

Synthesis and Crystal Structure of Cobalt(III) Complexes of Salen Type Schiff Bases and Tertiary Phosphanes as Ligands

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(Received 19 April 2015, Accepted 4 July 2016)

[Co(Salen)(PBU₃)₂]*X* (*X* = ClO₄, BF₄), [Co(Salpn)(PBU₃)₂]ClO₄ and [Co(Salen)(PMe₂Ph)₂]ClO₄ complexes (where salen = bis(salicylaldehyde)ethylenediimine) and salpn = bis(salicylaldehyde) 1,3-propanediimine) were synthesized and characterized by IR, UV-Vis, ¹H NMR spectroscopy and elemental analysis. The IR and ¹H NMR spectra confirmed that the synthesized complexes contain Schiff base ligand, phosphane and the corresponding counter ion and the elemental analysis is in good agreement with the theoretical data calculated for the proposed formula. The coordination geometry of [Co(Salen)(PBU₃)₂]ClO₄ and [Co(Salen)(PMe₂Ph)₂]ClO₄ complexes were determined by X-ray crystallography. It has been found that all the complexes are hexa coordinate in the solid state. Cobalt atom exhibits a distorted octahedral geometry and the salen ligand acts as N₂O₂ donor, occupying the equatorial positions.

Keywords: Schiff base, Phosphane, Cobalt(III) complexes, X-Ray crystal structure

INTRODUCTION

Cobalt complexes with ligands derived from salicylaldehyde have been well studied [1]. They are regarded as models for the Cobalamine (B₁₂) coenzymes [2-4] classified as an oxygen carrier [5] and used as a catalyst for the preparative oxygenation of phenols [6] indols [7] and amines [8]. The catalytic activity of Co(III) with salen complexes has been investigated. The reported results show that the catalytically active species contains cobalt in the Co(III) oxidation state [9-15].

Monophosphane cobalt(III) Schiff base complexes with the general formula of [CoL(PR₃)(OH₂)]⁺ (where L = tetradentate N₂O₂ Schiff bases) show that these types of complexes are in equilibrium with phosphanes and amines to form [CoL(PR₃)₂]⁺ and [CoL(PR₃)(amine)]⁺ [16-21], but there is not any information about their structure. So to extend the studies on the structure of these type of complexes, Salen (bis(salicylaldehyde)ethylenediimine) and

Salpn (bis(salicylaldehyde)propanediimine) Schiff bases were prepared by the condensation of 2-hydroxybenzaldehyde within 1,2-ethylenediamine and 1,3-propanediamine respectively. The tertiary phosphane cobalt(III) complexes of these ligands were prepared in methanol solvent (Fig. 1). The resulting complexes were identified by IR, ¹H NMR, UV-Vis spectroscopy and elemental analysis. The coordination geometry of [Co(Salen)(PMe₂Ph)₂]ClO₄ and [Co(Salen)(PBU₃)₂]ClO₄ were determined by X-ray crystallography.

EXPERIMENTAL

Chemicals and Apparatus

All of the chemicals and solvents used for synthesis were commercially available reagent grade and used without purification. Infrared spectra were recorded as KBr discs on a FT-IR JASCO-680 spectrophotometer in the 4000-400 cm⁻¹. The elemental analysis was determined on a CHN-O-Heraeus elemental analyzer. UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer in the 190-

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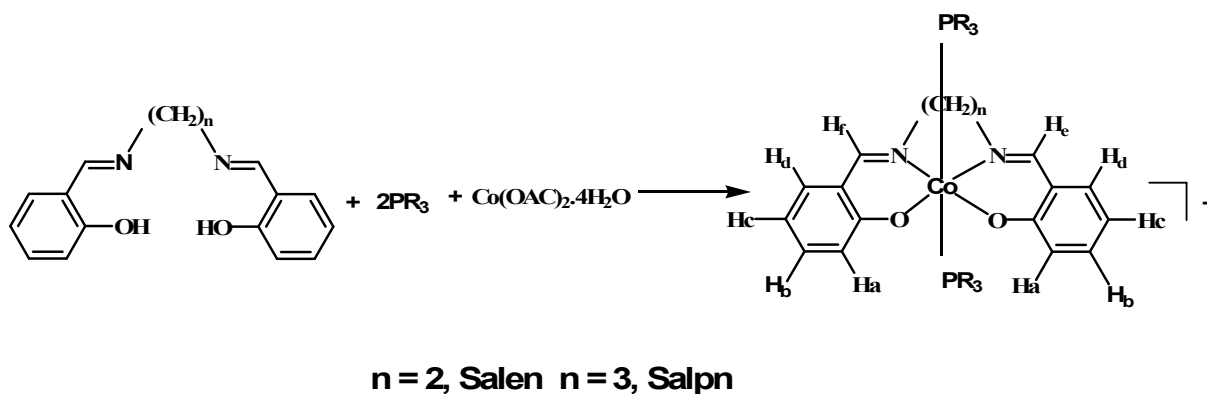


