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Synthesis and Structure of Heterometallic Compounds with Dimethyl Pyridine-2,6-dicarboxylate

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Abstract—Dimethyl pyridine-2,6-carboxylate (L) was prepared by refluxing pyridine-2,6-dicarbonyl dichloride in methanol. The reactions of L with Ca(II), Sr(II), and Ba(II) salts and with cobalt(II) thiocyanate resulted in the formation of three heterometallic complexes: $[CaL_3][Co(NCS)_4]$ (**I**), $[SrL_3][Co(NCS)_4]$ (**II**), and $[BaCoL_3(\mu\text{-}NCS)_2(NCS\text{-}\kappa N)_2]$ (**III**). The composition and structure of compounds L and **I**–**III** were determined by elemental analysis, infrared spectroscopy, and X-ray diffraction (CCDC nos. 2166019–2166022, respectively). It was found that isostructural Ca(II) and Sr(II) compounds are ionic and are formed by the $[CaL_3]^{2+}$ and $[SrL_3]^{2+}$ complex cations and $[Co(SCN)_4]^{2-}$ complex anion, while the Ba(II) derivative is a molecular complex in which $[BaL_3]^{2+}$ and $[Co(NCS)_4]^{2-}$ moieties are linked by two $(NCS)^-$ bridging units of the complex anions. In any of the three compounds, three tridentate L ligands are coordinated to the alkaline earth metal ion.

Keywords: heterometallic Ca(II), Sr(II), and Ba(II)/Co(II) complexes, dimethyl pyridine-2,6-dicarboxylate, IR spectra, X-ray diffraction

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INTRODUCTION

Dialkyl pyridine-2,6-dicarboxylate (L) moiety is present in the molecules of various organic compounds such as cyclic polyethers, cryptands, and macrocyclic ionophores and in their complexes [1–6]. In various complexes, they function as bridging polydentate ligands [7–9]. The coordination architectures of mono-, bi-, and polynuclear metal compounds depend mainly on two factors: the geometry of the metal coordination polyhedron and ligand characteristics [10–17]. Dialkyl pyridine-2,6-dicarboxylate is potentially a pentadentate ligand, as it has one donor nitrogen of the pyridine moiety and four oxygens of the two carboxylate groups. Since geometrical restrictions preclude simultaneous coordination of all these atoms to the same metal center, this ligand often forms complexes of different nuclearity. According to Cambridge Crystallographic Data Centre (CCDC) [18], although the coordination chemistry of compounds containing dialkyl pyridine-2,6-dicarboxylate ligands has been relatively little studied, this ligand is known to act as NO_2-, NO-, or N-donor ligand (O is either carbonyl oxygen or ester oxygen). The CCDC structural data [18] show that nitrogen atom participates in all types of coordination, and the coordination of carbonyl oxygen is more likely than the coordination of ester oxygen.

Since dialkyl pyridine-2,6-dicarboxylates and ligands based on them contain only C—H proton-donor groups, the crystal structure of these compounds is stabilized, most often, by weak intermolecular C—H···O hydrogen bonds and π···π interactions between the pyridine rings [19, 20].

This communication presents a new procedure for the preparation of L and the synthesis of three heterometallic complexes, $[CaL_3][Co(NCS)_4]$ (**I**), $[SrL_3][Co(NCS)_4]$ (**II**), and $[BaCoL_3(\mu\text{-}NCS)_2(NCS\text{-}\kappa N)_2]$ (**III**) (L = dimethyl pyridine-2,6-carboxylate), formed upon the reactions of various Ca(II), Sr(II), and Ba(II) salts with cobalt(II) thiocyanate and pyridine-2,6-dicarbonyl dichloride in methanol, and IR spectroscopic and X-ray diffraction data for the obtained compounds.

EXPERIMENTAL

Reagent grade commercial reactants and solvents were used as received. The initial compounds included pyridine-2,6-dicarbonyl dichloride, calcium thiocyanate tetrahydrate, cobalt thiocyanate trihydrate, strontium chloride, ammonium thiocyanate, barium thiocyanate trihydrate, and methanol (Sigma Aldrich). Although ligand L is a known compound [21], we prepared it using a simpler procedure: refluxing of pyridine-2,6-dicarbonyl dichloride in methanol (without methanol drying).

