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Preparations of sulfido-tricobalt clusters containing pyridyl type ligands: insertion of carbon monoxide into cobalt–carbon bond

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Abstract

The reaction of 2-mercaptopyridine with 1.5 M equivalent of $Co_2(CO)_8$ in THF at 25 °C for 1 h gave a sulfido-tricobalt cluster $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-C,N–}C_5H_4N)$ (**1**). Further reaction of **1** with diphenyl-2-pyridylphosphine (PPh_2py) under mild reaction condition afforded a PPh_2py bridged complex $(\mu_3\text{-S})Co_3(CO)_5[(\mu\text{-C(=O),N–}C_5H_4N(C{=}O))(\mu\text{-P,N–}PPh_2py)]$ (**3**). The X-ray structure analysis of **3** revealed that a carbonylation process occurred at the Co–C(pyridyl) bond of **1**. Carbonylation of **1** at the same position also took place under 1 atm of carbon monoxide at room temperature and formed $(\mu_3\text{-S})Co_3(CO)_7[(\mu\text{-C(=O),N–}C_5H_4N(C{=}O))]$ (**4**). Similar results were obtained in the reaction of 2-quinolinethiol with 1.5 M equivalent of $Co_2(CO)_8$. A sulfido-tricobalt cluster $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-C,N–}C_9H_6N)$ (**5**) and tris-quinolinethiolate chelated cobalt complex $[Co(\mu\text{-S,N–}SC_9H_6N)_3]$ (**6**) were obtained. In contrast to **1**, carbonylation did not occur in **5** at 1 atm of carbon monoxide even at 60 °C for prolonged reaction hours. However, treatment of **5** with PPh_2py yielded a PPh_2py coordinated $(\mu_3\text{-S})Co_3(CO)_6[(\mu\text{-C,N–}C_9H_6N)(PPh_2py)]$ (**7**) as the major product, which is accompanied with a small amount of PPh_2py bridged $(\mu_3\text{-S})Co_3(CO)_5[(\mu\text{-C(=O),N–}C_9H_6N(C{=}O))(\mu\text{-P,N–}PPh_2py)]$ (**8**). Carbonylation did occur at the Co–C(quinolinyl) bond of **5**, even though less efficient than that of **1**, while reacted with a PPh_2py ligand. The same reaction pattern was observed for the reaction of 2-mercapto-nicotinic acid methyl ester with 1.5 M equivalent of $Co_2(CO)_8$; a sulfido-tricobalt cluster $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-C,N–}C_5H_3NC(=O)OCH_3)$ (**9**) was obtained as the major product. The crystal structures of all eight new complexes have been determined. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sulfido-tricobalt clusters; Mercaptopyridine; CO insertion; Diphenyl-2-pyridylphosphine

1. Introduction

It has always been a difficult task to search for a systematic route in stabilizing the paramagnetic sulfido-tricobalt carbonyl $(\mu_3\text{-S})Co_3(CO)_9$ since its first preparation and characterization [1]. One of the most frequently employed methods is to prepare a diamagnetic sulfido-tricobalt clusters with the general formula $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-X})$ (X: a bridging, three-electron donating ligand) [2]. Apparently, most of the sulfido-tricobalt carbonyl clusters are stabilized by the assistance of those three-electron donating, bridging ligands. The pyridyl derivatives are chosen as prime candidates due to their unequivocal bonding capacities as a three-electron donating, bridging ligands. Since most of the sulfido-tricobalt clusters were obtained from the reaction of $Co_2(CO)_8$ with sulfur-containing compounds, it is natural for us to pick up mercaptopyridines as preferred reactants. In this paper, we report a general route of preparing pyridyl derivatives bridging sulfido-tricobalt carbonyl clusters from the reactions of various mercaptopyridines with $Co_2(CO)_8$. We will also describe an uncommon carbonylation that took place at the Co–C(pyridyl) bond of the sulfido-tricobalt carbonyl cluster while reacting with external ligands such as CO or diphenyl-2-pyridylphosphine (PPh_2py).

2. Results and discussion

2.1. Reaction of $Co_2(CO)_8$ with 2-mercaptopyridine

Reaction of $Co_2(CO)_8$ with 2-mercaptopyridine in THF at 25 °C for 1 h gave two compounds: a new sulfido-tricobalt cluster $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-C,N–}C_5H_4N)$

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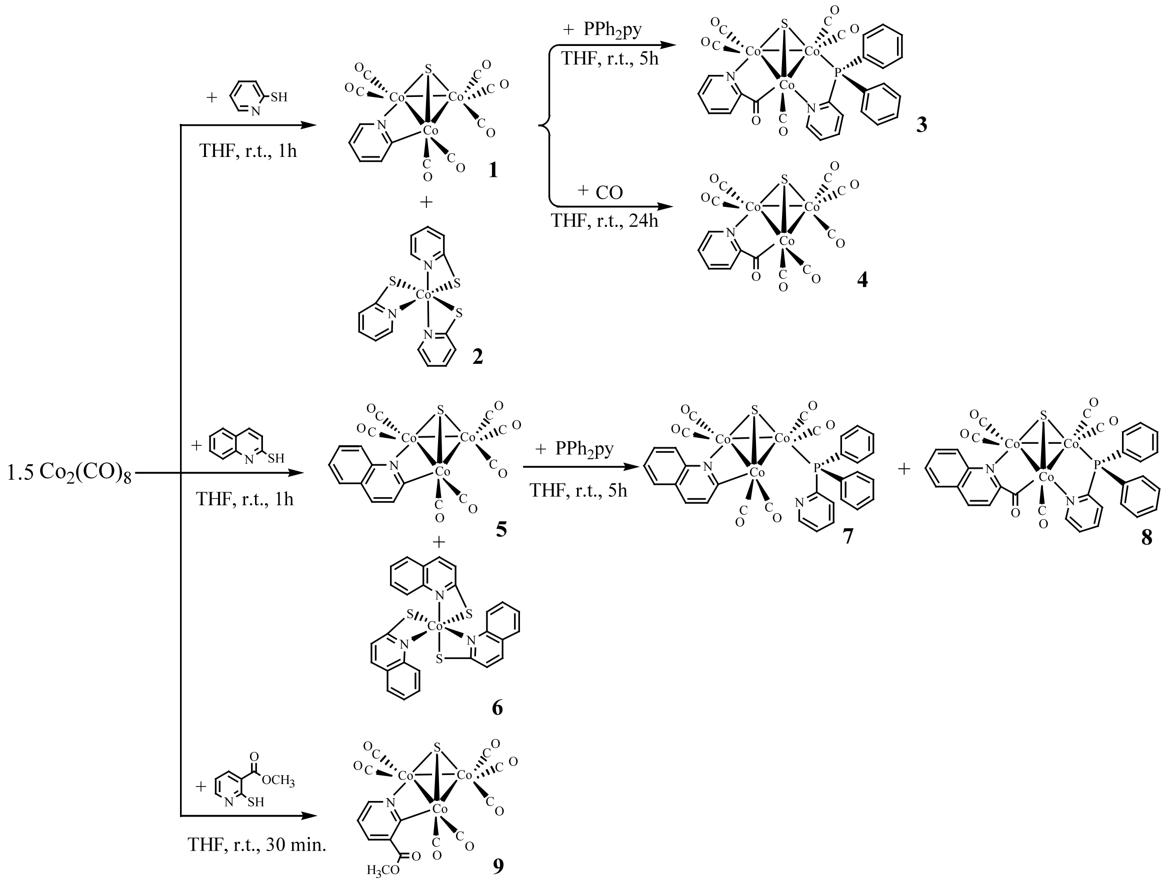

