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Four novel sulfur-rich complexes: syntheses, crystal structures of three nickel(II) and one cobalt(II) complex with derivatives of Lawesson's Reagent ☆

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Abstract

The reaction of 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's Reagent, LR) with $NiCl_2$ or $Co(CH_3COO)_2$ in methanol or ethanol gives novel sulfur-rich complexes: $C_{16}H_{20}NiO_4P_2S_4$ (**1**), $C_{18}H_{24}NiO_4P_2S_4$ (**2**) and $C_{24}H_{30}CoO_6P_3S_6$ (**4**). With the presence of ethylenediamine under the same conditions, complex $C_{24}H_{48}N_6NiO_4P_2S_4$ (**3**) is also obtained. These four novel sulfur-rich complexes were characterized by IR and X-ray crystallography, which indicate that the solvent can influence the crystal structure of complexes in the reaction between LR and metal.

Keywords: Lawesson's Reagent; Thiophosphoryl compound; Sulfur-rich complex; Nickel(II) complex; Cobalt(II) complex

1. Introduction

There is much literature that reports that 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's Reagent, LR, see Scheme 1) is a most effective thiation reagent for ketones, carboxamides, esters, *S*-substituted thioesters and a variety of other compounds [1–4]. LR can also participate in the preparation of many thiophosphoryl complexes [5,6]. It has been reported by Shabana and Atrees [7] and Fahmy [8] that thiophosphoryl compounds are of potential interest as fungicides, insecticide and herbicides. In order to study the influence of the thiophosphoryl metal on their biological activity, research of the syntheses and crystal structures of these thiophosphoryl metal compounds has an important role.

It has been reported that the P–S bonds in LR can easily be cleaved to offer $MeOC_6H_4PS_2$ as a ligand [9]. We found that LR can decompose into an alcohol derivative when heated in alcohol solvent (see Scheme 2).

Although a great deal of work has been reported [10–12] on thiophosphoryl compounds, these four complexes have not been reported before. We studied the syntheses and crystal structures of some metal complexes with $MeOC_6H_4P(OR)S_2$ ($R = CH_3-$ or C_2H_5-) using the direct reaction of LR with transition metal salts. In this paper, the syntheses and crystal structures of three nickel(II) and one cobalt(II) complex are reported.

2. Experimental

2.1. Materials and physical measurements

All chemicals except Lawesson's Reagent were of reagent analytical grade, purchased from Zhengzhou

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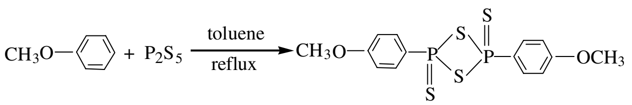
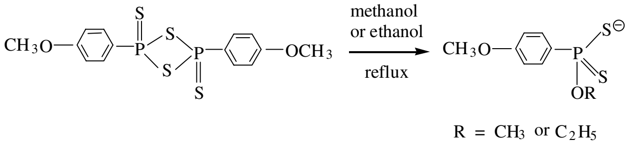


Scheme 1. Lawesson Reagent.



Scheme 2. The thermal decomposition reaction of Lawesson's Reagent in alcohol solvent.

Chemical Reagent Company and were used without any purification. Lawesson's Reagent ($R = p\text{-MeOC}_6H_4$) was prepared as described in the literature [13]. The single crystal structures were measured on a Rigaku-Raxis-IV X-ray diffractometer and IR spectra were recorded on a FTS-40 infrared spectrophotometer as KBr pellets in the range 4000–400 cm^{-1}.

2.2. Preparation of complexes **1**, **2**, **3** and **4**

Complex 1. 5 ml of 0.02 M solution of LR in methanol and 5 ml of 0.02 M solution of $NiCl_2$ in methanol were put into sealed vials, respectively, which were connected via a thin tube full of anhydrous ethanol. Purple crystals of complex **1** suitable for X-ray analysis were obtained in about three days.

Complex 2. With the same method mentioned above, purple crystals of complex **2** suitable for X-ray analysis were got using the mixed solution of ethanol and DMF (1:1, v/v).

