cobalt(II) salts, ClCH₂CH(OCH₃)₂ and Ph₂PK available from Sigma–Aldrich,

beforehand, hexane, CH₂Cl₂, and diethyl ether were distilled over calcium hydride, lithium aluminum hydride and from sodium / benzophenone, respectively.

^{"31}P{¹H}, ¹³C{¹H}, and ¹H NMR spectra were recorded on a Bruker DRX250 spectrometer at RT. Frequencies: ¹H NMR 250.12 MHz, ¹³C{¹H} NMR 62.9 MHz, and ³¹P{¹H} NMR 101.25 MHz. Chemical shifts in the ¹³C{¹H} and ¹H NMR spectra were measured relative to TMS using CDCl₃ as deuterated solvent. \Box p were measured relative to 85% H₃PO₄ ($\delta = 0$). IR data was recorded on a Bruker IFS 48 FT-IR spectrometer. Mass spectra: EI-MS; Finnigan TSQ70." Elemental analyses were carried out on an Elementar Varrio EL analyzer. FAB-MS; Finnigan 711A (8 kV), modified by AMD and reported as mass/charge (*m/z*). The Hirshfeld surface theoretical calculation of complex **1** was performed using CRYSTAL EXPLORER 3.1 program [13].

Procedure to synthesis of the (2,2-dimethoxyethyl)diphenylphosphine and (2,2dimethoxyethyl)diphenylphosphine oxide and their cobalt(II) complexes

(2,2-Dimethoxyethyl)diphenylphosphine

30.0 mmol of ClCH₂CH(OCH₃)₂ in (15 mL) dry THF was drop-wise added (within 60 min.) to 30.0 mmol of Ph₂PK in 50 ml of dry THF until all the red color of Ph₂PK solution was totally vanished, during addition the temperature of reaction was kept constant to 0 °C. Subsequently, at room temperature, the mixture was stirred for 3h to ensure the reaction completeness. Degassed saturated with NH₄Cl aqueous solution ~80 mL was placed to the reaction mixture, using separatory funnel. The organic layer that contains the ligand was separated then dried over MgSO₄ drying agent. After evaporation the solvent under vacuum, the viscous colorless oily air-sensitive pure ligand product was isolated in a good yield. Yield: 84%. MS: m/z = 274.22 (M+). FT-IR (KBr, cm⁻¹): 3160 (*v*PhH) and 2950 (*v*CH). 1530

(vC=C). UV-visible absorption: $\lambda_{max} = 245$ nm. Using CDCl₃ solvent, ³¹P{¹H} NMR: δp

(ppm) –22.20. ¹H NMR: δ (ppm) 2.45, 2.48 (d, J = 6.1 Hz, 2H, PCH₂), 3.29 (s, 3H, CH₃O), 4.42 (t, J = 5.2 Hz, H, O₂CH), 7.00–7.60 (2 m, 15H, Ar-H). ¹³C{¹H} NMR: δ (ppm) 32.87, 33.03 (d, 1C, PCH₂), 52.85 (s, 2C, OCH₃), 102.60, 102.70 (d, 1C, O₂CH), 128.7–137.9 (4 m, 12C, Ar). Elemental analysis, Calculated for C₁₆H₁₉O₂P. C, 70.06 and H, 6.98%. Found: C, 69.73 and H, 6.65%.

(2,2-Dimethoxyethyl)diphenylphosphine oxide

1.0 g of Ph₂PCH₂CH(OCH₃)₂ was dissolved in 60 ml of dichloromethane in 200 ml Erlenmeyer flask in an open atmosphere and at room temperature the solution was stirred for 3 h, by time, samples were taken and subjected to ³¹P NMR, in order to monitor the reaction conversions. Finally, the solvent was evaporated under vacuum and air-insensitive colorless powder was collected.