Fig. 1. The structure of Schiff bases and their complexes.

900 nm. The ^1H NMR spectra were recorded in CDCl_3 on DPX-400 MHz FT-NMR. The X-ray diffraction measurements were made on a STOE IPDS-2T diffractometer with graphite monochromated Mo- K_α radiation.

Synthesis

The Schiff base ligands, H_2Salen and H_2Salpn , were prepared according to the literature [22] by the condensation of 1,2-ethylenediamine, 1,3-propanediamine and 2-hydroxybenzaldehyde, (2:1 mole ratio) in methanol and recrystallized by dichloromethane/methanol mixed solvent through the partial evaporation of dichloromethane.

The general procedure for synthesis of $[\text{Co}(\text{Salen})(\text{PBU}_3)_2]\text{ClO}_4$, $[\text{Co}(\text{Salpn})(\text{PBU}_3)_2]\text{ClO}_4$, $[\text{Co}(\text{Salen})(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$ and $[\text{Co}(\text{Salen})(\text{PBU}_3)_2]\text{BF}_4$ complexes is as follows: an appropriate amount of cobalt(II)acetatetetrahydrate (0.249 g, 1.0 mmol), tributylphosphane (0.5 ml, 2.0 mmol) or dimethylphenylphosphane (0.31 ml, 2.0 mmol) were added to a methanolic solution (40 ml) of H_2Salen (0.268 g, 1.0 mmol) or H_2Salpn (0.282 g, 1.0 mmol). The reaction was refluxed for 1 h. The formed Co(II) complex was oxidized by blowing air into the solution for 2 h, and the final reaction mixture was filtered. An appropriate amount of sodium perchlorate monohydrate (0.140 g, 1.0 mmol) or sodium tetrafluoroborate (.110 g, 1.0 mmol) was then added to the filtrate. Red crystals were formed after 48 h. These crystals were filtered off, washed with methanol, and recrystallized from of dichloromethane/ethanol (2:1 ratio) and dried in vacuum at 65 °C.

$[\text{Co}(\text{Salen})(\text{PBU}_3)_2]\text{ClO}_4$ Yield (80%). Anal, Calcd. for $\text{C}_{40}\text{H}_{68}\text{N}_2\text{O}_6\text{P}_2\text{ClCo}$: C, 57.93; H, 8.26; N, 3.38%. Found; C, 57.74; H, 8.12; N, 3.41%. FT-IR (KBr cm^{-1}) ν_{max} 2959, 2924, 2867 (C-H), 1621, 1600 (C=N), 1452 (C=C), 1084 (ClO_4^-). ^1H NMR (CDCl_3 , δ , ppm): 0.80-0.84 (t, 18H, CH_3), 1.24-1.32 (m, 12H, CH_2), 1.36 (m, 12H, CH_2), 1.49-1.51 (m, 12H, CH_2), 3.92 (s, 4H, CH_2), 6.49-6.53 (t, 2H, H_a Aromatic), 6.81-6.84 (d, 2H, H_b Aromatic), 7.08-7.10 (d, 2H, H_c Aromatic), 7.19-7.23 (t, 2H, H_d Aromatic), 7.88 (s, 2H, HC=N). UV-Vis, λ_{max} (nm) (Ethanol): 395, 305, 254.