Complex 3. 3.0 ml (0.04 mol) of ethylenediamine and 8.10 g (0.02 mol) of LR were refluxed in 180 ml anhydrous toluene at 110 °C with stirring for about 6 h. After cooling to room temperature, insoluble materials were filtered off. Then the reaction mixture was concentrated to about 20 ml with a vacuum rotary evaporator. This 20 ml oil liquid was diluted with 80 ml methanol, and 5 ml of the diluted solution and 5ml methanol solution of $NiCl_2$ (0.2 mmol) were mixed and run into a small vial and allowed to evaporate slowly at room temperature. Filtered, washed with anhydrous ethanol and dried naturally, pink crystals of **3** suitable for single-crystal X-ray diffraction analyses were obtained in about two weeks.

Complex 4. Complex **4** can be obtained by the method used in the preparation of complex **1**. 5 ml of 0.02 M solution of LR in methanol and 5 ml of 0.02 M solution of $Co(CH_3COO)_2 \cdot 4H_2O$ in methanol were put into sealed vials, respectively, which were connected via a thin tube full of anhydrous ethanol. Red crystals of **4** suitable for X-ray analysis were obtained in about three days.

2.3. X-ray crystallography

Intensity data of these complexes were measured with a Rigaku-Raxis-IV X-ray diffractometer using mono-

Table 1
Crystallographic data and structure refinement for complexes **1**, **2**, **3** and **4**

	Complex **1**	Complex **2**	Complex **3**	Complex **4**
Formula	$C_{16}H_{20}NiO_4P_2S_4$	$C_{18}H_{24}NiO_4P_2S_4$	$C_{24}H_{48}N_6NiO_4P_2S_4$	$C_{24}H_{30}CoO_6P_3S_6$
T (K)	291(2)	291(2)	291(2)	291(2)
Molecular weight	525.21	553.26	733.57	758.68
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	11.974(2) A	6.5023(13)	15.364(3)	9.0075(18)
b (Å)	6.6343(13) A	7.6448(15)	18.929(4)	16.076(3)
c (Å)	14.750(3) A	13.109(3)	12.459(3)	23.034(5)
α (°)	90	99.37(3)	90	90
β (°)	109.69(3)	99.72(3)	94.76(3)	98.11(3)
γ (°)	90	104.09(3)	90	90
V (Å^3)	1103.3(4)	608.6(2)	3610.8(13)	3302.1(11)
D_{calc} (Mg m^{-3})	1.581	1.509	1.349	1.526
Z	2	1	4	4
Absorption coefficient (mm^{-1})	1.422	1.293	0.894	1.081
Reflections collected/unique (R_{int})	3234/1958 (0.0697)	1598/1598 (0.0000)	7464/4408 (0.0455)	8216/4758 (0.0591)
Data/restraints/parameters	1958/0/125	1598/8/134	4408/0/419	4758/0/362
R^a	0.0417	0.0737	0.0382	0.0454
$R_w{}^b$	0.0867	0.2060	0.0796	0.1133
Goodness-of-fit on F^2	0.970	1.122	0.897	0.987
$\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ (e Å^{-3})	0.310 and −0.336	1.097 and −0.696	0.372 and −0.215	0.423 and −0.482

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $R_w = [\sum(||F_o| - |F_c||)^2 / \sum w|F_o|^2]^{1/2}$.

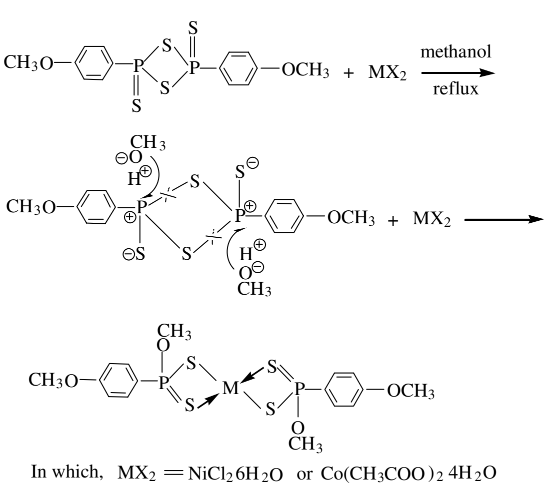
chromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Raw data were corrected and the structures were solved using the SHELXL-97 program. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. The full-matrix least-squares calculation on F^2 was applied on the final refinement. Details of the crystal structure determination are summarized in Table 1. Full atomic data are available as a file in CIF format.

