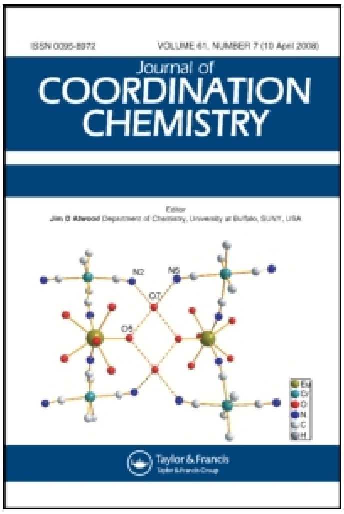

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Synthesis and characterization of 3-picoline adducts of bis(*O*,*O*′-ditolyl/dibenzyl/diphenyl dithiophosphato)cobalt(II) complexes: crystal structure of 3-picoline adducts $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$

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Bis(*O*,*O*′-ditolyl/dibenzyl/diphenyl dithiophosphato)cobalt(II) (**1**–**5**) with 3-picoline, $Co\{S_2P(OR)_2\}_2(NC_5H_4Me\text{-}3)_2$ ($R = o$-, m-, p-C_6H_4Me, CH_2Ph, Ph) have been synthesized by *in situ* reaction of 3-picoline and $CoCl_2{\cdot}6H_2O$ in aqueous medium followed by the addition of aqueous solution of $NH_4S_2P(OR)_2$. The single crystal structure of $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$ shows that geometry around cobalt(II) is distorted octahedral with two 3-picoline molecules in *trans* positions. These Co(II) dithiophosphate complexes (**1**–**5**) have been characterized by elemental analyses, spectroscopic techniques (UV-Vis, IR), and magnetic moment measurements.

Keywords: *O*,*O*′-Ditolyl dithiophosphate; 3-Picoline ligand; Lewis adduct; Cobalt(II) complex

1. Introduction

Cobalt dithiophosphate complexes have good antioxidant and antiwear properties with good viscosity index [1]. Polymerization of butadiene with catalytic cobalt dithiophosphate and organoaluminum compounds were studied [2, 3]. Coordination chemistry of cobalt(II)/(III) complexes with *O*,*O*′-dialkyl/alkylene dithiophosphates have received much attention in recent years [4–13]. The cobalt(II) complexes are very sensitive particularly with dialkyl/alkylene dithiophosphates and can be easily oxidized to cobalt(III) complexes. Cobalt(II) complexes with dialkyl and alkylene dithiophosphates have been synthesized by excluding air. Some adducts of the cobalt(II) complexes with nitrogen- and phosphorus-containing Lewis bases have been reported [13–19]. Dithiophosphate ligands are usually bidentate and X-ray crystal structures have been reported for a number of cobalt compounds with *O*,*O*′-dialkyl/alkylene dithiophosphate including $Co\{S_2P(OMe)_2\}_2(PPh_3)$ [15], $Co\{S_2P(OEt)_2\}_2(C_5H_5N)_2$ [16],

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$Co\{S_2P(OC_6H_{11})_2\}_2(C_5H_5N)_2$ [17], $Co\{S_2P(OEt)_2\}_2(C_{24}H_{26}O_2N_4)$ [18], $Co(S_2POCMe_2CH_2CHMeO)_2(2\text{-}MeNC_5H_4)$ [19], $Co(S_2POCMe_2CH_2CHMeO)_2(3\text{-}MeNC_5H_4)$ [19], $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(C_5H_5N)_2$ [14], and $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NH_3)$ [14].