Synthesis of dimethyl pyridine-2,6-dicarboxylate (L). Pyridine-2,6-dicarbonyl dichloride (0.19 g, 0.93 mmol) was dissolved in methanol (20 mL), and the solution was refluxed for 2 h, filtered, and allowed to stand at room temperature for crystallization. After 2 days, a white product was formed as large crystals. The yield was 0.17 g (94%).

For $C_9H_9NO_4$

Anal. calcd., %	C, 55.39	H, 4.65	N, 7.18
Found, %	C, 56.15	H, 5.05	N, 7.26

IR (ν, cm^{-1}): 3451 w, 3088 w, 3064 w, 2972 m, 2902 w.br, 2586 w, 2351 w, 1797 w, 1739 vs, 1731 sh, 1695 m, 1571 m, 1523 w, 1497 w, 1450 m, 1444 m, 1438 m, 1426 m, 1395 w, 1318 w, 1289 s, 1243 vs, 1197 s, 1164 s, 1145 m, 1081 m, 1034 w, 996 vs, 952 m, 862 w, 853 m, 812 m, 794 w, 756 vs, 722 m, 695 vs, 646 m, 521 w, 463 m, 434 m.

Synthesis of [Ca(L)$_3$][Co(NCS)$_4$] (I). A mechanical mixture of calcium thiocyanate tetrahydrate (0.05 g, 0.22 mmol), cobalt thiocyanate trihydrate (0.06 g, 0.26 mmol), and pyridine-2,6-dicarbonyl dichloride (0.15 g, 0.74 mmol) in 1 : 1 : 3 molar ratio was suspended in methanol (15 mL) and the mixture was refluxed for 3 h. After complete dissolution of all components, the blue-violet solution was filtered and allowed to stand at room temperature in air for crystallization. After 24 h, prismatic blue crystals suitable for X-ray diffraction were formed in the solution. The yield was 0.11 g (47%).

For $C_{31}H_{27}N_7O_{12}S_4CaCo$

Anal.	C,	H,	N,	S,	Ca,	Co,
calcd., %	40.61	2.97	10.70	13.99	4.37	6.43
Found, %	C,	H,	N,	S,	Ca,	Co,
	40.57	2.88	10.74	14.08	4.45	6.45

IR (ν, cm^{-1}): 3390 m, 3088 w, 2989 sh, 2958 m, 2902 w, 2057 vs, 1708 vs, 1588 c, 1489 w, 1462 m, 1435 s, 1423 m, 1324 vs, 1270 vs, 1205 w, 1180 m, 1148 m, 1082 m, 1013 m, 993 s, 951 m, 870 m, 846 m, 826 m, 795 vw, 756 s, 731 s, 693 s, 658 m, 540 w, 497 sh, 485 sh, 478 m, 429 m, 404 m.

Synthesis of [Sr(L)$_3$][Co(NCS)$_4$] (II). Strontium chloride (0.16 g, 1.01 mmol), cobalt thiocyanate trihydrate (0.23 g, 1.00 mmol), and ammonium thiocyanate (0.16 g, 2.10 mmol) were dissolved in methanol (10 mL) (solution 1). Pyridine-2,6-dicarbonyl dichloride (0.61 g, 3.00 mmol) was dissolved in methanol (12 mL) (solution 2). Solution 1 was added to solution 2 with continuous stirring, and the resulting blue-violet reaction mixture was refluxed for 3 h. The formed solution was filtered and allowed to stand at room temperature in air for crystallization. After 24 h, prismatic blue crystals suitable for X-ray diffraction were formed in the solution. The yield was 0.11 g (44%).

For $C_{31}H_{27}N_7O_{12}S_4CoSr$

Anal.	C,	H,	N,	S,	Co,	Sr,
calcd., %	38.61	2.82	10.17	13.30	6.11	9.09
Found, %	C,	H,	N,	S,	Co,	Sr,
	38.68	2.89	10.23	13.39	6.19	9.13

IR (ν, cm^{-1}): 3388 w, 3073 w, 2958 m, 2095 w, 2056 vs, 1709 vs, 1587 m, 1460 m, 1436 m, 1426 m, 1321 vs, 1268 vs, 1225 m, 1203 m, 1178 m, 1155 m, 1148 m, 1084 m, 1010 m, 993 s, 951 m, 871 m, 847 m, 839 w, 826 m, 796 w, 756 s, 730 m, 693 s, 657 m, 537 w, 485 w, 478 m, 428 m.