The IR spectra of the four complexes contain the expected bands due to the C_6H_4OMe groups. LR has two bands at 1267(s) and 1293(m) cm^{-1} due to ν_{as}(C–O–C) and a band at 2837(w) cm^{-1} of $\nu_s(CH_3)$. All these bands can be observed in complexes **1**–**4**. In the IR spectra of complex **1**, there are bands present at 1004(s), 1010(s), 1025(m) 829(w), 792(s), 666(m) and 644(m) cm^{-1} for ν_s(P–S). In that of complex **4**, the bands at 1025(m), 789(s) and 663(m) are for ν_s(P–S). All these are consistent with the literature [12]. As far as the IR spectra of the complex **3** is concerned, the bands at 3280(s) cm^{-1} for $\nu_{as}(NH_2)$, 2975(w) cm^{-1} for $\nu_{as}(CH_2)$, and 1028(vs) cm^{-1} for ν_s(CN) are also consistent with the literature [14] (s, strong; m, medium; w, weak; vs, very strong).

3. Results and discussion

3.1. The possible reaction mechanism of LR with transition metals

When Lawesson's Reagent and transition metals react in alcohol solvent the four above-mentioned complexes were obtained. The possible reaction mechanism, as shown in Scheme 3, may have one self-coordinating catalyst course. The sulfur atoms of the LR molecule have a strong coordinating tendency with the metal ion and the P–S bond of LR may easily be cleaved [9]. When Lawesson's Reagent was heated in alcohol solvent with transition metals, the fragment $CH_3OC_6H_4PS_2$, cleaved from LR, was produced and some alcohol molecules (such as methanol) were deprotonated in order to keep the phosphorus atoms with a five valence state. Finally, the fragments $CH_3OC_6H_4PS_2$ connect with a deprotonated alcohol molecule and coordinate to the metal ion. Therefore, the four title complexes (as shown in Scheme 3) are formed.



Scheme 3. The possible reaction mechanism of LR with transition metals.

3.2. The crystal structure description of complexes **1**, **2**, **3** and **4**

Crystallographic data and structure refinement for complexes **1**–**4** are given in Table 1. For complex **1**, it can be seen from Fig. 1 that the structural unit contains a crystallographic center of symmetry at the center of the four-member rings, and is therefore planar. Four sulfur atoms from two $MeOC_6H_4P(OCH_3)S_2$ ligands describe a parallelogram environment around the nickel atom, as is shown in these angles: S2AA–Ni1A–S2A = 180°, S1A–Ni1A–S1AA = 180° and S2AA–Ni1AA–S1A = 91.25°. Selected bond distances and angles for complex **1** are shown in Table 2. The two benzene rings of a certain crystal unit are parallel. The triangle P1A–S1A–S2A and another P1AA–S1AA–S2AA in the same unit lie *trans*-parallel along the central four-member ring S1A–S2A–S2AA–S1AA plane, and the dihedral angle is 19.2°.

From Figs. 1 and 2, it can be found that the molecular structure of complex **2** is similar to that of complex **1**. The only difference lies in the fact that the OCH_3 in complex **1** is replaced by OC_2H_5 in complex **2**. The nickel–sulfur bond lengths in complex **2** {2.2257(17) Å for Ni1A–S1AA and Ni1A–S1A; 2.2237(17) Å for Ni1A–S2AA and Ni1A–S2A} are a little shorter than those of complex **1** {2.2307(13) Å for Ni1A–S2AA and Ni1A–S2A; 2.2426(13) Å for Ni1A–S1AA and Ni1A–S1A}. Selected bond distances and angles for complex **2** are shown in Table 3.

As for complex **3**, it is in fact the complex $Ni(II)(en)_3^{2+}$ (en = ethylenediamine). The $MeOC_6H_4P(C_2H_5O)S_2$ can be seen as a substituted thiophosphate group which exists in the crystal structure as an electron-balancing anion. It can be seen from Fig. 3 that for every nickel(II), such as Ni1, three ethylenediamines offer four nitrogen atoms N1, N2, N4 and N5, existing in the equatorial geometry and forming a parallelogram, with the other two nitrogen atoms N3 and N6 from two ethylenediamines occupying the axial sites. So the Ni(II) ion is six-coordinated, in the center of a distorted