In our previous study, we reported the syntheses, characterization, and crystal structure of cobalt(II) complexes such as $[Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(C_5H_5N)_2]$ and $[Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NH_3)]$ with *O*,*O*′-ditolyl/dibenzyl dithiophosphate [14]. We also described the oxidation rate and reaction conditions for the salt of dithiophosphate, which was used in the preparation of cobalt(II) complexes [14]. Oxidation of ammonium salt was slow compared to sodium and potassium salts and complexes were oxidized easily into tris analogues [14]. However, the cobalt(II) complex with dibenzyl dithiophosphate was prepared by the one step stoichiometric reaction of $CoCl_2 \cdot 6H_2O$ and ammonium salt of dibenzyl dithiophosphate [14]. Pyridine adducts with (*O*,*O*′-ditolyl/dibenzyl/diphenyldithiophosphato)cobalt(II) and 2-picoline and 3-picoline adducts with bis(alkylene dithiophosphato)cobalt(II) complexes were synthesized previously [14, 19]. We found trigonal bipyramidal geometry of 2-picoline and 3-picoline adducts, while the pyridine adducts have distorted octahedral geometry. The distortion from octahedral to trigonal bipyramidal may either be due to steric effect of cyclic dithiophosphate or methyl group on the pyridine. The exact reason can be ascertained by using 3-picoline with bis(*O*,*O*′-ditolyl/dibenzyl/diphenyl dithiophosphato)cobalt(II) complexes. The crystal structure of **3** shows distorted octahedral geometry around cobalt, suggesting that the distortion from octahedral to trigonal bipyramidal occurs due the steric effect of the cyclic dithiophosphate moiety rather than picoline molecule. The cobalt(II) is coordinated octahedrally by four sulfurs in the equatorial plane and two picoline nitrogens in the axial positions. Herewith, we report syntheses and characterization of 3-picoline adducts of bis(*O*,*O*′-ditolyl/dibenzyl/diphenyl dithiophosphato)cobalt(II) complexes and single crystal structure of $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$.

2. Results and discussion

Syntheses of $Co\{S_2P(OR)_2\}_2(NC_5H_4Me\text{-}3)_2$, **1**–**5**, were carried out using indirect methods. The reaction of cobalt chloride hexahydrate with ammonium salts of *O*,*O*′-ditolyl/dibenzyl/diphenyl dithiophosphates in 1 : 2 molar ratio gave oxidation of blue Co(II) to brown Co(III). We attempted various methods to avoid decomposition, such as carrying out the reaction in foil-wrapped flasks at low temperature, but all failed decomposing into a brown solid. 3-Picoline adducts of bis(*O*,*O*′-ditolyl/dibenzyl/diphenyl dithiophosphato)cobalt(II) were prepared by *in situ* reaction of aqueous solution of $CoCl_2 \cdot 6H_2O$ and Lewis base followed by the addition of 1 : 2 stiochiometric amount of $NH_4S_2P(OR)_2$. These adducts were extracted in benzene from aqueous solution of the reaction mixture.

$$CoCl_2 \cdot 6H_2O + 2(NC_5H_4Me\text{-}3) + 2NH_4\{S_2P(OR)_2\} \rightarrow Co\{S_2P(OR)_2\}_2(NC_5H_4Me\text{-}3)_2$$

$$(R = o\text{-}, m\text{-}, p\text{-}C_6H_4Me, CH_2Ph, Ph)$$

Removal of the solvent followed by recrystallization from dichloromethane afforded a crystalline blue solid; in one attempt needle-like blue crystals of air-stable $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$ were obtained. All complexes are soluble in common organic solvents and characterized by elemental analyses, infrared (IR), UV-Vis, and magnetic moment measurement.

2.1. *IR spectra*

The relevant assignments of IR bands have been made on the basis of comparisons with the spectra of the ammonium salt of *O,O′*-ditolyl/dibenzyl/phenyl dithiophosphate [17] and the analogous adducts of cobalt(II) complexes [14]. In IR spectra two medium to strong bands observed at 1068–1047 and 892–853 cm^{-1} are assigned to ν[(P)–O–C] and ν[P–O–(C)] [13, 20], respectively. Peaks at 682–674 and 630–615 cm^{-1} may be assigned to ν(P=S) and ν(P–S) [13, 20]. The ν(Co–S) vibration at 420–410 cm^{-1} indicates complex formation through sulfur in these adducts. Weak to medium bands for ν(Co–N) are observed at 362–356 cm^{-1}. Additional medium intensity bands at 1623–1604 cm^{-1} may be assigned for ν(C–N) of the aromatic ring of the Lewis base confirming their presence in the adducts.