Scheme 1.

(**1**) and an known compound, *mer*-tris(pyridine-2-thiolato)cobalt(III) (**2**) [3] (Scheme 1).

Compound **1** was characterized by spectroscopic means as well as by X-ray crystal structure determination (Table 1). The molecular structure of **1** shows that it is a sulfido-tricobalt carbonyl unit $(\mu_3\text{-S})Co_3(CO)_7$ being bridged by a pyridyl ligand (Fig. 1) [4]. Obviously, the C–S and S–H bonds of the 2-mercaptopyridine were ruptured during the formation of **1**. A direct Co–C covalent bond and a pyridyl coordinated Co–N bond were formed through the pyridyl ligand. Four atoms, Co(1), Co(2), C(1), N(1), are almost coplanar. The bridged pyridyl ligand is located at the equatorial rather than the axial position of the sulfido-tricobalt cluster. The pyridyl ligand has to be close to the μ_3-S in sulfido-tricobalt cluster, which is at equatorial position, presumably due to the breaking of C–S bond of $S\text{–}C_5H_4N$ during the formation of cluster. It also shows that the pyridyl ligand bridged Co(1)–Co(2) bond length is the shortest among all three cobalt–cobalt bonds. The lengths of three Co–S bonds are almost identical (Table 2). The capped sulfur atom donates four electrons in cluster electron count [5].

Further reaction of **1** with PPh_2py in THF at 25 °C for 5 h gave a PPh_2py bridged complex $(\mu_3\text{-S})Co_3(CO)_5$-$[(\mu\text{-}C(=O),N\text{–}C_5H_4N(C=O))(\mu\text{-}P,N\text{–}PPh_2py)]$ (**3**) in 67%. Crystal structure of **3** discloses that a CO insertion took place at the Co–C(pyridyl) bond of **1** (Fig. 1). Interestingly, the carbonylation took place at room temperature without extra CO pressure [6]. The phosphorus and nitrogen atom of the PPh_2py ligand coordinate to the Co(1) and Co(2), respectively. The bridged PPh_2py ligand is also located at the equatorial position of the sulfido-tricobalt cluster. It is believed that the attack of PPh_2py ligand towards **1** comes from the top of the sulfido-tricobalt cluster in order to prevents severe steric hindrance. As a result, the PPh_2py ligand takes equatorial position in the sulfido-tricobalt cluster. The bond length of the pyridyl bridged Co(1)–Co(3) is the shortest among the three cobalt–cobalt bonds, which is consistence with **1**. All these three bonds are within common Co–Co bond lengths region [7]. The five atoms Co(1), C(6), C(1), N(1) and Co(3) are almost coplanar. The facts that the corresponding bond angles of Co(1)–C(6)–O(1), C(1)–C(6)–O(1) and Co(1)–C(6)–C(1) are 123.8(8), 115.5(9) and 120.8(7)°, respectively, and the bond length for C(6)–O(1) is 1.523(13) Å, all point to the existence of a carbonyl group.

Compound **4**, $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-}C(=O),N\text{–}C_5H_4N(C=O))$, was obtained from the reaction of **1**

Table 1
Crystal data of **1**, **3**–**8** and **9**

Compound	**1**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Formula	$C_{12}H_4Co_3NO_7S$	$C_{28}H_{18}Co_3N_2O_6PS$	$C_{13}H_4Co_3NO_8S$	$C_{16}H_6Co_3NO_7S$	$C_{27}H_{18}CoN_3S_3$	$C_{32}H_{20}Co_3N_2O_6PS$	$C_{32}H_{20}Co_3N_2O_6PS$	$C_{14}H_6Co_3NO_9S$
Formula weight	483.01	718.26	511.02	533.07	539.55	768.32	768.32	541.05
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$	$P2(1)/n$	$C2/c$	$P\bar{1}$
a (Å)	8.4341(18)	14.927(3)	7.9683(15)	8.0896(8)	10.212(3)	12.2792(9)	31.794(4)	8.0578(7)
b (Å)	9.427(2)	10.964(2)	9.856(2)	9.0519(9)	14.894(4)	14.0826(10)	11.1481(15)	8.8640(8)
c (Å)	11.557(2)	18.262(4)	12.557(2)	13.7107(14)	15.853(4)	18.9166(14)	18.686(3)	14.1571(13)
α (°)	95.038(4)		77.374(4)	75.474(2)				79.865(2)
β (°)	100.725(4)	104.085(4)	71.848(4)	84.961(2)	94.545(5)	105.0420(10)	108.888(3)	82.106(2)
γ (°)	108.548(4)		67.253(4)	73.277(2)				70.876(2)
V (Å^3)	845.1(3)	2899.2(9)	858.8(3)	930.65(16)	2403.7(11)	3159.0(4)	6266.5(15)	936.99(15)
Z	2	4	2	2	4	4	8	2
D_{calc} (Mg m^{-3})	1.898	1.646	1.976	1.902	1.491	1.615	1.629	1.918
λ (Mo–K$_\alpha$) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	3.064	1.868	3.026	2.793	0.996	1.720	1.735	2.783
2θ Range (°)	2.31–26.04	2.18–26.08	2.25–26.02	2.42–26.00	1.88–26.43	2.23–26.02	1.95–26.04	1.47–26.04
Observed reflections [$F > 4\sigma(F)$]	1761	1969	1887	2130	2820	4603	4297	2937
Refined parameters	217	370	235	253	307	406	406	253
R_1 for significant reflections [a]	0.0596	0.0527	0.0622	0.0482	0.0553	0.0364	0.0932	0.0460
wR_2 for significant reflections [b]	0.1402	0.0932	0.1423	0.1172	0.1380	0.1012	0.0818	0.1219
Goodness-of-fit [c]	0.853	0.807	0.899	0.804	0.928	0.845	0.950	0.993

[a] $R_1 = |\Sigma (|F_o| - |F_c|)/|\Sigma F_o||$.