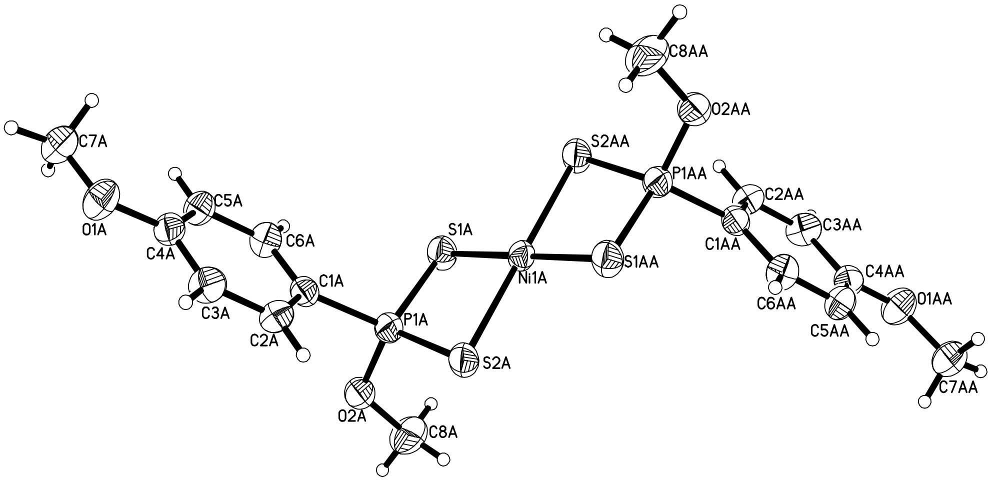


Fig. 1. The crystal structural unit of complex **1**.

Table 2
Selected bond distances (Å) and angles (°) for complex **1**

Ni1A–S2AA	2.2307(13)	S1A–Ni1A–P1AA	134.99(5)
Ni1A–S2A	2.2307(13)	S1AA–Ni1A–P1AA	45.01(5)
Ni1A–S1A	2.2426(13)	S2AA–Ni1A–P1A	135.00(4)
Ni1A–S1AA	2.2426(13)	S2A–Ni1A–P1A	45.00(4)
Ni1A–P1AA	2.8098(15)	S1A–Ni1A–P1A	45.01(5)
Ni1A–P1A	2.8098(15)	S1AA–Ni1A–P1A	134.99(5)
		P1AA–Ni1A–P1A	180.00(7)
S2AA–Ni1A–S2A	180.00(10)	S1A–Ni1A–S1AA	180.00(5)
S2AA–Ni1A–S1A	91.25(5)	S2AA–Ni1A–P1AA	45.00(4)
S2A–Ni1A–S1A	88.75(5)	S2A–Ni1A–P1AA	135.00(4)
S2AA–Ni1A–S1AA	88.75(5)		

Symmetry transformations used to generate equivalent atoms: #1, $-x, -y, -z$.

Table 3
Selected bond distances (Å) and angles (°) for complex **2**

NiA–S1AA	2.2257(17)	S1A–NiA–P1AA	135.63(6)
NiA–S1A	2.2257(17)	S2A–NiA–P1AA	135.18(6)
NiA–S2A	2.2273(17)	S2AA–NiA–P1AA	44.82(6)
NiA–S2AA	2.2273(17)	S2A–NiA(1)-P1A	180.00(5)
NiA–P1A	2.8311(19)	S1AA–NiA–S2AA	88.04(7)
NiA–P1AA	2.8311(19)	S1A–NiA–S2AA	91.96(7)
		S2A–NiA–S2AA	180.00(11)
S1AA–NiA–S1A	180.00(13)	S1AA–NiA–P1A	135.63(6)
S1AA–NiA–S2A	91.96(7)	S1A–NiA–P1A	44.37(6)
S1A–NiA–S2A	88.04(7)		

Symmetry transformations used to generate equivalent atoms: #1, $-x, -y, -z$.

octahedron. The selected bond distances and angles for complex **3** are shown in Table 4a. It is evident that in the crystal structure of complex **3** there exist numerous N–H–S hydrogen bonds which stabilize the crystal structure. The hydrogen bonds are stated in Table 4b.

For complex **4**, it can be seen from Fig. 4 that for every Co(II), such as Co1, three $MeOC_6H_4P(CH_3O)S_2$