2.2. *Electronic absorption spectra*

Electronic spectra of the 3-picoline adducts were carried out in 3-picoline solution. Peaks corresponding to $^4T_1g(F) \rightarrow {}^4T_1g(P)$, $^4T_1g(F) \rightarrow {}^4A_2g(F)$, and $^4T_1g(F) \rightarrow {}^4T_2g(F)$ were seen in the ranges 505–559, 582–800, and 1187–1205 nm, respectively. Similar electronic transitions have been observed for octahedral $Co\{S_2CN(C_2H_5)_2\}_2(C_5H_5N)_2$ [21] and pyridine adducts of bis(*O,O′*-ditolyl/dibenzyl dithiophosphates)cobalt(II) [14], suggesting an octahedral coordination in these adducts. We have also recorded electronic spectra of these complexes in benzene, CH_2Cl_2, or $CHCl_3$ and found pentacoordinate adducts and free Co(II) dithiophosphate complexes.

2.3. *Magnetic moment measurements*

Octahedral coordination of these adducts is further supported by magnetic moment values. The magnetic moment for adducts is in the range 4.9–5.2 B.M. These μ_{eff} values may arise due to electron pairing in the formation of strong covalent bond involving the use of 3d electrons of Co(II) or spin–spin interaction. The magnetic moment values of these complexes are in the range of the other octahedral cobalt(II) dithiophosphate complexes [14]. The magnetic moment values are slightly higher than the tetrahedral cobalt(II) dithiophosphate complexes. The tetrahedral cobalt(II) complex $Co\{S_2P(OCH_2Ph)_2\}_2$ [11] has magnetic moment of 4.34 B.M.

The ligand is bidentate coordinating *via* four sulfurs and two nitrogens forming a distorted octahedral geometry. Plausible structure is suggested for these newly synthesized complexes in figure 1.

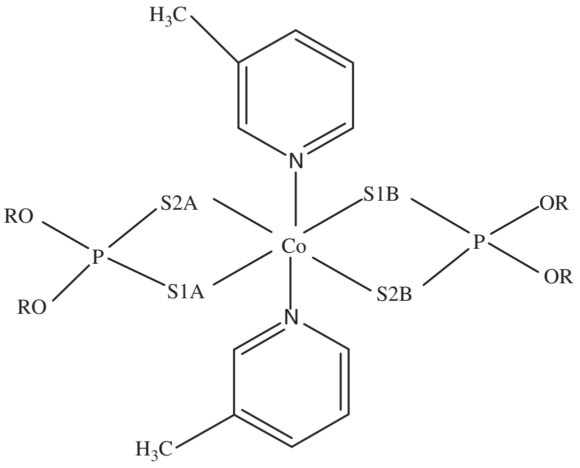

Figure 1. Proposed distorted octahedral geometry (R = *o*-, *m*-, *p*-C_6H_4Me, CH_2Ph, Ph).

2.4. *Molecular structure determination of* $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$

The crystal of $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$ crystallizes as monoclinic in *P121/n1* space group. The two dithiophosphates are symmetrically anisobidentate coordinated with cobalt(II) in the equatorial plane and the two 3-picoline molecules lie in *trans* positions. Complex **3** contains two crystallographically independent molecules but is chemically identical shown in the ORTEP diagram (figure 2) and the immediate environment around cobalt is distorted octahedral, apparent from the deviations of atoms from least square planes CoS_4 and CoN_2. The structure of the adduct is very similar to that of $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(C_5H_5N)_2$, however, the formation of the bis(3-methyl picoline) adduct of $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2$ not only decreases the Co–S and P–S bond distances, but also the bond angles of S–Co–S and S–P–S are somewhat enlarged. The Co–N bond distances in the title complexes are larger than $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(C_5H_5N)_2$, suggesting that the Co–N bond distance varies with the group attached to pyridine.

The average Co–N distance (2.1755(3) Å) is slightly longer than that of $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(C_5H_5N)_2$ (2.162(2) Å) [14] and $Co\{S_2P(OEt)_2\}_2(C_5H_5N)_2$ (2.164(3) Å) [22]. The average Co–S bond distance is 2.52 Å which is similar to the average Co–S distance of $Co\{S_2P(OEt)_2\}_2(C_5H_5N)_2$ (2.515(1) Å) [22] and suggests partial double bond character in the Co–S bond. The average P–S distance of 1.966(11) Å is similar to the average P–S bond distance 1.975(1) Å in $Co\{S_2P(OEt)_2\}_2(C_5H_5N)_2$ and 1.964(3) Å in $Co\{S_2P(OEt)_2\}_2 \cdot C_{24}H_{26}N_4O_2$ [23]. The average P–O distances (1.608(2) Å) are similar to $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(C_5H_5N)_2$ (1.599(2) Å) and $Co\{S_2P(OEt)_2\}_2(C_5H_5N)_2$ (1.593(3) Å).