Synthesis of [BaCoL$_3$(μ-NCS)$_2$(NCS-κN)$_2$] (III). Barium thiocyanate trihydrate (0.08 g, 0.28 mmol) and cobalt thiocyanate trihydrate (0.06 g, 0.26 mmol) were dissolved in methanol (7 mL) (solution 1). Pyridine-2,6-dicarbonyl dichloride (0.016 g, 0.078 mmol) was dissolved in methanol (15 mL) (solution 2). Solution 1 was added to solution 2 with continuous stirring, and the resulting violet reaction mixture was refluxed for 3 h (the Ba^{2+} : Co^{2+} : pyridine-2,6-dicarbonyl dichloride molar ratio was 1 : 1 : 3). Then the solution was filtered and allowed to stand at room temperature in air for crystallization. On the second day, prismatic blue crystals suitable for X-ray diffraction were formed in the solution. The yield was 0.11 g (43%).

For $C_{31}H_{27}N_7O_{12}S_4CoBa$

Anal.	C,	H,	N,	S,	Co,	Ba,
calcd., %	36.72	2.68	9.67	12.65	5.81	13.54
Found, %	C,	H,	N,	S,	Co,	Ba,
	36.75	2.76	9.74	12.67	5.84	13.51

IR (ν, cm^{-1}): 3408 br.w, 3178 w, 3088 w, 2956 m, 2292 br.w, 2069 s, 2032 s, 1715 vs, 1584 m, 1454 m, 1435 m, 1428 sh, 1349 w, 1311 vs, 1261 vs, 1222 sh, 1200 m, 1174 m, 1149 w, 1084 m, 1067 sh, 1058 w, 1028 vw, 1001 sh, 990 s, 948 m, 870 m, 848 m, 838 w, 824 m, 796 w, 756 s, 728 m, 695 s, 654 w, 533 br.w, 499 m, 480 m, 429 m.

The key and most intense absorption bands in the spectra of L and **I**–**III** are summarized in Table 1.

The composition of compounds L and **I**–**III** was established using elemental analysis and IR spectroscopy, and the structure was determined by single crystal X-ray diffraction. IR spectra were measured on a FT-IR Perkin-Elmer Spectrum 100 instrument in mineral oil in the 4000–400 cm^{-1} range and ATP in the 4000–650 cm^{-1} range.

X-ray diffraction. The experimental data for L and **I**–**III** were collected at room temperature on a Xcalibur E diffractometer, MoK_α radiation (λ = 0.71073 Å),

Table 1. Main frequencies in the IR spectra of compounds L and **I**–**III**

Compound	ν(C≡N) [21]	ν(C=O) [21]	ν_{as}(C–O–C) [22, 23]	ν_s(C–O–C) [22, 23]	$\delta_{ip}(CH)_{arom}$ [24]	$\delta_{oop}(CH)_{arom.}$ [24]	ν(CS) [21]	δ(NCS) [21]	ν(M-N) [25]
L		1739	1243	1034	1164, 1081, 996	756, 722			
I	2057	1708	1270	1013	1180, 1082, 993	756, 731	826	485	540
II	2056	1709	1268	1010	1178, 1084, 993	756, 730	826	485	537
III	2069, 2032	1715	1261	1001	1174, 1084, 990	756, 728	824	499	533

graphite monochromator, ω-scan mode. The unit cell parameters were refined considering all measured reflections. The crystal structures were solved by direct methods and refined by least squares in the full-matrix anisotropic approximation for non-hydrogen atoms (SHELX-97) [22]. The hydrogen atom positions were determined from the difference Fourier maps and refined isotropically in the rigid body model. The crystallographic data and X-ray experiment details for L and **I**–**III** are summarized in Table 2, the interatomic distances and bond angles in the coordination polyhedra are given in Table 3, and the geometric parameters of hydrogen bonds are presented in Table 4.