$[\text{Co}(\text{Salen})(\text{PBU}_3)_2]\text{BF}_4$ Yield (75%). Anal., Calcd. for $\text{C}_{40}\text{H}_{68}\text{N}_2\text{O}_2\text{P}_2\text{F}_4\text{BCo}$: C, 58.82; H, 8.39; N, 3.43%. Found; C, 58.91; H, 8.31; N, 3.46%. FT-IR (KBr cm^{-1}) ν_{max} 2956, 2930, 2868 (C-H), 1623, 1599 (C=N), 1451 (C=C), 1058 (BF_4^-). ^1H NMR (CDCl_3 , δ , ppm): 0.80-0.84 (t, 18H, CH_3), 1.24-1.31 (m, 12H, CH_2), 1.36 (m, 12H, CH_2), 1.48-1.50 (m, 12H, CH_2), 3.82 (s, 4H, CH_2), 6.49-6.53 (t, 2H, H_a Aromatic), 6.82-6.84 (d, 2H, H_b Aromatic), 7.09-7.10 (d, 2H, H_c Aromatic), 7.19-7.23 (t, 2H, H_d Aromatic), 7.85 (s, 2H, HC=N). UV-Vis, λ_{max} (nm) (Ethanol): 394, 306, 255.

$[\text{Co}(\text{Salpn})(\text{PBU}_3)_2]\text{ClO}_4$ Yield (75%). Anal., Calcd. for $\text{C}_{41}\text{H}_{70}\text{N}_2\text{O}_6\text{P}_2\text{ClCo}$: C, 57.57; H, 8.18; N, 3.28%. Found; C, 57.95; H, 8.15; N, 3.45%. FT-IR (KBr cm^{-1}) ν_{max} 2954, 2928, 2869 (C-H), 1620, 1600 (C=N), 1449 (C=C), 1084 (ClO_4^-). ^1H NMR (CDCl_3 , δ , ppm): 81-85 (t, 18H, CH_3), 1.26-1.33 (m, 12H, CH_2), 1.41 (m, 12H, CH_2), 1.61-1.68 (m, 12H, CH_2), 2.22 (s, 2H, CH_2), 3.84 (s, 4H, CH_2), 6.47-6.50 (t, 2H, H_a Aromatic), 6.80-6.82 (d, 2H, H_b Aromatic), 6.98-7.00 (d, 2H, H_c Aromatic), 7.15-7.19 (t, 2H, H_d Aromatic), 7.44 (s, 2H, HC=N). UV-Vis, λ_{max} (nm)

(Ethanol): 393, 304, 253.

[Co(Salen)(PMe₂Ph)₂]ClO₄ Yield (80%). Anal., Calcd. for C₃₂H₃₆N₂O₆P₂ClCo: C, 54.82; H, 5.17; N, 3.99%. Found; C, 54.76; H, 5.21; N, 4.07%. FT-IR (KBr cm⁻¹) ν_{\max} 3053, 2914 (C-H), 1628, 1597 (C=N), 1448 (C=C), 1085 (ClO₄⁻). ¹H NMR (CDCl₃, δ , ppm): 1.57-1.59 (d, 12H, CH₃), 3.58 (s, 4H, CH₂), 6.42-6.46 (t, 2H, Aromatic), 6.71-6.72 (d, 2H, H Aromatic), 7.07-7.13(m, H Aromatic), 7.18-7.24(m, H Aromatic), 7.29 (s, 2H, HC=N), ppm., UV-Vis, λ_{\max} (nm) (Ethanol): 395, 305, 254.

Crystal Structure Determination and Refinement of [Co(Salen)(PMe₂Ph)₂]ClO₄ and [Co(Salen)(PBU₃)₂]ClO₄ Complexes

The X-ray diffraction measurements were made on a STOE IPDS-2T diffractometer with graphite monochromated Mo-K α radiation.

For [Co(Salen)(PMe₂Ph)₂]ClO₄ complex red plate crystal with a dimension of 0.50 × 0.30 × 0.15 mm were chosen and mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 8668 unique reflections. Data were collected at a temperature of 120(2) K to a maximum 2θ value of 58.34° in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [23] software package. The numerical absorption coefficient, μ , for Mo-K α radiation is 0.758 mm⁻¹.

For [Co(Salen)(PBU₃)₃]ClO₄ complex red block crystal with a dimension of 0.45 × 0.10 × 0.36 mm were chosen and mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 12280 unique reflections. Data were collected at a temperature of 120(2) K to a maximum 2θ value of 29.17° in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [23] software package. The numerical absorption coefficient, μ , for Mo-K α radiation is 0.544 mm⁻¹.