The S(1A)–Co(1)–S(1B), S(2B)–Co(1)–S(2A), and N(2)–Co(1)–N(1) bond angles are 177.25(3)°, 177.41(4)°, and 177.36(10)°, respectively, slight deviation from 180°. The S(2A)–Co(1)–S(1A) (81.50(3)°), S(2B)–Co(1)–S(1B) (81.55(3)°) bite angles and other inter-ligand angles show the greatest deviation from 90°. The N–Co–S bond angles of 87.27°–92.40° show slight variation from regular octahedral geometry. The two

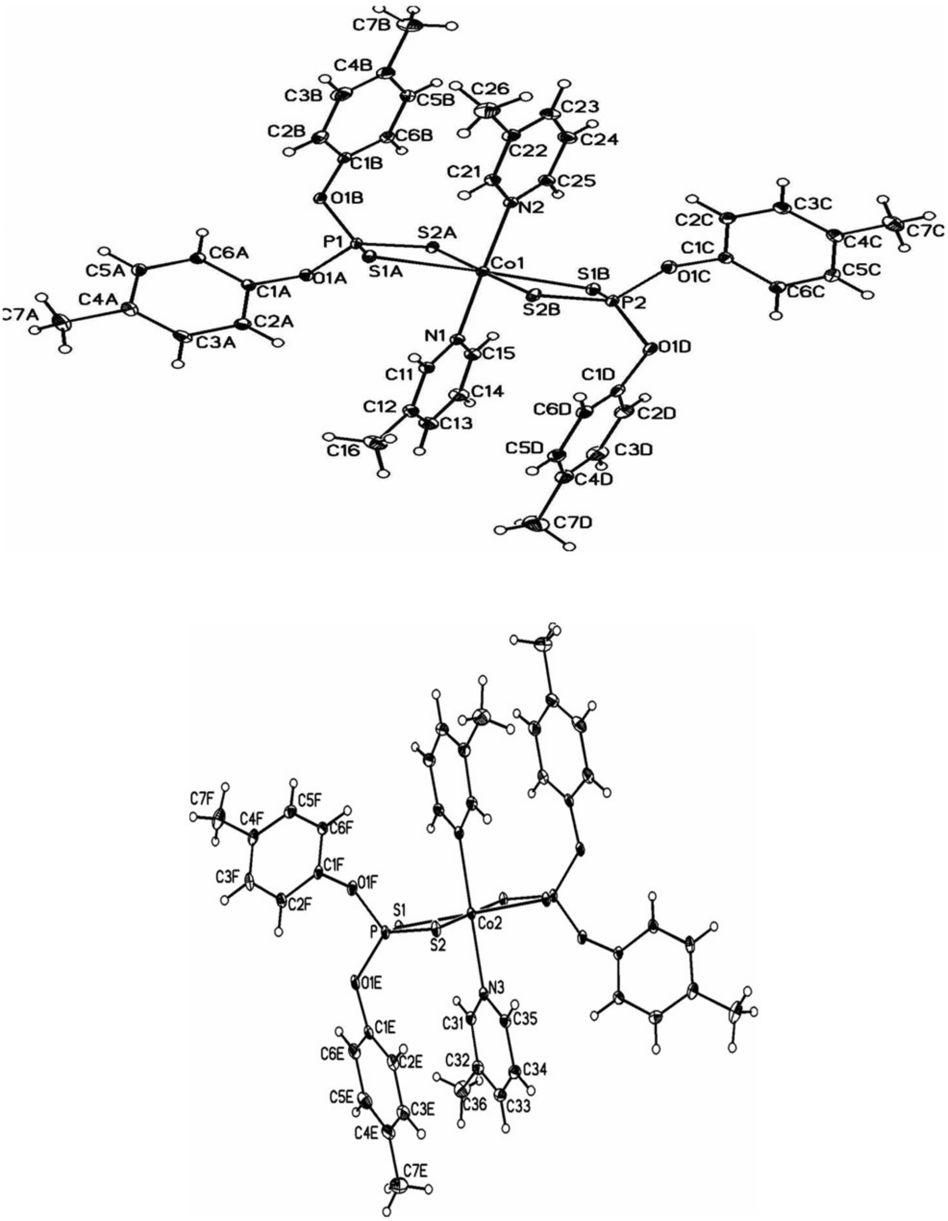

Figure 2. ORTEP plot of two crystallographically independent molecules of $[Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$. The non-hydrogen atoms are drawn with 30% probability ellipsoids.

nitrogens have the distances of 2.1757 Å (for N1) and 2.1721 Å (for N2) from the CoS_4 least square plane, suggesting *trans* 3-picolines.