[b] $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2 / \Sigma [w(F_o^2)^2]\}^{1/2}$; $w = 0.10$ for **1**, **3**–**5**.

[c] Goodness-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2 / (N_{rflns} - N_{params})]^{1/2}$.

with 1 atm of CO in THF at 25 °C for 24 h with the yield of 38%. Carbonylation of **1** took place under 1 atm of carbon monoxide, nevertheless, which was less efficient while compared with the previous reaction. It is seen clearly that the phosphine ligand, PPh_2py, played a vital role in enhancing the reaction rate. The structural analysis of **4** shows that a CO insertion took place at the Co–C(pyridyl) bond of **1** (Fig. 1). Except for the bridging PPh_2py ligand, the mainframe of **3** is almost identical with **4**.

The proton chemical shifts of the bridged pyridyl ligand of **1** and **4** were assigned with the aid of ^1H–^1H COSY spectra as shown in Fig. 5. The most down-fielded doublet signal of **1** was assigned to Ha because of the adjacent electron-withdrawing nitrogen. The most up-fielded signal is assigned as Hb due to its strong

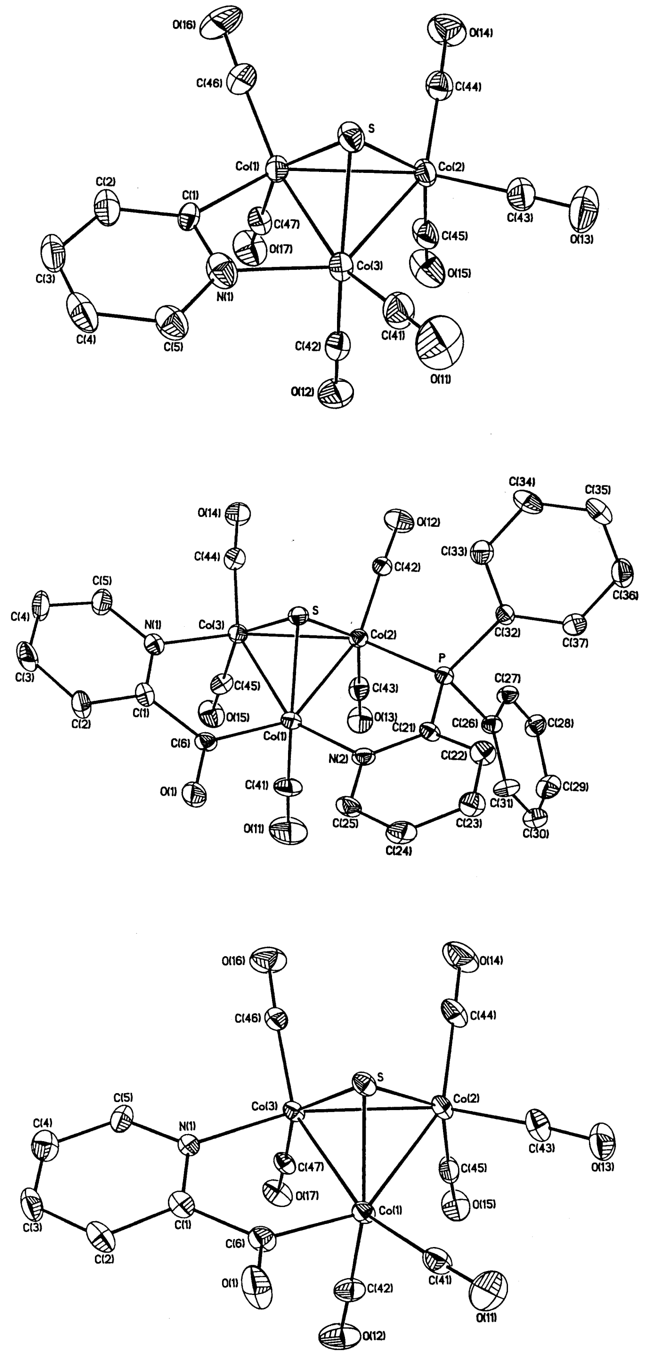

Fig. 1. Molecular structures of: (a) (μ_3-S)$Co_3(CO)_7$(μ-C,N–C_5H_4N) (**1**); (b) (μ_3-S)$Co_3(CO)_5$[(μ-C(=O),N–C_5H_4N(C=O))(μ-P,N–PPh_2py)] (**3**); (c) (μ_3-S)$Co_3(CO)_7$[(μ-C(=O),N–C_5H_4N(C=O))] (**4**).

correlation with Ha. The remaining doublet and doublet of doublet signals are assigned as Hd and Hc, respectively. Slightly different patterns of the bridged pyridyl ligands were observed for **4** and **1** in ^{1}H-NMR. It seems that the corresponding doublet signal of Hd has a notable up-fielded shift from **1** to **4**. This large up-fielded shift might be caused by the neighboring carbonyl group. The relative positions of the three protons, Ha, Hc, Hb, are remained the same.

2.2. Reaction of $Co_2(CO)_8$ with 2-quinolinethiol

The reaction of 2-quinolinethiol with $Co_2(CO)_8$ was carried out for the purpose of comparison. Similar results, a major product, sulfido-tricobalt cluster (μ_3-S)$Co_3(CO)_7$(μ-C,N–C_9H_6N) (**5**), accompanied with a relatively small amount of tris-quinolinethiolate chelated cobalt complex [Co(μ-S,N–SC_9H_6N)$_3$] (**6**), were obtained. In contrast to the case of **1**, no carbonylation of **5** was observed at additional one atmospheric pressure of carbon monoxide even at 60 °C for 16 h, instead it decomposed. The resistance of CO insertion is probably due to a stronger bonding between Co–C(quinolinyl) in **5**. As expected, the crystal structure of **5** reveals that the main framework is quite similar as **1**. The bridged ligand, quinolinyl, is also located at the equatorial position of the sulfido-tricobalt cluster. Interestingly, the structure of **6** shows that the three bridged quinolinethiolate ligands are not arranged in the same manner as that of **2**. Each sulfur atom is in the *trans*-position of a corresponding nitrogen atom; **6** is a facial isomer [8]. The averaged bond length of Co–N and Co–S is 1.986 and 2.2728 Å, respectively. Complexes **6** could not convert to **5** while reacted with excess of $Co_2(CO)_8$ (Fig. 2).