A numerical absorption correction was applied using X-RED [24] and X-SHAPE [25] softwares. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods [26] and subsequent difference Fourier maps and then refined on F^2 by a full-

matrix least-squares procedure using anisotropic displacement parameters [27]. All of hydrogen atoms were located in a difference Fourier map and then refined isotropically. Atomic factors are from International Tables for X-ray Crystallography [28]. All refinements were performed using the X-STEP32 crystallographic software package [29].

A summary of the crystal data, experimental details and refinement results are given in Tables 1 and 2 for [Co(Salen)(PMe₂Ph)₂]ClO₄ and [Co(Salen)(PBU₃)₃]ClO₄ complexes, respectively. It is notable that although the structure was refined correctly for [Co(Salen)(PMe₂Ph)₂]ClO₄, the high values of R_{int} (0.2152) and R_{sigma} (0.1404) are due to cracking of the crystal. In the case of [Co(Salen)(PBU₃)₃]ClO₄ complex however, the asymmetric unit also contains solvents molecules, which could not be modeled. Therefore, the diffraction contribution of the solvent water molecules was removed by the subroutine SQUEEZE in PLATON

RESULTS AND DISCUSSION

IR Characteristics

The IR spectra of the cobalt(III) Schiff base complexes synthesised here are listed in section 2.2. The IR spectra of the cobalt(III) complexes exhibit several bands in the 400-4000 cm⁻¹ region.

The characteristic C=N vibration appears in 1597-1628 cm⁻¹ region for the synthesised complexes. The C=N stretching in the complexes is generally shifted to a lower frequency relative to the free Schiff bases, indicating a decrease in the C=N bond order due to the coordinate bond formation between the metal and the imine nitrogen lone pair [30]. The C-H stretching of the coordinated PBU₃ ligands appears in 2867-2959 cm⁻¹ region. The stretching vibrations of BF₄⁻ and ClO₄⁻ counter ions appear at about 1058 and 1085 cm⁻¹, respectively.

Electronic Spectra

The spectral data of the synthesised complexes are listed in section 2.2. In all complexes, the band in the 253-255 nm region, involves $\pi \rightarrow \pi^*$ transition related to the aromatic rings. The band in the 304-307 nm region, involves $\pi \rightarrow \pi^*$ transition related to azomethine group. The cobalt(III)

Table 1. Crystallographic and Structure Refinements Data for [Co(Salen)(PMe₂Ph)₂](ClO₄) (A) and [Co(Salen)(PBu₃)₂](ClO₄) (B)

Compound	A	B
Formula	C ₃₂ H ₃₆ Cl ₁ Co ₁ N ₂ O ₆ P ₂	C ₄₀ H ₆₈ Cl ₁ Co ₁ N ₂ O ₆ P ₂
Formula weight	700.95	829.28
Temperature (K)	120(2)	120(2)
Wavelength λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>p</i> -1
Crystal size (mm ³)	0.50×0.30×0.15	0.45 x 0.10 x 0.36
<i>a</i> (Å)	13.5631(6)	12.6562(5)
<i>b</i> (Å)	6.0273(8)	12.6739(4)
<i>c</i> (Å)	16.0467(7)	16.0688(6)
α	90.00	104.124(3)
β (°)	111.955(3)	106.138(3)
γ	90.00	101.710(3)
Volume (Å ³)	3235.3(3)	2297.40(14)
<i>Z</i>	4	2
Density (Calcd.) (g cm ⁻³)	1.439	1.199
θ ranges for data collection	2.11-29.22	2.07-29.17
<i>F</i> (000)	1456	888
Absorption coefficient	0.758	0.544
Index ranges	-18 ≤ <i>h</i> ≤ 18 -21 ≤ <i>k</i> ≤ 21 -19 ≤ <i>l</i> ≤ 21	-17 ≤ <i>h</i> ≤ 16 -17 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 22
Data collected	24762	12280
Unique data (<i>R</i> _{int})	8668, (0.2152)	12280, (0.0750)
Parameters, restraints	402, 0	469, 0
Final <i>R</i> ₁ , <i>wR</i> ₂ ^a (Obs. data)	0.1109, 0.2839	0.0696, 0.1637
Final <i>R</i> ₁ , <i>wR</i> ₂ ^a (All data)	0.1409, 0.3163	0.0932, 0.1738
Goodness of fit on <i>F</i> ² (<i>S</i>)	1.075	1.024
Largest diff peak and hole (e Å ⁻³)	1.547, -1.502	1.187, -0.845