Yield: 92%. MS: m/z = 290.29 [M+]. m.p = 53 °C, IR (KBr, cm⁻¹): 3120 (vPhH) and 2920 (vCH). 1125 (vP=O). 1410 (vC=C), UV-visible absorption: $\lambda_{\text{max}} = 255 \text{ nm}$. Using CDCl₃ solvent, ³¹P{¹H} NMR: δp (ppm) 28.7. ¹H NMR: δ (ppm) 2.67 (t, J = 6.2 Hz, 2H, PCH₂), 3.20 (s, 3H, CH₃O), 4.82 (t, J = 5.0 Hz, H, O₂CH), 7.20–7.90 (2 m, 15H, Ph-H). ¹³C{¹H} NMR: δ (ppm) 34.70, 35.40 (d, 1C, PCH₂), 52.85 (s, 2C, OCH₃), 100.32, 100.44 (d, 1C, O₂CH), 128.7–139.1 (4 m, 12C, Ar). Calculated for C₁₆H₁₉O₃P. C, 66.20 and H, 6.60; %. Found: C, 66.05 and H, 6.45%.

Complexes preparation

The desired complexes were prepared by mixing 40 ml ethanolic solutions of CoX2.6H₂O with equivalent amount of (2,2-dimethoxyethyl)diphenylphosphine in inert atmosphere. Orange

solution is formed after 5 min. The reaction mixture was stirred for 1.0 h at room temperature and inert atospehere before it concentrated to \sim 3 ml volume under vacuum, adding 40 ml of hexane to the concentrated mixture cases the desired complexes to precipitate, the precipitate was filtered (P4), washed (30 ml of diethyl ether) then finally dried under vacuum.

CoCl_{2.6}H₂O (1.0 mmol) in 20 ml of EtOH was mixed with (2,2-dimethoxyethyl)diphenylphosphine (2.1 mmol) in 20 ml of EtOH to produce complex **1**. 88% Yield of light orange powder, m.p 180 °C. FAB-MS (m/z) 677.2 [M⁺] (*theoretical 677.8*). Calc., for $C_{32}H_{38}Cl_2CoO_4P_2$: C, 56.65 and H, 5.60. Found: C, 56.38 and H, 5.47%.

CoBr2.6H₂O (1.0 mmol) was treated with (2,2-dimethoxyethyl)diphenylphosphine (2.1 mmol) to produce complex **2**. 80% Yield, light brown powder, m. p. = 160 °C. FAB-MS (m/z) 764.2 (theoretical 764.9) [M⁺]. Anal. Calc., for $C_{32}H_{38}Br_2CoO_4P_2$: C, 50.09 and H, 4.99. Found: C, 49.88 and H, 4.87%.

X-ray structural analyses for complex 1

Crystals of complex **1** was grown by slowly diffusion of Et₂O solvent into a solution of complex **1** dissolved in CH₂Cl₂. The XRD data was collected at 173(2) K on a BRUKER APPEX-II CCD diffractometer, using graphite mono-chromated Mo-K_{α} radiation (λ = 0.71073 Å). Details of crystal data is illustrated in Table 1. Direct methods were served to solve the structure using SHELXS-97 program [14].

Table 1. Structure refinement and crystal data for complex 1

Crystal data	
$C_{32}H_{38}Cl_2CoO_4P_2$	Z = 2
$M_r = 678.39$	F(000) = 706
Triclinic, P1	$D_{\rm x} = 1.403 {\rm ~Mg} {\rm ~m}^{-3}$
a = 9.274 (2) Å	Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
<i>b</i> = 12.145 (3) Å	Cell parameters from 1939 reflections
c = 14.885 (4) Å	$\theta = 2.4 - 26.1^{\circ}$
$\alpha = 99.618 \ (3)^{\circ}$	$\mu = 0.84 \text{ mm}^{-1}$
$\beta = 93.398 \ (3)^{\circ}$	T = 100 K
$\gamma = 102.506 \ (3)^{\circ}$	Prism, Colourless
V = 1605.8 (7) Å ³	$0.44 \times 0.31 \times 0.12 \text{ mm}$
Refinement	
Refinement on F^2	Primary atom site location: Structure-invariant direct methods
Least-squares matrix: Full	Secondary atom site location: Difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.030$	Hydrogen site location: Inferred from neighbouring sites
$wR(F^2) = 0.074$	H-atom parameters constrained
<i>S</i> = 1.03	$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 1.4025P]$ where $P = (F_o^2 + 2F_c^2)/3$
5869 reflections	$(\Delta/\sigma)_{ m max} < 0.001$
374 parameters	$\Delta \rho_{\text{max}} = 0.45 \text{ e} \text{ Å}^{-3}$
0 restraints	$\Delta \rho_{\rm min} = -0.28 \ e \ {\rm \AA}^{-3}$