The adducts of bis(alkylene dithiophosphato)cobalt(II) have distorted trigonal bipyramidal geometry due to steric hindrance of the cyclic alkylene moiety, while the adducts of bis(*O,O′*-dialkyl/diaryl dithiophosphato)cobalt(II) complexes have distorted octahedral geometries.

3. Experimental

All chemicals (Emerk) were used after purification and solvents were dried before use by standard methods. Literature methods were used for the preparation of the *O,O*-ditolyl/dibenzyl/biphenyl dithiophosphoric acids [20]. The ammonium salts of these dithiophosphoric acids were prepared by the reaction of the parent acids with an equimolar amount of ammonia in benzene. Cobalt and sulfur were estimated by pyridine thiocyanate and Messenger's methods, respectively. Elemental analyses (C, H, and N) were carried out on a Vario EL elemental analyzer. Electronic spectra were recorded on a Perkin-Elmer UV-Vis-NIR spectrometer in 3-picoline. IR spectra were recorded on a Perkin-Elmer 983G spectrometer as Nujol mulls between CsI discs from 4000 to 180 cm^{-1}. The magnetic moments of the solid compounds were measured using a Gouy balance at room temperature.

3.1. *Syntheses*

3.1.1. $Co\{S_2P(OC_6H_4Me\text{-}o)_2\}_2(NC_5H_4Me\text{-}3)_2$ (1). $Co\{S_2P(OC_6H_4Me\text{-}o)_2\}_2(NC_5H_4Me\text{-}3)_2$ was synthesized by the *in situ* reaction of an aqueous solution (10 mL) of $CoCl_2{\cdot}6H_2O$ (0.245 g, 1.02 mmol) and 3-picoline (0.192 g, 2.06 mmol), followed by the addition of an aqueous solution (10 mL) of $NH_4S_2P(OC_6H_4Me\text{-}o)_2$ (0.674 g, 2.05 mmol) with stirring. The green adduct was thus extracted in benzene (50 mL), dried under vacuum, and recrystallized by dichloromethane. Yield: 0.770 g (86.5%); Anal. Calcd for $C_{38}H_{42}N_2O_4P_2S_4Co$ (%): C, 54.34; H, 5.04; N, 3.33; S, 14.84; Co, 6.82. Found (%): C, 54.30; H, 5.01; N, 3.29; S, 14.80; Co, 6.79. UV-Vis spectral data [λ_{max}, nm(A); ε ($L\,mol^{-1}\,cm^{-1}$)] in 0.005 $mol\,L^{-1}$ 3-picoline solution 553(57), 582(67), 650(43), 790(29), 1187(43); IR (KBr): 1604s (C–N), 1047s [(P)–O–C], 889m [P–O–(C)], 679s (P=S), 615s (P–S), 410m (Co–S), 362m (Co–N); μ_{eff} 4.9 B.M.

3.1.2. $Co\{S_2P(OC_6H_4Me\text{-}m)_2\}_2(NC_5H_4Me\text{-}3)_2$ (2). The method is the same as described for **1** and the product is isolated as a green crystalline solid. Yield: 1.019 g (87.2%); Anal. Calcd for $C_{38}H_{42}N_2O_4P_2S_4Co$ (%): C, 54.34; H, 5.04; N, 3.33; S, 14.84; Co, 6.82. Found (%): C, 54.28; H, 5.02; N, 3.27; S, 14.81; Co, 6.79. UV-Vis spectral data [λ_{max}, nm(A); ε ($L\,mol^{-1}\,cm^{-1}$)] in 0.006 $mol\,L^{-1}$ 3-picoline solution 556(230), 593(109), 619(56), 800(45), 1205(41); IR (KBr): 1605s (C–N), 1050s [(P)–O–C], 881m [P–O–(C)], 674s (P=S), 622s (P–S), 420m (Co–S), 360m (Co–N); μ_{eff} 5.1 B.M.