^a*R*₁ = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, *wR*₂ = $[\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (°) for [Co(Salen)(PMe₂Ph)₂](ClO₄) (A) and Co(Salen)(PBU₃)₂](ClO₄) (B)

Bond distances	A	B	Bond angles	A	B
Co1-N1	1.905(5)	1.896(2)	P1-Co1-N1	91.2(1)	92.5(1)
Co1-N2	1.909(5)	1.901(2)	P1-Co1-N2	95.8(1)	95.1(6)
Co1-O1	1.927(4)	1.919(2)	P1-Co1-O1	91.2(1)	86.6(1)
Co1-O2	1.907(4)	1.914(4)	P1-Co1-O2	85.1(1)	84.4(9)
Co1-P1	2.289(2)	2.319(1)	P1-Co1-P2	169.2(1)	170.2(8)
Co1-P2	2.303(1)	2.319(1)	P2-Co1-N1	95.2(2)	94.6(1)
O1-C1	1.323(6)	1.316(3)	P2-Co1-N2	92.7(1)	92.0(3)
O2-C16	1.313(6)	1.318(3)	P2-Co1-O1	86.6(1)	86.3(5)
N1-C7	1.287(7)	1.290(4)	P2-Co1-O2	85.5(1)	88.6(1)
N2-C10	1.279(7)	1.284(4)	O1-Co1-N2	178.6(2)	178.0(5)
N1-C8	1.479(8)	1.467(4)	O2-Co1-N1	178.3(2)	176.5(5)
N2-C9	1.464(7)	1.478(4)	O1-Co1-O2	86.8(2)	87.9(7)
C8-C9	1.498(9)	1.519(4)	N1-Co1-N2	85.3(2)	93.5 (3)
			O1-Co1-N1	93.6(22)	93.0(6)
			O2-Co1-N2	94.3(22)	85.5(4)
			Torsion angle	-	-
			C17-P1-P2-C25	13.2(8)	-
			N1-C8-C9-N2	-39.2(6)	39.2(3)
			O1-C1-C6-C7	-2.3(8)	1.7(5)
			C1-C6-C7-N1	7.0(8)	-7.0(5)
			O2-C16-C11-C10	-1.1(8)	1.1(5)
			C16-C11-C10-N2	1.7(8)	0.4(5)

complexes show an absorption band related to charge transfer transition (LMCT) at about 395-412 nm region [16, 31-37].

¹H NMR Spectra

The chemical shift (δ, ppm) of different protons of the cobalt(III) complexes is presented in section 2.2.

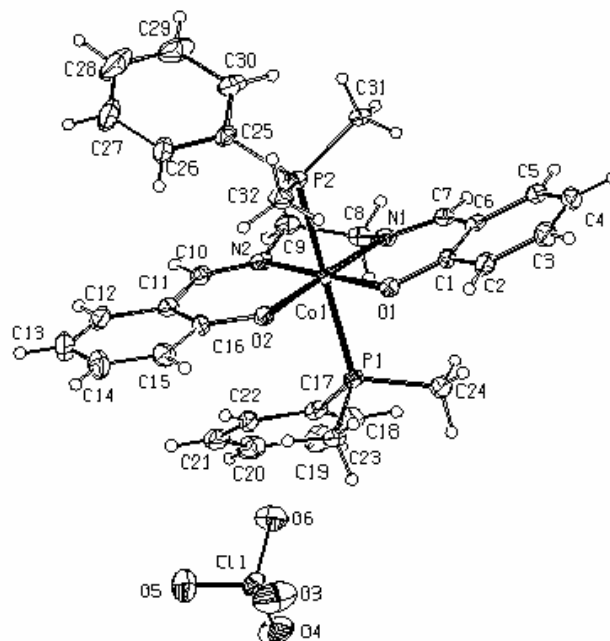


Fig. 2. The labeled diagram of $[\text{Co}(\text{Salen})(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$. Thermal ellipsoids are at 30% probability level.