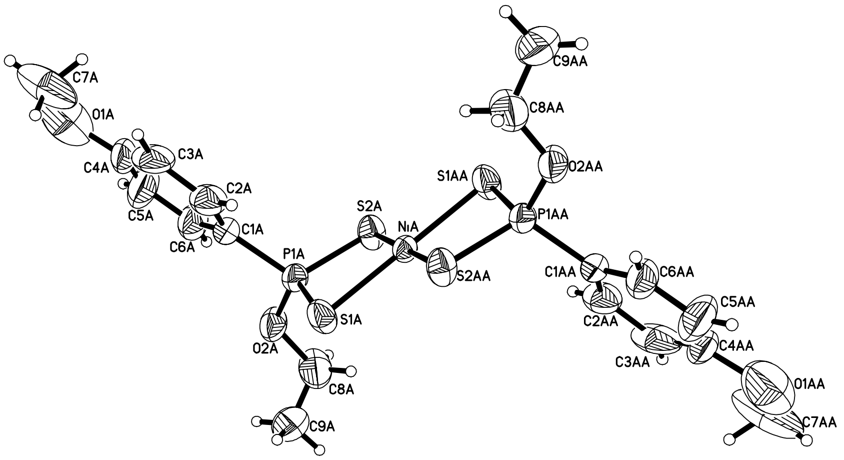


Fig. 2. The crystal structural unit of complex **2**.

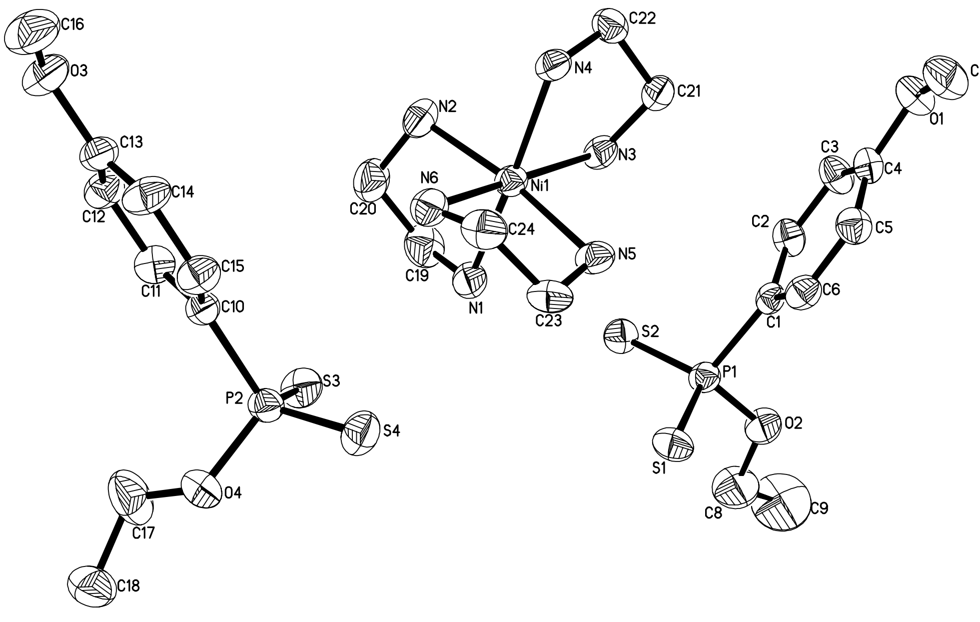


Fig. 3. The crystal structural unit of complex **3**.

Table 4a
Selected bond distances (Å) and angles (°) for complex **3**

Ni1–N3	2.113(4)	N1–Ni1–N6	94.24(19)
Ni1–N4	2.115(4)	N3–Ni1–N5	92.28(19)
Ni1–N1	2.122(4)	N4–Ni1–N5	92.7(2)
Ni1–N6	2.136(4)	N1–Ni1–N5	94.50(19)
Ni1–N5	2.145(4)	N6–Ni1–N5	80.92(19)
Ni1–N2	2.150(5)	N3–Ni1–N2	93.9(2)
		N4–Ni1–N2	91.8(2)
N3–Ni1–N4	81.51(17)	N1–Ni1–N2	81.54(19)
N3–Ni1–N1	93.04(18)	N6–Ni1–N2	93.3(2)
N4–Ni1–N1	171.1(2)	N5–Ni1–N2	172.8(2)
N3–Ni1–N6	170.4(2)		

groups offer four sulfur atoms S1, S4, S3 and S6, existing in the equatorial geometry and forming a parallelogram, with the other two sulfur atoms S2 and S5 occupying the axial sites. So the Co(II) ion is six-coordinated, in the center of a distorted octahedron. Selected bond distances and angles are shown in Table 5.