Results and discussion

Synthesis of the $Ph_2PCH_2CH(OCH_3)_2$ ether-phosphine, ether-phosphine oxide $Ph_2P(P=O)CH_2CH(OCH_3)_2$ and (ether-phosphine)_2Cobalt(II) complexes

Tridentate ether-phosphine {P, 2O} hybrid ligand was prepared by reacting equivalent amount of 2-chloro-1,1-dimethoxyethane with Ph₂PK in dry THF under inert atmosphere, as seen in Scheme1. The prepared ligand showed a high sensitivity to atmospheric oxygen, the ether–phosphine oxide was form directly by subjecting the ether-phosphine to an open atmospheric oxygen under stirring conditions. The oxidation reaction of ether-phosphine to ether-phosphine oxide was monitored by ³¹P NMR.

When the ether-phosphine ligand was treated with $CoX_2.6H_2O$ salt (X = Cl or Br) in EtOH (Scheme 1), the X₂Co[η^1 -Ph₂PCH₂CH(OCH₃)₂]₂ complexes are formed directly in very high yields. The complexes showed somewhat air-sensitivity in solution, while in solid state they are stable for months. The desired complexes found to be soluble in alcohol, dichloromethane, chloroform and water solvents and insoluble in most of aliphatic hydrocarbons.



Scheme 1. Synthesis of hemilabile ligands and their complexes.

Mass Spectral Studies

Mass spectra of the $Ph_2PCH_2CH(OCH_3)_2$, $Ph_2P(=O)CH_2CH(OCH_3)_2$ ligands, complex **1** and complex **2** exhibited molecular ion peak [M]+, *m/z* at 274.22, 290.29, 677.2 and 764.2, respectively, corresponding to their molecular weights, the full fragments pattern of complex **2** was illustrated in Figure **1**.

Figure 1 reported a typical FAB-MS spectrum of complex 2. Good agreement between real structure formula and expected molecular ion $[M^+]$ m/z = 764.2 (764.8 theoretical) with a

58% peak intensity was recorded. Relevant fragments seen in the spectrum (Figure 1) reconcile to m/z at 684.2 (20%) [M-Br]⁺ and 606.2 (20%) [M-2Br]⁺



Figure 1. FAB-MS of complex 2.

X-Ray structural determination of complex 1

To collect better insight on structural parameters, complex 1 was subjected to X-ray structural investigation since good crystals were collected. The crystal structure and packing mode are presented in Figure 2 and 3, respectively.



Figure 2. ORTEP of complex 1 with labelled atoms. Thermal ellipsoids are drawn at the 50%

probability level.



Figure 3. A crystal packing of complex 1 viewed along the crystallographic *a* axis.

The complex crystallizes as $Cl_2Co[\eta^1-Ph_2PCH_2CH(OCH_3)_2]_2$ isomer with approximate $C_{2\nu}$ symmetry. In the complex structure, cobalt exhibited distorted tetrahedral geometrical coordination, being surrounded by the phosphprous atoms belong to ether-phosphine in monodetate coordination mode and two chloride ions ligands, relevant angles and bond distances are collected in Table 2.

							_
Bond	angle	(°)		Bond	distan	ces (Å)	_
Cl1	Col	Cl2	121.58(2)	Col	Cl1	2.2325(7)	
Cl1	Col	P1	117.54(2)	Col	Cl2	2.2390(7)	
Cl1	Col	P2	94.65(2)	Col	P1	2.3742(8)	
Cl2	Col	P1	100.34(2)	Col	P2	2.3822(7)	
Cl2	Col	P2	109.97(2)				
P1	Col	P2	113.18(2)				
Col	P1	C1	111.34(7)				
Col	P1	C7	119.10(7)				
Col	P1	C13	109.59(7)				_
					-		

Table 2. Selected bond distances (Å) and, angles (°) of complex 1.

An analysis of the packing showed seveal polar short intermolecular contacts, the molecules being separated by Co—Cl....Hph and $-CH_2)_2$ —O.....H_{CHP} as well as normal van-der-Waals distances. The complex crystallize in the triclinic/*P-1* space group with two molecules per asymmetric unit.