The atom positions and thermal parameters for L and **I**–**III** are deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2166019–2166022, respectively; deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reaction of pyridine-2,6-dicarbonyl dichloride with methanol gave dimethyl pyridine-2,6-dicarboxylate (L), which was allowed to react with various Ca(II), Sr(II), and Ba(II) salts and cobalt(II) thiocyanate to furnish three heterometallic complexes: $[CaL_3][Co(NCS)_4]$ (**I**), $[SrL_3][Co(NCS)_4]$ (**II**), and $[BaCoL_3(\mu\text{-}NCS)_2(NCS\text{-}\kappa N)_2]$ (**III**).

The key and most intense bands in the absorption spectra of compounds L and **I**–**III** are caused by the ν(C≡N), ν(C=O), and ν_{as}(C–O–C) stretching modes and $\delta_{oop}(CH)_{arom}$ (out-of-plane) mode (Table 1). The ν(C≡N) band is manifested at 2057 (**I**), 2056 (**II**), and 2069, 2032 (**III**) cm^{-1}. These frequencies are typical of NCS$^-$ groups coordinated to a metal via nitrogen [23]. The spectrum of compound **III**, unlike the spectra of **I** and **II**, exhibits two ν(C≡N) bands at 2069 and 2032 cm^{-1} with approximately equal intensity. The higher-frequency band corresponds to the bridging NCS$^-$ group [23]. These results are in full agreement with X-ray diffraction data, which indicate that all four NCS$^-$ groups are coordinated to cobalt(II), and two of them are additionally coordinated to barium in the bridging fashion. The spectra of L and **I**–**III** show strong ν(C=O) absorption bands: 1739 (L), 1708 (**I**), 1709 (**II**), and 1715 (**III**) cm^{-1}. Lower ν(C=O) frequencies in the spectra of the complexes compared to the spectrum of L are due to the coordination of the carbonyl groups to alkaline earth metal atoms.

In the spectra of ethers, esters, and coordination compounds containing methyl esters, important information is provided by the ν_{as}(C–O–C) band at ~1250 cm^{-1}, which is known as the "1250 band," and also by the ν_s(C–O–C) band in the 1060–1000 cm^{-1} range [24, 25]. It can be seen from Table 1 that the compounds studied here give rise to bands at 1243 (L), 1270 (**I**), 1268 (**II**), and 1261 (**III**) cm^{-1} for ν_{as}(C–O–C) and at 1034 (L), 1013 (**I**), 1010 (**II**), and 1001 cm^{-1} (**III**) for ν_s(C–O–C). The obtained data on the bands for the $\delta_{ip}(CH)_{arom}$ (in-plane) modes and especially $\delta_{oop}(CH)_{arom}$ (out-of-plane) modes are important for determining the type of substitution in aromatic rings, in this case, 1,2,3-substitution (three adjacent unsubstituted hydrogen atoms). The absorption bands at 1164, 1081, 996 (L), 1180, 1082, 993 (**I**), 1178, 1084, 993 (**II**), and 1174, 1084, 990 (**III**) cm^{-1} are due to the $\delta_{ip}(CH)_{arom}$ vibrations [26]. The bands for the $\delta_{oop}(CH)_{arom}$ vibrations are highly intense and occur in the range of 810–750 cm^{-1}: 756 and 722 (L), 756 and 731 (**I**), 756 and 730 (**II**), and 756 and 728 (**III**) cm^{-1} [26]. The type of coordination of the NCS$^-$ group (through nitrogen or sulfur atom) affects the position of absorption bands for the ν(CS) and δ(NCS) modes. The spectra of compounds **I**–**III** exhibit absorption bands at 826/485 (**I**), 826/485 (**II**), and 824/499 (**III**) cm^{-1}, which are due to the ν(CS)/δ(NCS) modes. This is in line with the metal coordination of NCS$^-$ anions through the nitrogen atom. The M–N and M–O vibrations are usually manifested below 400 cm^{-1}. Presumably, the bands at 540 (**I**), 537 (**II**), and 533 (**III**) cm^{-1} can be assigned to ν(M–N) [27].