3.3. Discussion

Through the research of the syntheses and crystal structures of these four novel sulfur-rich complexes, we found that the product can be influenced by the sort of solvent used in the preparation of such complexes of LR derivatives. For example, when the solvent is methanol or ethanol, the deprotonated methanol or ethanol can attack the phosphorus atom of LR, and the product cleaved from LR containing methoxy or ethoxy was produced. It is suggested that when LR is heated in a solvent containing an active proton, solvation decomposition can easily take place.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic

Table 4b
Hydrogen-bond distances (Å) and angles (°) for complex **3**

D–H	d(D–H)	d(H···A)	∠DHA	d(D···A)	Assignment
N5–H5F	0.797	2.862	163.69	3.635	S1
N4–H4F	0.900	2.610	154.76	3.446	S4 $[x, -y+3/2, z+1/2]$
N1–H1F	0.954	2.581	153.18	3.459	S2
N3–H3E	0.864	2.908	140.57	3.617	S2
N1–H1E	1.020	2.586	153.08	3.525	S3
N6–H6F	0.923	2.907	171.65	3.823	S3
N2–H2E	0.953				
N6–H6E	0.936	2.523	157.24	3.405	S3 $[x, -y+3/2, z+1/2]$
N4–H4E	0.864	2.654	147.61	3.415	S1 $[x, -y+3/2, z+1/2]$
N5–H5E	0.884	2.692	148.20	3.475	S1 $[x, -y+3/2, z+1/2]$
N3–H3F	0.994	2.628	148.74	3.516	S4 $[-x+1, y+1/2, -z+3/2]$
N2–H1F	0.915	2.732	147.50	3.538	S4 $[-x+1, y+1/2, -z+3/2]$

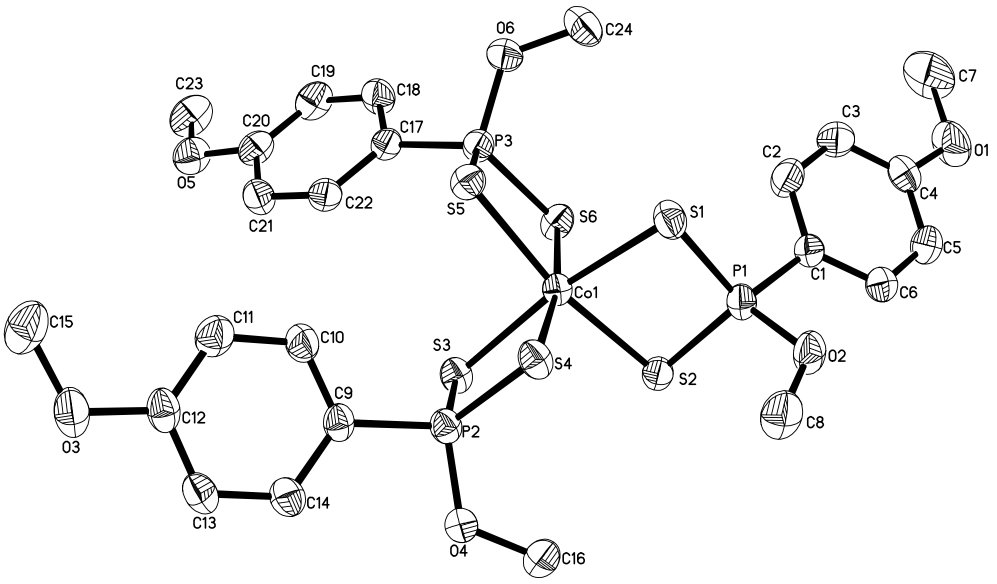


Fig. 4. The crystal structural unit of the complex **4**.

Table 5
Selected bond distances (Å) and angles (°) for complex **4**

Bond lengths					
Co1–S1	2.3029(17)	S1–Co1–S4	88.21(6)	S1–Co1–S5	89.42(6)
Co1–S4	2.3042(16)	S1–Co1–S6	97.43(6)	S4–Co1–S5	89.76(6)
Co1–S6	2.3190(16)	S4–Co1–S6	171.50(6)	S6–Co1–S5	83.97(5)
Co1–S3	2.3211(17)	S1–Co1–S3	169.98(6)	S3–Co1–S5	96.62(6)
Co1–S5	2.3292(15)	S4–Co1–S3	83.85(6)	S1–Co1–S2	84.05(6)
Co1–S2	2.3362(15)	S6–Co1–S3	91.16(6)	S4–Co1–S2	98.31(6)
Bond angles					
S3–Co1–S2	91.06(6)	S5–Co1–S2	169.42(6)	S6–Co1–S2	88.63(5)

Data Center, CCDC Nos. 222648, 222650 222647 and 228385 for complexes **1**, **2**, **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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