The reaction of PPh_2py with **5** gave a PPh_2py coordinated (μ_3-S)$Co_3(CO)_6$[(μ-C,N–C_9H_6N)(PPh_2py)] (**7**) as the major product, which is accompanied with a small amount of PPh_2py bridged (μ_3-S)$Co_3(CO)_5$[(μ-C(=O),N-C_9H_6N(C=O))(μ-P,N–PPh_2py)] (**8**). The structure of **7** shows that the phosphine coordinates to Co(2) through phosphorous site as a mono-dentate ligand (Fig. 3). On the contrast, PPh_2py acts only as a bridging ligand in the reaction of **1** with it. The expected CO insertion occurred at the Co–C(quinolinyl) bond of **8**. Nevertheless, it is much less efficient than in the case of **1** (Fig. 3). The phosphorus and nitrogen atom of the PPh_2py ligand had coordinated to the Co(2) and Co(3), respectively. This newly bridged PPh_2py is also located at the equatorial position of the sulfido-tricobalt cluster. The bond length of the pyridyl bridged Co(1)–Co(3) is the shortest among the three cobalt–cobalt bonds, which is consistent with that for **1**. All these three bonds are within usual Co–Co bond lengths region. The five atoms Co(1), C(6), C(1), N(1) and Co(3) are almost coplanar. The facts that the respective bond angles of 123.7(3), 114.8(3) and 121.4(3)° for Co(1)–C(6)–O(1), C(1)–C(6)–O(1) and Co(1)–C(6)–C(1) and the bond length of 1.529(5) Å for C(6)–O(1) all support the fact of the existence of a carbonyl group.

2.3. Reaction of $Co_2(CO)_8$ with 2-mercapto-nicotinic acid methyl ester

A reaction was carried out between 2-mercapto-nicotinic acid methyl ester, mercaptopyridine with a

Table 2
Comparison of selected structural parameters of **1**, **3**–**5**, **7**, **8** and **9**

	1	**3**	**4**	**5**	**7**	**8**	**9**
Bond lengths (Å)							
S–Co(1)	2.151(2)	2.158(3)	2.135(2)	2.1405(19)	2.1512(10)	2.1550(10)	2.1510(12)
S–Co(2)	2.157(2)	2.175(3)	2.188(2)	2.1671(18)	2.1659(9)	2.1892(10)	2.1642(12)
S–Co(3)	2.151(3)	2.169(3)	2.154(2)	2.1703(19)	2.1839(9)	2.1752(11)	2.1531(11)
Co(1)–Co(2)	2.5427(6)	2.5224(19)	2.5417(16)	2.5425(13)	2.5633(6)	2.5188(8)	2.5402(8)
Co(2)–Co(3)	2.5350(15)	2.5263(19)	2.5358(16)	2.5658(12)	2.5508(6)	2.5403(7)	2.5591(8)
Co(3)–Co(1)	2.4141(17)	2.4460(19)	2.4420(15)	2.4185(12)	2.4467(6)	2.4558(7)	2.4182(7)
Co(1)–C(1)	1.952(7)			1.934(6)	1.937(3)		1.948(4)
Co(3)–N(1)	1.963(8)	1.967(8)	2.002(6)	1.982(5)	1.999(3)	2.042(3)	1.967(4)
C(1)–N(1)	1.316(11)	1.363(12)	1.367(10)	1.323(8)	1.319(4)	1.339(5)	1.347(5)
Co(1)–C(6)		1.923(10)	1.917(9)			1.901(4)	
C(1)–C(6)		1.523(13)	1.495(12)			1.529(5)	
P–Co(2)		2.155(3)			2.2206(9)	2.1602(11)	
N(2)–Co(1)		2.021(8)				2.031(3)	
Bond angles (°)							
Co(1)–C(1)–N(1)	105.9(6)			110.3(4)	110.6(2)		106.8(3)
C(1)–N(1)–Co(3)	106.7(6)	120.6(7)	121.1(6)	102.3(4)	102.8(2)	117.2(2)	104.8(2)
N(1)–Co(3)–Co(1)	73.3(3)	91.3(3)	89.1(2)	74.80(15)	74.00(8)	91.39(9)	74.18(9)
Co(3)–Co(1)–C(1)	74.2(2)			72.64(19)	72.62(10)		73.97(11)
Co(3)–Co(1)–C(6)		89.0(3)	90.7(3)			89.15(11)	
Co(1)–C(6)–C(1)		120.8(7)	119.9(6)			121.4(3)	
Co(1)–Co(2)–P		87.09(9)			107.56(3)	86.18(3)	
Co(2)–Co(1)–N(2)		98.6(2)				99.21(9)	
Dihedral angles (°)							
Plane1–Plane2 [a]	9.0	18.2	14.4	9.5	5.2	17.9	10.6
Plane2–Plane3		18.3				17.8	

[a] Plane 1: Co(1), Co(3), N(1), C(1); Plane 2: Co(1), Co(2), Co(3); Plane 3: Co(1), Co(2), P, N(2).