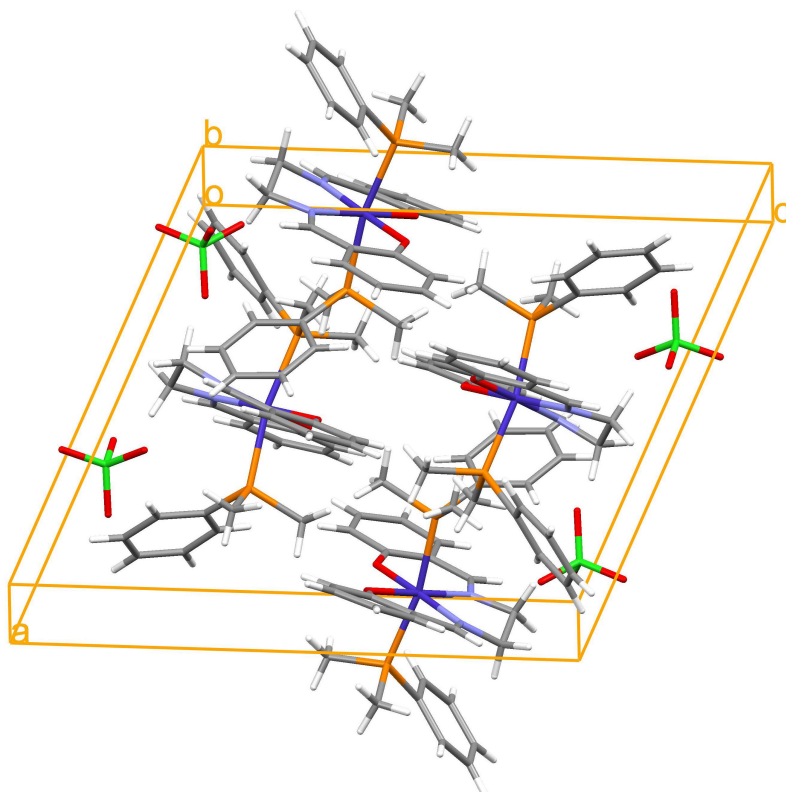


Fig. 3. Crystal packing diagram of $[\text{Co}(\text{Salen})(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$.

The ^1H NMR of complexes is in line with the proposed structures. The hydrogens of the tributyl phosphane appear in the range of 0.80-1.68 ppm. The CH_3 of butyl appears as a triplet and the methylene groups as multiplet in three set. The hydrogens of methyl groups of PMe_2Ph appear as a triplet (two mixed doublet) and it is evident that the hydrogens of methyls have a little different chemical environment and so different chemical shift. The bridging ethylene protons in salen complexes appear as a singlet at about 3.58-3.92 ppm. The bridging propylene protons in salpn complex appear at 2.22 and 3.82 ppm as singlets. The hydrogens of aromatic rings appear as triplet, doublet, doublet and triplet in the range of 6.42-7.23 and are attributed to the H_a , H_b , H_c , H_d , respectively (Fig. 1). The azomethine hydrogens are seen as a singlet. These hydrogens are shifted to high field in $[\text{Co}(\text{Salen})(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$ because of phenyle rings of dimethylphenylphosphane ligands.

Description of the Molecular Structure of $[\text{Co}(\text{Salen})(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$

The complex $[\text{Co}(\text{Salen})(\text{PMe}_2\text{Ph})]\text{ClO}_4$ crystallizes in the Monoclinic space group $P2_1/a$. Relevant X-ray diffraction data and selected bond lengths and angles are listed in Tables 1 and 2, respectively. The structure of this complex is shown in Fig. 2, which includes the atom labelling scheme. The packing diagram of complex is shown in Fig. 3. In the six-coordinate $[\text{Co}(\text{Salen})(\text{PMe}_2\text{Ph})_2]\text{ClO}_4$, cobalt atom exhibits a distorted octahedral geometry, the salen ligand has the N_2O_2 coordinated in the equatorial plane. P-Co-N/O angles are distributed from 85.5(1) to 96.2(2)°. The PMe_2Ph groups occupy the two opposite axial positions. The Co-N1, Co-N2, Co-O1 and Co-O2 distances of 1.905(5), 1.909(5), 1.927(4) and 1.907(4) Å, respectively, are similar to those in N_2O_2 -salen cobalt complexes [38-40]. The Co-P bond distances of apical positions are 2.289(1) and 2.303(1) for Co-P1 and Co-P2 respectively. The phenyl groups in axial ligands are oriented in one side of the molecule and the C17-P1-P2-C25 dihedral angle is 13.22°. The angle between phenyl main planes is 68.85°.