Hirshfeld surface analysis for complex 1

Using the cif file crystal structure information of complex **1** Hirshfeld surface theoreticalx caclualation was carried out, the sufficient intermolecular forces and atoms_{inside} /atom_{outside} fingerprint map interactions were figured out as in Figure **4** and **5** respectively. Figure 4 showed surfaces mapped over a d_{norm}, d_e and d_i [15-17]. The red dark-spots on the d_{norm} surface may reveal the short interatomic contacts, i.e., Co—Cl....H_{Ph} with distance = 2.839 Å with four interactions per molecule and $-CH_2)_2$ —O.....H_{CHP} with distance 2.708 Å with two interactions per molecule, the other interactions cited as light-spots, i.e., C— H.....H/C due to several van-der-Waals interactions [17-18].



Figure 4. *d_{norm}* on Hirshfeld surface intermolecular forces of complex 1.

The 2D-fingerprint plots over the Hirshfeld surfaces of complex **1** revealed the most important differences between the interaction patterns. Total interactions, H...H (64.3 %), H...Cl (5.6 %), H...C (4.8 %) and H...O (3.5 %) were illustrated in Figure 5. The detailed fingerprints intermolecular interaction between atoms inside and outside in molecules were presented in Table 3



Figure 5. Hirshfeld surface atom per atom fingerprint with their d_{norm} of complex 1.

100%	H _{inside}	Cl _{inside}	Oinside	Cinside	P _{inside}	Co _{inside}
Houtside	64.3	10.4	7.5	17.0	0	0
Cl _{outside}	10.4	0	0.3	0	0	0
O _{outside}	7.5	0	0	0.7	0	0
Coutside	17.0	0	0.7	0	0	0
P _{outside}	0	0	0	0	0	0
Co _{inside}	0	0	0	0	0	0

|--|

NMR of the $Ph_2PCH_2CH(OCH_3)_2$ and $Ph_2P(P=O)CH_2CH(OCH_3)_2$ ligands

The ¹H NMR spectra belong to the desired ether–phosphine $Ph_2PCH_2CH(OCH_3)_2$ and ether–phosphine oxide $Ph_2P(P=O)CH_2CH(OCH_3)_2$ ligands characterized several sets of signals, phenylic and aliphatic protons were recorded. The correlations between O₂CH and CH₂P function groups in the desired ligands were established by 2D-H,H-COSY experiments, chemical shifts and the splitting of the signals together with integrations of the ¹H resonances are in accordance with ligands compositions, as seen in S1, (for ether-phosphine ligand).

The ${}^{13}C{}^{1}H$ NMR spectrum collaborated the schemed structures illustrated in Scheme 1. ${}^{13}C$ signals belong to aliphatic and aromatic ether-phosphine carbons are recorded, as seen in S2, (see the experimental part).

The stepwise oxidation of ether-phosphine to ether-phosphine oxide is monitored by ${}^{31}P{}^{1}H$ NMR spectroscopy. The signal of ether-phosphine at $\delta_{p} = -22.2$ ppm was displanced to the positive phosphine oxide chemical shift ($\delta_{p} = 28.7$ ppm) due to the oxide-phosphine new double bond fomation (see Scheme 1 and S3). Complete oxidation was recorded after 2h from stirring of 0.1g of ether-phosphine dissolved in 40 ml of chloroform at RT open atomsphere, look up Figure 8c S3, which reflects the degree of air-sensitivity of such ligand.

Electronic spectra and solvatochromism of desired complexes

In order to demonstrate the effect of solvent on the coordination structures around Co(II) species, UV–Vis. spectroscopy was performed for the desired complexes in different suitable solvents.

The spectra of the desired complexes in chloroform revealed typical tetrahedral coordination around the Co^{2+} center, having several maxima from ~550 to 750 nm, due to the ${}^{4}\text{A2}(\text{F}) \rightarrow {}^{4}\text{T1}(\text{P})$ electron transition, as seen in Figure 6, significantly higher values than the ${}^{4}\text{T1g}(\text{F}) \rightarrow {}^{4}\text{T1g}(\text{P})$ octahedral electron transition with splitting belongs to either doublet state transitions effects or spin-orbit coupling [19-23].

Complex **1** in chloroform has absorptions at 580, 645 and 785 nm (sh) see Figure 6a, while complex **2** shows absorptions at 610 (sh), 650 and 780 nm see Figure 6b.