3.1.3. $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$ (3). The method is the same as described for **1** and the product is isolated as a green crystalline solid. Yield: 1.096 g (86.3%); Anal. Calcd for $C_{38}H_{42}N_2O_4P_2S_4Co$ (%): C, 54.34; H, 5.04; N, 3.33; S, 14.84; Co, 6.82. Found (%): C, 54.29; H, 5.01; N, 3.31; S, 14.83; Co, 6.80. UV-Vis spectral data [λ_{max}, nm(A); ε ($L\,mol^{-1}\,cm^{-1}$)] in 0.005 $mol\,L^{-1}$ 3-picoline solution 559(203),

Table 1. Crystal data and structure refinement for $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$.

Empirical formula	$C_{40}H_{42}N_2O_4P_2S_4Co$
Formula weight	863.87
Temperature (K)	293(2)
Wavelength (Å)	1.54184
Crystal system	Monoclinic
Space group	*P121/n1*
Unit cell dimensions (Å, °)*a*	20.6331(2)
b	14.1279(2)
c	21.8742(3)
β	97.65(10)
Volume (Å^3), *Z*	6319.63(14), 6
Calculated density (mg m^{-3})	1.362
Absorption coefficient (mm^{-1})	6.098
F(000)	2694
Crystal size (mm^3)	$0.52 \times 0.45 \times 0.34$
θ range for data collection	4.08–77.83
Limiting indices	$-25 \le h \le 24$, $-16 \le k \le 17$, $-27 \le l \le 25$
Reflections collected	31,016
Independent reflections	13,010 [$R(\text{int}) = 0.0525$]
Completeness to $\theta = 67.50°$	99.1%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	1.00000 and 0.28502
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13010/0/727
Goodness-of-fit on F^2	0.926
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0506$, $wR_2 = 0.1145$
R indices (all data)	$R_1 = 0.0868$, $wR_2 = 0.1256$
Largest difference peak and hole (Å^{-3})	0.474 and −0.430

Table 2. Selected bond distances [Å] and angles [°] for $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$.

Co(1)–N(2)	2.174(3)	Co(1)–N(1)	2.177(3)
Co(1)–S(2B)	2.4891(10)	Co(1)–S(2A)	2.5085(9)
Co(1)–S(1A)	2.5322(9)	Co(1)–S(1B)	2.5518(10)
Co(2)–N(3)	2.169(3)	Co(2)–N(3)#1	2.169(3)
Co(2)–S(2)#1	2.4975(8)	Co(2)–S(2)	2.4975(8)
Co(2)–S(1)#1	2.5444(8)	Co(2)–S(1)	2.5444(8)
N(2)–Co(1)–N(1)	177.36(10)	N(2)–Co(1)–S(2B)	88.99(7)
N(1)–Co(1)–S(2B)	92.40(8)	N(2)–Co(1)–S(2A)	89.36(7)
N(1)–Co(1)–S(2A)	89.34(8)	S(2B)–Co(1)–S(2A)	177.25(3)
N(2)–Co(1)–S(1A)	90.72(8)	N(1)–Co(1)–S(1A)	91.37(8)
S(2B)–Co(1)–S(1A)	96.31(3)	S(2A)–Co(1)–S(1A)	81.50(3)
N(2)–Co(1)–S(1B)	90.71(8)	N(1)–Co(1)–S(1B)	87.27(8)
S(2B)–Co(1)–S(1B)	81.55(3)	S(2A)–Co(1)–S(1B)	100.68(3)
S(1A)–Co(1)–S(1B)	177.41(4)	N(3)–Co(2)–N(3)#1	180.0
N(3)–Co(2)–S(2)#1	91.11(7)	N(3)#1–Co(2)–S(2)#1	88.89(7)
N(3)–Co(2)–S(2)	88.89(7)	N(3)#1–Co(2)–S(2)	91.11(7)
S(2)#1–Co(2)–S(2)	180.0	N(3)–Co(2)–S(1)#1	89.41(7)
N(3)#1–Co(2)–S(1)#1	90.59(7)	S(2)#1–Co(2)–S(1)#1	81.65(3)
S(2)–Co(2)–S(1)#1	98.35(3)	N(3)–Co(2)–S(1)	90.59(7)
N(3)#1–Co(2)–S(1)	89.41(7)	S(2)#1–Co(2)–S(1)	98.35(3)
S(2)–Co(2)–S(1)	81.65(3)	S(1)#1–Co(2)–S(1)	180.0