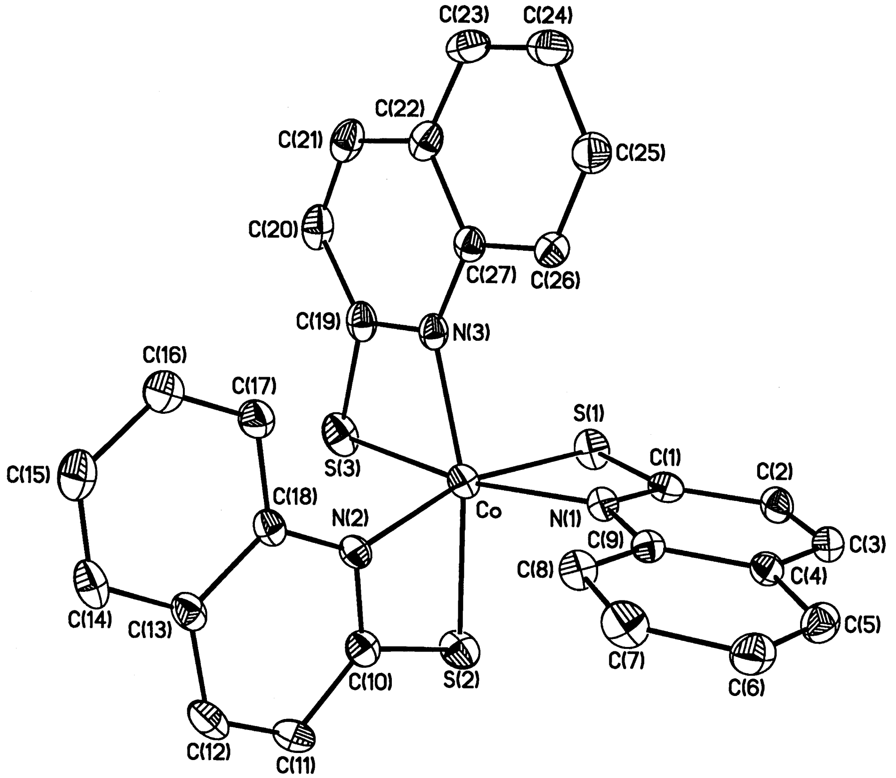

Fig. 2. Molecular structures of [Co(μ-S,N–SC_9H_6N)$_3$] (**6**).

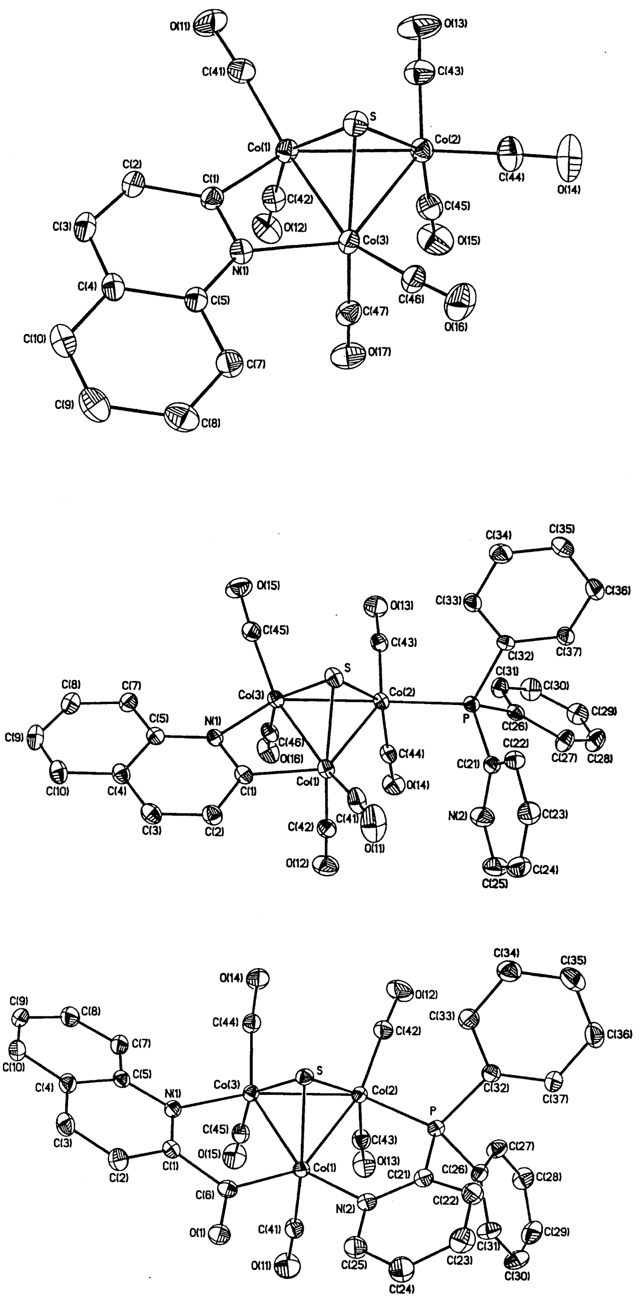

Fig. 3. Molecular structures of: (a) (μ_3-S)$Co_3(CO)_7$(μ-C,N–C_9H_6N) (**5**); (b) (μ_3-S)$Co_3(CO)_6$[(μ-C,N–C_9H_6N)(PPh_2py)] (**7**); (c) (μ_3-S)$Co_3(CO)_5$[(μ-C(=O),N–C_9H_6N(C=O))(μ-P,N–PPh_2py)] (**8**).

strong electron-withdrawing group, and $Co_2(CO)_8$, for the purpose of comparison [9]. Contrast to the previous reaction, only the sulfido-tricobalt cluster (μ_3-S)$Co_3(CO)_7$(μ-C,N–$C_5H_3NC(=O)OCH_3$) (**9**) was obtained. There was no sign of the presence of tris-pyridyl chelated cobalt complex. Crystal structure of **9** shows the main framework of it is quite similar to **1** or **5**. The bridged ligand is also located at the equatorial position of the sulfido-tricobalt cluster. Some structural parameters of compound **1**, **3**, **4**, **5**, **7**, **8** and **9** are selected and listed in Table 2 for comparison (Fig. 4).

3. Summary

Several pryidyl derivatives bridged sulfido-tricobalt carbonyl clusters were prepared through the reaction of mercaptopyridines with $Co_2(CO)_8$. Intramolecular CO insertion took place at the Co–C(pryidyl) bond of **1** or the Co–C(quinolinyl) bond of **5** under a rather mild condition in the presence of the bidentate ligand, PPh_2py. The carbonylation of **1** also took place, with less efficiency, under 1 atm of carbon monoxide. Contrast to the willingness for CO insertion at the Co–C(pryidyl) bond of **1**, carbonylation of **5** at the Co–C(quinolinyl) bond requires the additional bidentate ligand like PPh_2py.