All angles around the cobalt center deviate significantly from 90° indicating a regular distortion. The ligand - cobalt-ligand bond angles in the equatorial plane consist of two

that are larger than 90° (O1-Co1-N1) (93.6(22)), (O2-Co1-N2) (94.3(22)) and two smaller angles (O1-Co1-O2) (86.8(2)), (N1-Co1-N2) (85.3(2)) and are similar to those in N_2O_2 -salen cobalt complexes [41]. Also the summation of these angles are 360° and shows that the cobalt atom is in a square planar environment of N_2O_2 atoms.

Description of the Molecular Structure of $[\text{Co}(\text{Salen})(\text{PBU}_3)_2]\text{ClO}_4$

The complex $[\text{Co}(\text{Salen})(\text{PBU}_3)_2]\text{ClO}_4$ crystallizes in the Triclinic space group $P\bar{1}$. Relevant X-ray diffraction data and selected bond lengths and angles are listed in Tables 1 and 2, respectively. The structure of this complex is shown in Fig. 4, which includes the atom labelling scheme. The packing diagram of complex is shown in Fig. 5. In the six-coordinate $[\text{Co}(\text{Salen})(\text{PBU}_3)_2]\text{ClO}_4$, cobalt atom exhibits a distorted octahedral geometry, the salen ligand has the N_2O_2 coordinated in the equatorial plane. P-Co-N/O angles range from 84.5(1) to 95.2(2)°. The PBU_3 groups occupy the two opposite axial positions. The Co-N1, Co-N2, Co-O1 and Co-O2 distances of 1.896 (2), 1.896 (2), 1.919 (2) and 1.914 (7) Å, respectively, are slightly shorter than those in $[\text{Co}(\text{Salen})(\text{PMe}_2\text{Ph})]\text{ClO}_4$ complex. The Co-P bond distances of apical positions of 2.319 (0) and 2.336 (3) for Co-P1 and Co-P2, respectively are slightly longer than those in $[\text{Co}(\text{Salen})(\text{PMe}_2\text{Ph})]\text{ClO}_4$ complex. This may be due to the higher cone angle for PBU_3 (145°) than PMe_2Ph (135°) [42].

All angles around the cobalt center deviate significantly from 90° indicating a regular distortion. The ligand - cobalt-ligand bond angles in the equatorial plane consist of two that are larger than 90° (O1-Co1-N1) (93.5 (3)), (O2-Co1-N2) (93.0(6)) and two smaller angles (O1-Co1-O2) (87.9(7)), (N1-Co1-N2) (85.5(4)) and are similar to those in $[\text{Co}(\text{Salen})(\text{PMe}_2\text{Ph})]\text{ClO}_4$ complex. The summation of these angles are 360° with a square planar environment for the cobalt atom.

CONCLUSIONS

By considering the spectroscopic properties and structural behavior of cobalt(III) complexes the following conclusions have been drawn.