X-ray diffraction analysis confirmed that refluxing of pyridine-2,6-dicarbonyl dichloride in methanol results in the formation of C_2-symmetric dimethyl pyridine-2,6-dicarboxylate, which has been prepared previously by a more cumbersome method that included the reactions of pyridine-2,6-dicarboxylic

Table 2. Crystallographic data and X-ray experiment details for structures of L and **I**–**III**

Parameter	Value			
	L	**I**	**II**	**III**
Molecular formula	$C_9H_9NO_4$	$C_{31}H_{27}N_7O_{12}S_4CaCo$	$C_{31}H_{27}N_7O_{12}S_4SrCo$	$C_{31}H_{27}N_7O_{12}S_4CoBa$
M	195.17	916.84	964.38	1014.10
System	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$P\bar{1}$
a, Å	13.307(6)	15.7908(90)	16.0759(6)	10.6515(5)
b, Å	6.7994(10)	15.6777(10)	15.4392(12)	11.0221(5)
c, Å	12.616(5)	17.157(2)	17.1841(8)	18.1814(8)
α, deg	90	90	90	85.125(4)
β, deg	129.57(7)	102.172(9)	99.516(4)	83.249(4)
γ, deg	90	90	90	82.707(4)
V, Å^3	879.9(9)	4152.0(6)	4206.4(4)	2097.27(16)
Z	4	4	4	2
ρ(calcd.), g/cm^3	1.473	1.467	1.523	1.606
μ, mm^{-1}	0.118	0.802	1.925	1.591
F(000)	408	1876	1948	1010
Crystal size, mm	0.12 × 0.11 × 0.05	0.34 × 0.20 × 0.07	0.40 × 0.20 × 0.20	0.44 × 0.42 × 0.10
Range of θ, deg	3.47–25.50	2.87–24.99	3.19–25.50	3.03–25.49
Ranges of reflection indices	$-14 \le h \le 16$, $-5 \le k \le 8$, $-15 \le l \le 14$	$-18 \le h \le 18$, $-18 \le k \le 17$, $-11 \le l \le 20$	$-19 \le h \le 19$, $-12 \le k \le 18$, $-20 \le l \le 20$	$-11 \le h \le 12$, $-13 \le k \le 13$, $-21 \le l \le 22$
Number of measured/unique reflections (R_{int})	1708/818 (0.0188)	7275/3651 (0.0524)	7731/3908 (0.0385)	13971/7780 (0.0273)
Filling, %	100	99.6	99.5	99.7
Number of reflections with $I > 2\sigma(I)$	592	1720	2604	6710
Number of refined parameters	66	258	256	511
GOOF	1.002	1.000	1.003	1.001
R-factor ($I > 2\sigma(I)$)	$R_1 = 0.0488$, $wR_2 = 0.1319$	$R_1 = 0.0656$, $wR_2 = 0.1016$	$R_1 = 0.0592$, $wR_2 = 0.1216$	$R_1 = 0.0353$, $wR_2 = 0.0805$
R-factor (for the whole array)	$R_1 = 0.0683$, $wR_2 = 0.1505$	$R_1 = 0.1501$, $wR_2 = 0.1259$	$R_1 = 0.1013$, $wR_2 = 0.1373$	$R_1 = 0.0443$, $wR_2 = 0.0847$
$\Delta\rho_{max}/\rho_{min}$, e Å^{-3}	0.196/–0.250	0.376/–0.327	0.551/–0.415	0.527/–0.663

acid with thionyl chloride and then with the appropriate alcohol [21] (Fig. 1). Compound L crystallizes in the monoclinic space group $C2/c$ (Table 2), and its unit cell parameters are in line with the previously published data.

Isostructural compounds **I** and **II** crystallize in the monoclinic space group $C2/c$, and **III** crystallizes in the triclinic space group $P\bar{1}$ (Table 2). It was found that Ca(II)- and Sr(II)-containing compounds are ionic and are formed by the $[CaL_3]^{2+}$ and $[SrL_3]^{2+}$ complex cations, respectively, and the $[Co(NCS)_4]^{2-}$ complex anions, while the Ba(II) compound is a molecular complex in which $[BaL_3]^{2+}$ and $[Co(NCS)_4]^{2-}$ moieties are connected by two nitrogen atoms of two bridging $(NCS)^-$ ligands (Fig. 2). The coordination environment of Co(II) in each of the three compounds is a tetrahedron formed by the N_4 set of donor atoms, which belong to four $(NCS)^-$ anions, while the polyhedra of alkaline earth metals are different. Indeed, the coordination numbers of Ca and Sr are 9, while the

Table 3. Selected interatomic distances and bond angles in the structures of **I**–**III***