4. Experimental

4.1. General

All operations were performed in a nitrogen flushed glove box or in a vacuum system. Freshly distilled solvents were used. All processes of separations of the products were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924). ^1H-NMR spectra were recorded (Varian VXR-300S spectrometer) at 300.00 MHz; chemical shifts are reported in ppm relative to internal Me4Si. ^{31}P- and ^{13}C-NMR spectra were recorded at 121.44 and 75.46 MHz, respectively. Some other ^1H-NMR spectra were recorded at Gemini-200 spectrometer at 200.00 MHz or Varian-400 spectrometer at 400.00 MHz.COSY spectra: standard pulse sequence, acquisition time 0.213 s, pulse width 21 μs, relaxation delay 1 s, 128 scans, 256 increments. IR spectra of solution in CH_2Cl_2 were recorded on a Hitachi 270-30 spectrometer. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyzes were recorded on Heraeus CHN–O–S–Rapid. Accurate elemental analyzes were precluded for some of the following compounds probably due to their chemical labilities.

4.1.1. Synthesis of $Co_3(CO)_7(\mu_3\text{-}S)(\mu\text{-}C,N\text{–}C_5H_4N)$ (1)

Into a 100 cm^3 flask was placed a solution of $Co_2(CO)_8$ (0.60 g, 0.175 mmol) and 2-mercaptopyridine (0.195 g, 1.75 mmol) in 20 cm^3 THF. The solution was stirred at 25 °C for 1 h. Subsequently, the solvent of the resulting red solution was removed and the residue was chromatographed by CTLC. The first brown band of the title compound $Co_3(CO)_7$(μ_3-S)(μ-C,N–C_5H_4N) (0.1381 g, 0.268 mmol) with 16% yield was separated out.

Complex **1**: Brown crystalline solid; ^1H-NMR (CD_2Cl_2, δ, ppm): 7.74 (d, 1H, $J_{H-H} = 2.60$ Hz), 7.35

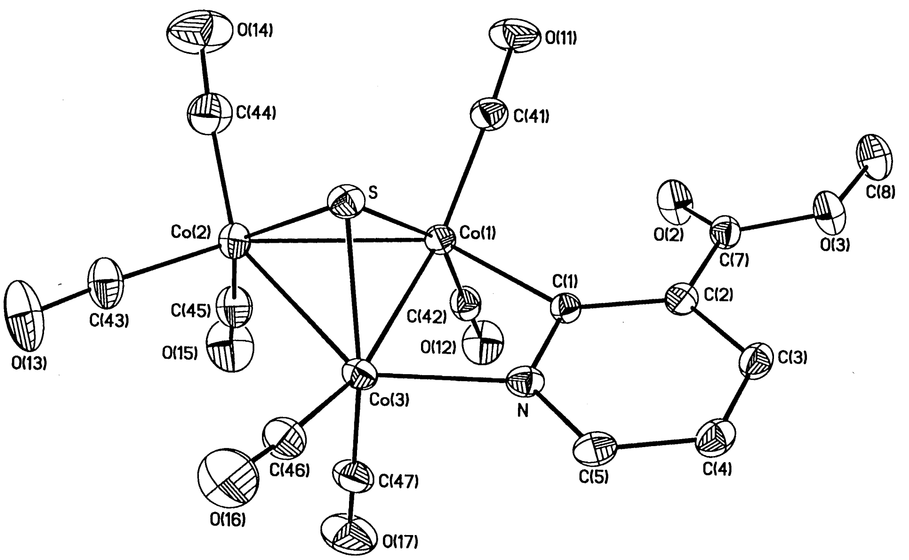

Fig. 4. Molecular structure of (μ_3-S)$Co_3(CO)_7$(μ-C,N–$C_5H_3NC(=O)OCH_3$) (**9**).

(d, 1H, $J_{H-H} = 8.80$ Hz), 7.00 (dd, 1H), 6.63 (dd, 1H); ^{13}C-NMR: 154.92 (s, 1C), 137.44 (s, 1C), 132.52 (s, 1C), 120.87 (s, 1C); IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)} = 2081$ (m), 2035 (s), 2007 (s); MS (FAB): 483 [M$^+$].

4.1.2. Synthesis of (μ_3-S)$Co_3(CO)_5$[(μ-C(=O),N–C_5H_4N(C=O))(μ-P,N–PPh_2py) (3)

In a dry box, PPh_2py (0.152 g, 0.58 mmol) and **1** (0.2800 g, 0.58 mmol) were placed in a 100 cm^3 flask with 20 cm^3 THF. The solution was stirred at 25 °C for