1- The IR and ^1H NMR confirmed that the synthesised

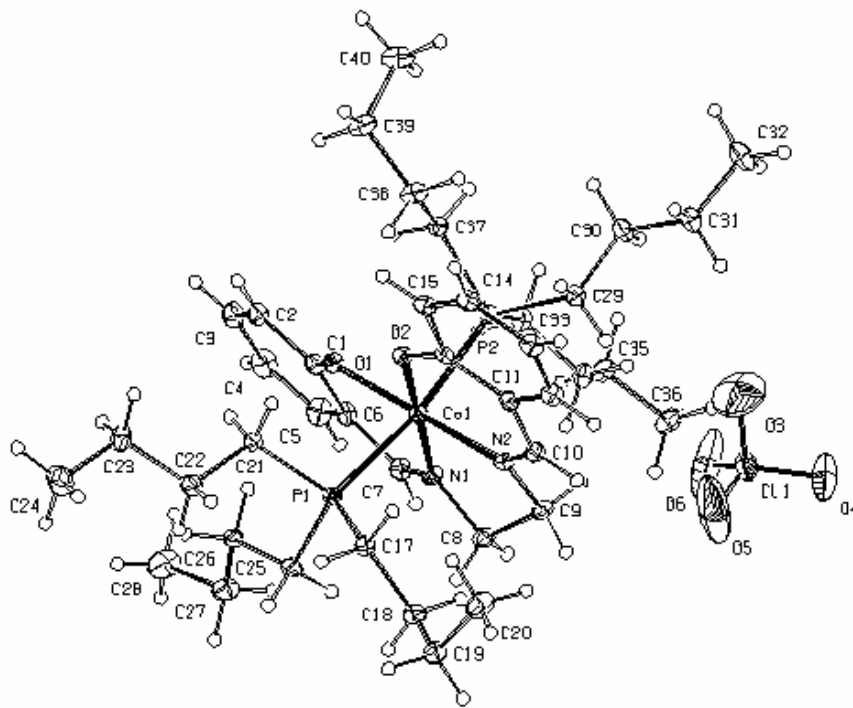


Fig. 4. The labeled diagram of $[\text{Co}(\text{Salen})(\text{PBu}_3)_2]\text{ClO}_4$. Thermal ellipsoids are at 30% probability level.

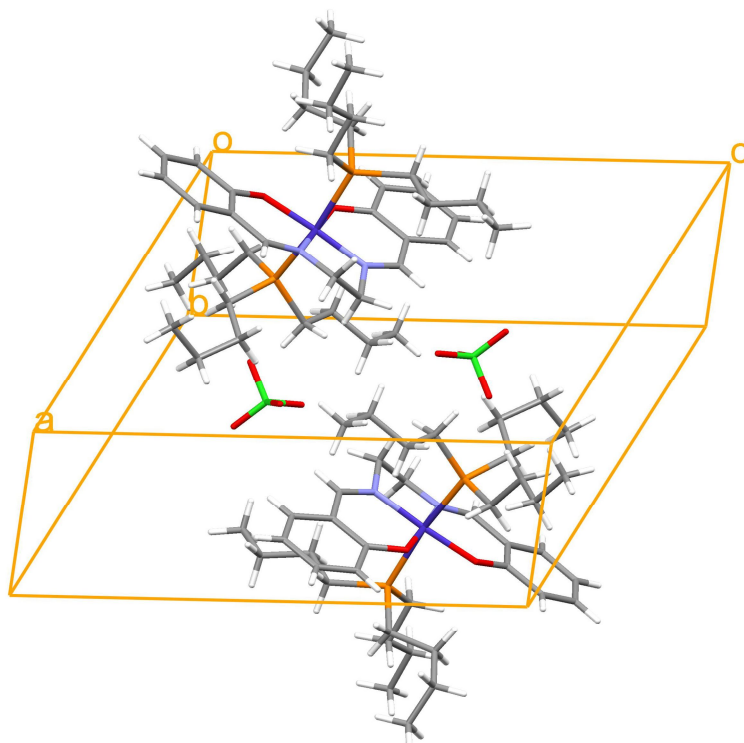


Fig. 5. Crystal packing diagram of $[\text{Co}(\text{Salen})(\text{PBu}_3)_2]\text{ClO}_4$.

complexes contain schiff base, phosphane and conter ion.

2- The synthezised complexes are hexacoordinated in the solid state.

3- Cobalt atom exhibits a distorted octahedral geometry.

4- The Schiff base ligands have the N2O2 coordinated environment in the equatorial plane.

SUPPLEMENTARY MATERIAL

CCDC No. 888598 and 888599 contains the supplementary crystallographic data for [Co(Salen)(PMe₂Ph)₂](ClO₄) and [Co(Salen)(PBu₃)₂](ClO₄) respectively. These data can be obtained at www.ccdc.cam.ac.uk/deposit {or from the Cambridge Crystallographic Data Center 12, Union Road Cambridge CB2 1EZ, UK; Fax: (internet) +44-1223/336-033; E. mail: deposit@ccdc.cam.ac.uk).

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