Figure 6. Vis. spectra of: a) complex 1 and b) complex 2 dissolved in chloroform at RT.

In ethanol, the tetrahedral structure of complex **1** exhibited four weak maxims with higher chemical shift, an extra absorptions in the "octahedral region" ~550 nm was recorded, an additional coordination of ethanol solvent [20-24], leading to octahedral $Co(P)_2Cl_2(EtOH)_2$ complex formation toghther with the orginal tetrahedral $Co(P)_2Cl_2$ complex, see Figure 7b. Typical pure octahedral [$Co(P)_2Cl_2(H_2O)_2$] coordinated around Co^{2+} center was recorded when complex **1** was dissolved in water (strong polar solvent), all the maxims (in chloroform or EtOH solvents) were replaced by one broad maximum at ~600 nm, see Figure 7c.



Figure 7. Vis. spectra of complex 1: a) in chloroform, b) in EtOH, c) in water at RT.

FT-IR investigation

The FT-IR spectra of the desired ether-phosphine and its complexes were compared under identical measurement conditions, as seen in S4, three main sets of functional groups stretching vibrations in the ranges 3600-3300 (special in complexes), 3150-3050 and 2900-

2700 cm⁻¹, which assigned to H₂O, Ph-H, and alkyl-H groups, respectively. Appearance of two new bands at 440 and 420 cm⁻¹ in the complexes spectra only (not in the free ligand) were due to $v_{(Co-P)}$ new bond formation.

Thermogravimetric analysis of complex 1

The weigh lost of complex **1** over 0–1000 °C temprature range was carried out at 10 °C min⁻¹ heating rate and in an open atomsphere. The TG/DTG spectrum of complex **1** proceed through two steps of Wt. loss mechanism (Figure 8). The first step is the major one, 80% of the complex Wt. was lost over 180-250 °C temp. range, due to destruction of the two ether-phosphine ligands from the desired complex structure ended to $CoCl_2$ complex (79%, theoretical wt. loss). The second step was removing of Cl ions from $CoCl_2$ and reacting with atomspheric oxygen to preduce cobalt oxide (as final products), occuring at 430-620 °C with a 10.5% Wt. lost (theoretical 10%).



Figure 8. TG-DTG thermal curves of complexes 1.

Conclusion

Novel tridentate ether-phosphine {P, 2O}, ether-phosphine oxide {OP, 2O} and their tetrahedral $Co(\eta^{1}$ ether-phosphine)₂X₂ complexes (X= Cl or Br) were synthesized and spectrally characterized. ³¹P-NMR was investigated to monitor the oxidation process of Ph₂PCH₂CH(OCH₃)₂ to Ph₂P(=O)CH₂CH(OCH₃)₂. The tetrahedral Cl₂Co[η^{1} -Ph₂PCH₂CH-(OCH₃)₂]₂ structure was solved by X-ray single crystal and showed Triclinic unit cells with *P*-*1* space group. Solvatochromism (solvents effect) on complexes revealed the formation of pure tetrahedral structure Co(P)₂Cl₂ (EtOH)₂ in ethanol, meanwhile in water, a pure octahedral structure Co(P)₂Cl₂(H₂O)₂ was detected. Together XRD and Hirshfeld surface theoretical analysis confirmed the formation of several polar and non-polar intermolecular short contacts in the crystal lattice of complex **1**. Complex **1** exhibited a good thermal stability with two steps thermal decomposition mechanism.

Acknowledgements

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the research group project Number (RGP- 257 - 1435-1436). I. W. thanks Prof. Avelino Corma for UPV-CSIC. De los Naranjos, Spain for providing free X-ray measurement and for his continuous encouragement.

Appendix A. Supplementary materials

"Crystallographic data for the structural analyses have been deposited with the Cambridge crystallographic data center, CCDC No. 1486394. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from thee CCDC, 12 union Road, Cambridge CB2 IEZ, UK; fax: +44-1223-33633; e-mail: deposit@ccdc.ca.ac.uk)".