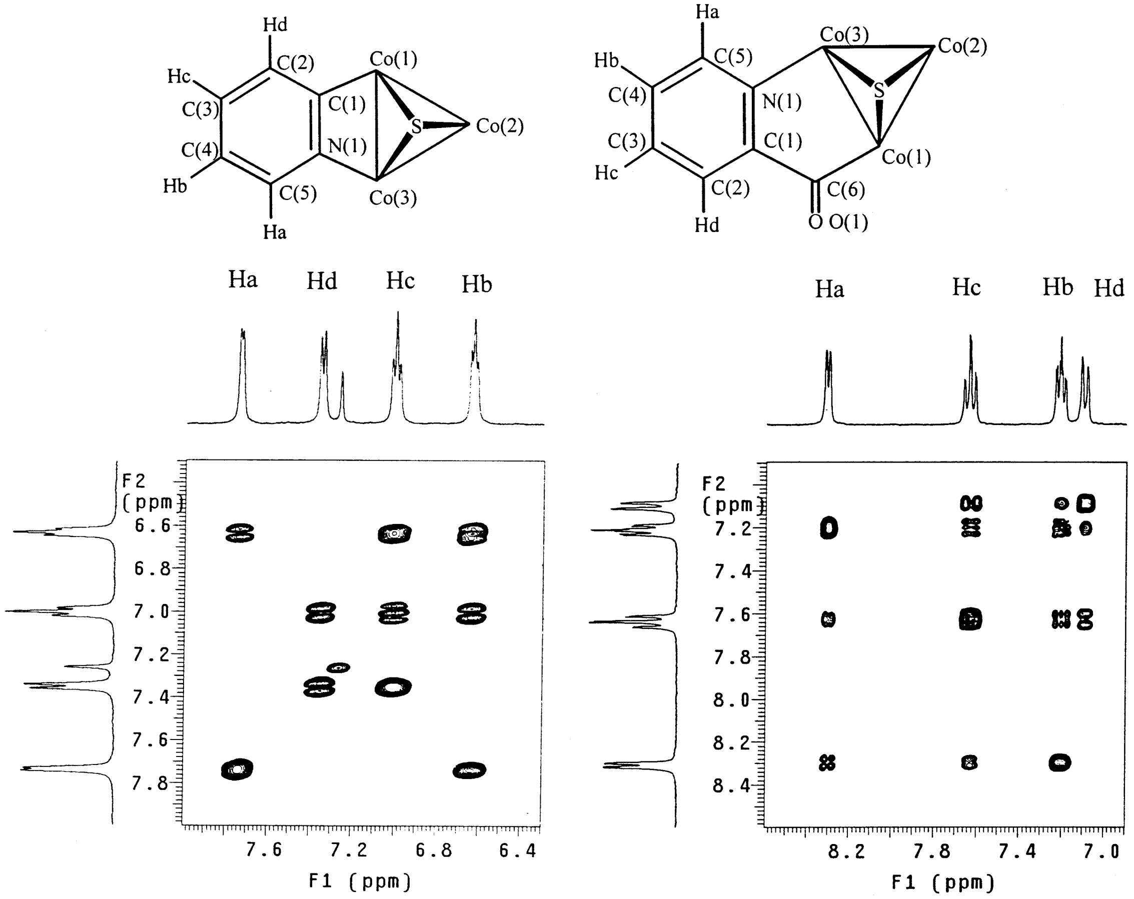

Fig. 5. ^{1}H–^{1}H COSY spectra of the bridged pyridyl of **1** (left) in $CDCl_3$ (400 MHz) and **4** (right) in CD_2Cl_2 (300 MHz).

5 h. Subsequently, the solvent of the resulting brown solution was removed and the residue was chromatographed by CTLC in a $CH_2Cl_2–C_6H_{14} = 1:1$ mixed solvent. The second band, brown in color of the title compound **3** (0.282 g, 0.392 mmol) was obtained. The yield is 67%.

Complex **3***:* Brown crystalline solid; ^{1}H-NMR (CD_2Cl_2, δ, ppm): 9.55 (d, 1H, $J_{H-H} = 4.8$ Hz), 8.37 (d, 1H, $J_{H-H} = 2.2$ Hz), 7.74 (m, 2H), 7.44–7.57 (m, 10H), 7.21–7.00 (m, 3H), 6.63 (d, 1H, $J_{H-H} = 6.4$ Hz); ^{13}C-NMR: 162.98 (s, 1C, PPh_2Py), 156.07 (d, 1C, $J_{PC} = 13.0$ Hz, py), 155.37 (s, 1C, PPh_2Py), 137.87 (s, 1C, Py), 136.83 (s, 1C, PPh_2Py), 135.68 (d, 1C, $J_{PC} = 30$, *ipso* of arene), 135.30 (d, 1C, $J_{PC} = 40$ Hz, *ipso* of arene), 133.77 (d, 2C, $J_{PC} = 12.3$ Hz, arene), 131.55 (d, 2C, $J_{PC} = 10.8$ Hz, arene), 130.88 (s, 1C, *p*-arene), 130.29 (s, 1C, Py), 130.39 (s, 1C, *p*-arene), 129.0–129.2 (m, 4C, arene), 126.7 (s, 1C, PPh_2Py), 125.38 (s, 1C, Py), 115.63 (s, 1C, Py); ^{31}P-NMR ($CDCl_3$): 46.9 (s); IR (KBr, cm^{-1}): $\nu_{(CO)} = 1577$ (w), 1978 (s), 2030 (s); MS (FAB): 719 [M$^+$]; Anal. Calc. for **3**: C, 46.82; H, 2.52; N, 3.90. Found: C, 45.62; H, 3.89; N, 3.86%.

4.1.3. Synthesis of $(\mu_3\text{-}S)Co_3(CO)_7[(\mu\text{-}C(=O),N–C_5H_4N(C=O))]$ (4)

Into a 100 cm^3 flask was placed **1** (0.314 g, 0.652 mmol) with a jointed balloon. THF (20 cm^3) was added and the solution was stirred at 25 °C for 24 h. Subsequently, the solvent of the resulting brown solution was removed and the residue was chromatographed by CTLC in a $CH_2Cl_2–C_6H_{14} = 1:1$ mixed solvent. First brown band which was nothing but unreacted **1** (51%) was collected. The second orange band of the title compound $(\mu_3\text{-}S)Co_3(CO)_7[(\mu\text{-}C(=O),N–C_5H_4N(C=O))$ (0.1264 g, 0.247 mmol) with 38% yield was separated out.

Complex **4***:* Orange crystalline solid; ^{1}H-NMR (CD_2Cl_2, δ, ppm): 8.31 (d, 1H, $J_{H-H} = 4.40$ Hz), 7.64 (dd, 1H), 7.21 (dd, 1H), 7.10 (d, 1H, $J_{H-H} = 7.20$ Hz); ^{13}C-NMR: 217.99 (s, 1C, C=O), 163.24 (s, 1C, py), 155.97 (s, 1C, py), 139.13 (s, 1C, py), 128.21 (s, 1C, py), 118.50 (s, 1C, py); IR (KBr, cm^{-1}): 1635 (m), 1980 (m), 2033 (s), 2083 (m); MS (FAB): 511 [M$^+$ −6CO]; Anal. Calc. for **4**: C, 30.55; H, 0.79; N, 2.74. Found: C, 30.64; H, 0.94; N, 2.75%.

4.2. Reaction of 2-quinolinethiol with $Co_2(CO)_8$

Similar processes were undertaken as in the preparation of **1**. Into a 100 cm^3 flask was placed a solution of $Co_2(CO)_8$ (0.6360 g, 1.86 mmol) and 2-quinolinethiol (0.200 g, 1.24 mmol) in 25 cm^3 THF and was stirred at 25 °C for 1 h. Subsequently, the solvent of the resulting red solution was removed and the residue was chromatographed by CTLC. The first band, brown in color of the compound $(\mu_3\text{-}S)Co_3(CO)_7(\mu\text{-}C,N–C_9H_6N)$ (**5**) (0.4635 g, 0.8695 mmol) was eluted out by C_6H_{14}. The yield is 70%. A small amount of greenish brown $[Co(\mu\text{-}S,N–SC_9H_6N)_3]$ (**6**) was eluted out by the mixture solvent of $MeOH–CH_2Cl_2 = 1/2$.