599(98), 669(67), 786(42), 1189(39); IR (KBr): 1610s (C–N), 1057s [(P)–O–C], 892m [P–O–(C)], 674s (P=S), 630s (P–S), 415m (Co–S), 356m (Co–N); μ_{eff} 5.2 B.M.

3.1.4. Co{$S_2P(OCH_2Ph)_2$}$_2$(NC_5H_4Me-3)$_2$ (4).

The method is the same as described for **1** and the product is isolated as a green crystalline solid. Yield: 0.987 g (88.5%); Anal. Calcd for $C_{38}H_{42}N_2O_4P_2S_4Co$ (%): C, 54.34; H, 5.04; N, 3.33; S, 14.84; Co, 6.82. Found (%): C, 54.36; H, 5.08; N, 3.28; S, 14.82; Co, 6.81. UV-Vis spectral data [λ_{max}, nm(A); ε (L mol^{-1} cm^{-1})] in 0.004 mol L^{-1} 3-picoline solution 545(196), 608(87), 660(74), 792(59), 1200(78); IR (KBr): 1616s (C–N), 1049s [(P)–O–C], 890m [P–O–(C)], 676s (P=S), 621s (P–S), 416m (Co–S), 361m (Co–N); μ_{eff} 5.1 B.M.

3.1.5. Co{$S_2P(OPh)_2$}$_2$(NC_5H_4Me-3)$_2$ (5).

The method is the same as described for **1** and the product is isolated as a green crystalline solid. Yield: 1.010 g (89.2%); Anal. Calcd for $C_{32}H_{34}N_2O_4P_2S_4Co$ (%): C, 50.59; H, 4.5; N, 3.69; S, 16.88; Co, 7.76. Found (%): C, 50.53; H, 4.46; N, 3.66; S, 16.87; Co, 7.75. UV-Vis spectral data [λ_{max}, nm(A); ε (L mol^{-1} cm^{-1})] in 0.005 mol L^{-1} 3-picoline solution 505(160), 610(78), 674(65), 764(100), 1197(43); IR (KBr): 1623s (C–N), 1068s [(P)–O–C], 853m [P–O–(C)], 682s (P=S), 618s (P–S), 416m (Co–S), 357m (Co–N); μ_{eff} 5.0 B.M.

3.2. *Crystallography*

A green crystal of Co{$S_2P(OC_6H_4Me$-*p*)$_2$}$_2$(NC_5H_4Me-3)$_2$ was mounted on a glass fiber. Crystal data were collected using Cu-Kα radiation (graphite monochromated, $\lambda = 1.54184$ Å) and data collected on a Bruker-Nonius Kappa CCD area detector diffractometer. Cell refinements [24] gave cell constants corresponding to a monoclinic cell, whose dimensions are given in table 1 along with other experimental parameters. An absorption correction was applied [25]. The structures were solved by direct methods [26] and refined using the WINGX version [27] of SHELX-97 [28]. All non-hydrogen atoms were treated anisotropically. Hydrogens were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atoms to which they were attached. Selected distances and angles are given in table 2 and the molecules are displayed as ORTEP diagrams in figure 2.

4. Conclusion

We have shown a method to synthesize 3-picoline adducts of bis(*O*,*O′*-ditolyl/dibenzyl/diphenyl dithiophosphato)cobalt(II) complexes of the type, Co{$S_2P(OR)_2$}$_2$(NC_5H_4Me-3)$_2$ (R = *o*-, *m*-, *p*-C_6H_4Me, CH_2Ph, Ph). The IR and UV-Vis spectra and magnetic moments of these compounds are consistent with the proposed distorted octahedral structures. The molecular structure of Co{$S_2P(OC_6H_4Me$-*p*)$_2$}$_2$(NC_5H_4Me-3)$_2$ was determined to have a distorted octahedron around cobalt.