References

- [1] E. Lindner, St. Pautz, M. Haustein, Coord. Chem. Rev. 155 (1996) 145-162
- [2] Y. Mitsushige, B. P. Carrow, Sh. Ito, K. Nozaki, Chem. Sci., 7 (2016) 737-744
- [3] G. Leone, M. Mauri, F. Bertini, M. Canetti, D. Piovani and G. Ricci, Macromolecules, 48 (2015) 1304-1312
- [4] E. Lindner, Z-L. Lu, A.H. Mayer, B. Speiser, C. Tittel, I. Warad: Electrochem. Commun.7 (2005) 1013-1020
- [5] Z. Jian, M. C. Baier and S. Mecking, J. Am. Chem. Soc., 137 (2015) 2836-2839
- [6] A. Bader, E. Lindner, Coord. Chem. Rev. 27 (1991) 108-110
- [7] A.A. Batista, M.O. Santiago, C.L. Donnici, I.S. Moreira, P.C. Healy, S.J. Berners-Price,S.L. Queiroz, Polyhedron 20 (2001) 2123-2128
- [8] M. Al-Noaimi, A. Nafad, I. Warad, R. Alshwafy, A. Husein, W. H. Talib, T. Ben Hadda, Spectrochim. Acta, Part A, 122 (2014) 273–282
- [9] E. Lindner, I. Warad, K. Eichele, H.A. Mayer, Inorg. Chim. Acta. 350 (2003) 49-56
- [10] I. Warad, H. Al-Hussen, R. Al-Far, R. Mahfouz, B. Hammouti, T. Ben Hadda, Spec.Acta A. 95 (2012) 37-43
- [11] I. Warad, E. Lindner, K. Eichele, HA. Mayor, Inorg chim Acta. 357 (2004) 1847-1853
- [12] I. Warad, Molecules 15 (2010) 4652-4669
- [13] S. K. Wolff, D. J. Grimwood, J. J. McKinnon, D. Jayatilaka, M. A. Spackman, (2007).
- Crystal Explorer 2.1 University of Western Australia, Perth, Australia.
- [14] G. M. Sheldrick, SHELXS-97; University of Göttingen, Göttingen, Germany 1997
- [15] M. A. Spackman, J. J. McKinnon, Cryst. Engg. Comm. 4 (2002) 378–392
- [16] M. A. Spackman, D. Jayatilaka, Cryst. Engg. Comm. 11 (2009) 19-32

- [17] R. N. Patel, N. Singh, K. K. Shukla, J. Niclós-Gutiérrez, A. Castineiras, V. G.,Vaidyanathan, B. U. Nair, Spectrochim. Acta, Part A, 62 (2005) 261–268
- [18] K.P. Balasubramanian, R. Karvembu, R. Prabhakaran, V. Chinnusamy, K. Natarajan, Spectrochim. Acta, Part A, 68 (2007) 50-54
- [19] G. Gritzner, J. Küta, Pure Appl. Chem. 4 (1984) 46-466
- [20] V. Ramírez-Delgado, R. E. Morales León, L. Ayala, V. Coutiño, F. J. Rodríguez, G. Osorio-Monreal, J. C. García-Ramos, M. F Ruiz-Azuara, L. Ortiz-Frade, Polyhedron 74 (2014) 72–78
- [21] N. Levesanos, A. Grigoropoulos, C. P. Raptopoulou, V. Psycharis, P. Kyritsis Inorg.Chem. Comm. 30 (2013) 34–38
- [22] A. Romerosa, C. Saraiba-Bello, M. Serrano-Ruiz, A. Caneschi, V. McKee, M. Peruzzini,
- L. Sorace, F. Zanobini Dalton Trans. (2003) 3233-3239.
- [23] R. Bou-Moreno, S. A. Cotton, V. Hunter, K. Leonard, A. W. G. Platt, P. R. Raithby, S. Schiffers Polyhedron, 30 (2011) 2832-2836
- [24] S. A. Cotton, J. Fawcett, V. Franckevicius, Transition Met. Chem., 27 (2002) 38-41.

Highlights

- New tridentate ether-phosphine, ether-phosphine oxide ligands and their Co(II) complexes were made available
- The NMR, spectral, solvatochromic, CV and thermal properties were reported
- Complex 1 was solved by XRD crystal structure as novel *cis*-Cl₂Co[η¹-Ph₂PCH₂CH(OCH₃)₂]₂ Tetrahedral geometry

Chilling and a second