Complex **5***:* Brown crystalline solid; ^{1}H-NMR (CD_2Cl_2, δ, ppm): 7.399–7.731 (m, 6H, arene); ^{13}C-NMR ($CDCl_3$): 122.91, 125.56, 127.42, 128.93, 130.32, 130.89, 133.38, 148.30 (arene); IR (KBr, cm^{-1}): 2009 (s), 2080 (s); Anal. Calc. for **5**: C, 36.05; H, 1.13; N, 2.63. Found: C, 36.47; H, 1.26; N, 2.22%.

Complex **6***:* Greenish brown crystalline solid; ^{1}H-NMR (CD_2Cl_2, δ, ppm): 8.83 (d, $J_{H-H} = 8.20$ Hz, arene), 8.32 (d, $J_{H-H} = 8.80$ Hz, arene), 8.21 (d, $J_{H-H} = 8.80$ Hz, arene), 7.87 (d, $J_{H-H} = 8.20$ Hz, arene), 7.74 (dd, 1H, arene), 7.56 (dd, 1H, arene); ^{13}C-NMR ($CDCl_3$): 156.12, 147.81, 136.67, 129.81, 129.47, 128.34, 127.57, 126.87, 119.35 (arene).

4.2.1. Synthesis of $(\mu_3\text{-}S)Co_3(CO)_6[(\mu\text{-}C,N–C_9H_6N)(PPh_2py)]$ (7) and $(\mu_3\text{-}S)Co_3(CO)_5[(\mu\text{-}C(=O),N–C_9H_6N(C=O))\text{-}(\mu\text{-}P,N–PPh_2py)]$ (8)

Following the same procedures, 0.588 mmol (0.3134 g) of **5** and molar equivalent of PPh_2py (0.1548 g, 0.588 mmol) were dissolved in 5 cm^3 of THF each, then were transferred into a 100 cm^3 flask. The solution was stirred at 25 °C for 1 h. Subsequently, the solvent of the resulting dark brown solution was removed and the residue was chromatographed by CTLC in a $CH_2Cl_2–C_6H_{14} = 1:1$ mixed solvent. The first band, dark brown in color of the title compound **7** (0.3038 g, 0.396 mmol) was obtained. The yield is 67%. A small amount of the brown compound was eluted by CH_2Cl_2 as the second band and was characterized as **8**.

Complex **7***:* Dark brown crystalline solid; ^{1}H-NMR ($CDCl_3$, δ, ppm): 8.79 (d, 1H, py), 7.26–7.68 (m, 19H, arene); ^{13}C-NMR (CD_2Cl_2): 160.26 (d, $J_{PC} = 64.7$ Hz, 1C, py), 150.16 (d, $J_{PC} = 15.8$ Hz, 1C, py), 148.17 (s, 1C, arene), 135.70 (d, $J_{PC} = 7.3$ Hz, 1C, py), 134.87 (d, $J_{PC} = 42.1$ Hz, 1C, *ipso*), 134.54 (d, $J_{PC} = 42.8$ Hz, 1C, *ipso*); 133.64 (s, arene), 133.51 (s, 2C, Ph), 133.39 (s, 2C, Ph), 130.28 (s, 1C, arene), 129.82 (s, 2C,Ph), 129.63 (s, 1C, arene), 128.63 (s, 1C, arene), 128.36 (s, 2C, Ph), 128.28 (s, 2C, Ph), 127.87 (s, 1C, py), 127.15 (s, 1C, arene), 124.89 (s, 1C, arene), 123.53 (s, 1C, py), 123.26 (s, 1C, arene); ^{31}P-NMR ($CDCl_3$): 48.86; Anal. Calc. for **7**: C, 50.02; H, 2.62; N, 3.65. Found: C, 52.55; H, 4.42; N, 3.62%; IR (KBr, cm^{-1}): $\nu_{(CO)} = 1980.3$ (s), 2014.3 (s); MS (FAB): 769 [M$^+$ +1].

Complex **8***:* Brown crystalline solid; ^{1}H-NMR ($CDCl_3$, δ, ppm): 9.60 (d, 1H, Py), 8.90 (d, 1H, arene), 8.06 (d, 1H, arene), 6.69–7.83 (m, 17H, arene); ^{31}P-NMR: 36.57; IR (KBr, cm^{-1}): $\nu_{(CO)} = 1575.2$ (s), 1979.3 (s), 2013.6 (s); MS (FAB): 769 [M$^+$ +1]. Elemental analysis and ^{13}C-NMR for **8** were precluded due to its small quantity.

4.2.2. Synthesis of (μ_3-S)$Co_3(CO)_7$(μ-C,N–$C_5H_3NC(=O)OCH_3$) (9)

Compound **9** was prepared by the same procedures adapted from the synthesis of **1**. Into a 100 cm^3 flask was placed 2-mercapto-nicotinic acid methyl ester (0.200 g, 1.182 mmol) with 1.5 M equivalent of $Co_2(CO)_8$ (0.606 g, 1.733 mmol) in 10 cm^3 THF. The solution was stirred at 0 °C for half an hour then it was allowed to warm up to 25 °C for another 30 min. Subsequently, the solvent of the resulting dark brown solution was removed and the residue was chromatographed by CTLC. The second brown band of the title compound (μ_3-S)$Co_3(CO)_7$(μ-C,N–$C_5H_3NC(=O)OCH_3$) (**9**) (0.1537 g, 0.2840 mmol) with 24% yield was separated out. A large amount of the decomposed materials remains uncharacterized.

Complex **9**: Brown crystalline solid; ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.86 (d, 1H, $J_{H-H} = 4.8$ Hz, py), 7.71 (d, 1H, $J_{H-H} = 7.5$ Hz, py), 6.68 (dd, 1H, py), 3.98 (s, 3H,CH_3); ^{13}C-NMR: 166.97 (s, 1C, C=O), 156.99 (s, 1C, CH), 138.19 (s, 1C, CC=O), 135.31 (s, 1C, CH), 119.52 (s, 1C, CH), 52.33 (s, 1C, CH_3); Anal. Calc. for **9**: C, 31.08; H, 1.12; N, 2.59. Found: C, 31.29; H, 1.34; N, 2.23%; IR (KBr, cm^{-1}): $\nu_{(CO)} = 2084$ (s), 2038 (s), 1726 (m), 1555 (m), 1392 (m), 1275 (m); MS (FAB): 512 [$M^+ - CO$].

5. X-ray crystallographic studies

Suitable crystals of **1**, **3**–**8** and **9** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Crystallographic data of **1**, **3**–**8** and **9** are summarized in Table 1.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 176592–176599 for compounds **1**, **3**–**9**, 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; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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