Supplementary material

CCDC 772115 contains the supplementary crystallographic data for $Co\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(NC_5H_4Me\text{-}3)_2$. This can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 2EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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References

[1] T.J. Moon. *J. Korean Chem. Soc.*, **23**, 52 (1979).
[2] F.A. Nasirov. *Iran. Polym. J.*, **12**, 217 (2003).
[3] F.A. Nasirov, F.M. Novruzova, S.S. Salmanov, A.H. Azizov, N.F. Janibayov. *Iran. Polym. J.*, **18**, 521 (2003).
[4] V.F. Toropova, R.A. Cherkasova, N.I. Savel'eva, E.J. Petrova. *Zh. Obshch. Khim.*, **44**, 531 (1974).
[5] V.V. Ovchinnikov, V.I. Galkin, A.R. Garifzyanov, V.F. Toropova, R.A. Cherkasov. *Zh. Obshch. Khim.*, **55**, 357 (1985).
[6] J.D. Lebedda, R.A. Palmer. *Inorg. Chem.*, **10**, 2704 (1971).
[7] U.N. Tripathi, M.S. Singh. *J. Indian Chem. Soc.*, **76**, 360 (1999).
[8] R.G. Cavell, E.D. Day, W. Byars, P.M. Wathins. *Inorg. Chem.*, **11**, 1759 (1972).
[9] B.F. Hoskins, R. Robson, G.A. Williams. *Inorg. Chim. Acta*, **16**, 121 (1976).
[10] J.F. McConnell, A. Schwartz. *Acta Crystallogr.*, **28**, 1546 (1972).
[11] T.V. Evgen'evich. *Mater Vses Nauchn Stud Konf: Khim*, **13**, 12 (1975).
[12] R. Micu-Semeniuc, L. Dumitrescu-Silaghi, I. Haiduc. *Inorg. Chim. Acta*, **33**, 281 (1979).
[13] Y. Yamada, M. Shimoi, A. Ouchi. *Chem. Lett.*, 867 (1978).
[14] S.C. Bajia, J.E. Drake, M.E. Light, M. Nirwan, S.K. Pandey, R. Ratnani. *Polyhedron*, **28**, 85 (2009).
[15] I.M. Oglezneva, V.N. Kirichenko. *Zh. Strukt. Khim.*, **25**, 164 (1984).
[16] M. Shimoi, A. Ouchi, T. Uehiro, Y. Yoshino, S. Sato, Y. Saito. *Bull. Chem. Soc. Jpn.*, **55**, 2371 (1982).
[17] X. Zheng, L. Jianhua, Y. Yunpeng, X. Jie, Y. Xiaozeng, L. Shixiong, L. Chichang. *Huaxue Xuebao*, **47**, 623 (1989).
[18] M.Q. He, X.P. Shen, W.L. Zhang, Y.L. Wu, X.N. Cheng, Y.P. Yu. *Huaxue Xuebao*, **18**, 739 (2002).
[19] S. Bajia, R.J. Butcher, J.E. Drake, R. Ratnani. *Polyhedron*, **28**, 1556 (2009).
[20] J.E. Drake, C.L.B. Macdonald, A. Kumar, S.K. Panday, R. Ratnani. *J. Chem. Crystallogr.*, **35**, 447 (2005).
[21] K.S. Siddiqi, S.A.A. Nami, Lutfullah Y. Chebude. *Synth. React. Inorg. Met-Org. Nano-Met. Chem.*, **35**, 445 (2005).
[22] Z. Xhu, J.H. Lin, Y.P. Yu, J. Xu, X.Z. You, S.X. Liu, C.C. Lin. *Huaxue Xuebao*, **7**, 623 (1989).
[23] G.A. Williams, R. Robson. *Aust. J. Chem.*, **34**, 65 (1981).
[24] A.J.M. Duisenberg. *J. Appl. Crystallogr.*, **25**, 92 (1992).
[25] G.M. Sheldrick. *SADABS V2.10*, University of Gottingen, Gottingen, Germany (2003).
[26] G.M. Sheldrick. *Acta Crystallogr.*, **46**, 467 (1990).
[27] L.J. Farrugia. *J. Appl. Crystallogr.*, **32**, 837 (1999).
[28] G.M. Sheldrick. *SHELXL97, Structure Determination Software*, University of Gottingen, Gottingen, Germany (1997).