Bond	*d*, Å	Angle	ω, deg
I			
Ca(1)–N(1)	2.542(3)	N(1)Ca(1)N(2)	112.01(8)
Ca(1)–N(2)	2.544(6)	N(1)Ca(1)N(1)$^{\#1}$	136.0(2)
Ca(1)–O(1)	2.513(3)	N(1)Ca(1)O(1)	60.52(11)
Ca(1)–O(3)	2.549(3)	N(1)Ca(1)O(3)	63.11(11)
Ca(2)–O(5)	2.522(4)	O(1)Ca(1)O(3)	126.10(10)
Co(1)–N(3)	1.952(5)	N(2)Ca(1)O(5)	63.21(8)
Co(1)–N(4)	1.934(5)	O(5)Ca(1)O(5)$^{\#1}$	126.4(2)
		N(3)Co(1)N(4)	106.2(2)
		N(3)Co(1)N(3)$^{\#2}$	116.3(3)
		N(3)Co(1)N(4)$^{\#2}$	110.6(2)
		N(4)Co(1)N(4)$^{\#2}$	106.7(3)
II			
Sr(1)–N(1)	2.710(3)	N(1)Sr(1)N(2)	108.15(8)
Sr(1)–N(2)	2.717(7)	N(1)Sr(1)N(1)$^{\#1}$	143.7(2)
Sr(1)–O(1)	2.623(3)	N(1)Sr(1)O(1)	60.25(9)
Sr(1)–O(3)	2.659(3)	N(1)Sr(1)O(3)	59.71(10)
Sr(1)–O(5)	2.643(4)	O(1)Sr(1)O(3)	119.75(9)
Co(1)–N(3)	1.937(5)	N(2)Sr(1)O(5)	60.09(10)
Co(1)–N(4)	1.944(5)	O(5)Sr(1)O(5)$^{\#1}$	120.2(2)
		N(3)Co(1)N(4)	105.9(2)
		N(3)Co(1)N(3)$^{\#2}$	116.1(3)
		N(3)Co(1)N(4)$^{\#2}$	110.8(2)
		N(4)Co(1)N(4)$^{\#2}$	107.2(3)
III			
Ba(1)–N(1)	2.979(2)	N(1)Ba(1)N(2)	99.77(7)
Ba(1)–N(2)	2.984(3)	N(1)Ba(1)N(3)	168.71(7)
Ba(1)–N(3)	2.946(2)	N(1)Ba(1)N(4)	106.99(7)
Ba(1)–N(4)	3.325(3)	N(1)Ba(1)N(5)	64.54(7)
Ba(1)–N(5)	3.220(3)	N(2)Ba(1)N(3)	90.45(7)
Ba(1)–O(1)	2.786(2)	N(2)Ba(1)N(4)	148.56(7)
Ba(1)–O(3)	2.835(2)	N(2)Ba(1)N(5)	151.02(7)
Ba(1)–O(5)	2.810(2)	N(3)Ba(1)N(4)	61.86(7)
Ba(1)–O(7)	2.877(3)	N(3)Ba(1)N(5)	108.09(7)
Ba(1)–O(9)	2.833(2)	N(4)Ba(1)N(5)	59.18(7)
Ba(1)–O(11)	2.833(2)	N(1)Ba(1)O(1)	55.52(7)
Co(1)–N(4)	1.956(3)	N(1)Ba(1)O(3)	55.21(7)
Co(1)–N(5)	1.976(3)	O(1)Ba(1)O(3)	110.67(7)
Co(1)–N(6)	1.957(4)	N(2)Ba(1)O(5)	56.07(8)
Co(1)–N(7)	1.964(3)	N(2)Ba(1)O(7)	54.69(7)
		O(5)Ba(1)O(7)	110.54(8)
		N(3)Ba(1)O(9)	55.71(6)
		N(3)Ba(1)O(11)	56.24(6)
		O(9)Ba(1)O(11)	111.80(6)

Table 3. (Contd.)

Bond	d, Å	Angle	ω, deg
		N(4)Co(1)N(5)	110.6(1)
		N(4)Co(1)N(6)	104.9(1)
		N(4)Co(1)N(7)	115.5(1)
		N(5)Co(1)N(6)	111.2(1)
		N(5)Co(1)N(7)	107.0(1)
		N(6)Co(1)N(7)	107.7(2)

* Symmetry codes: $^{\#1}$ $-x + 2, y, -z + 1/2$; $^{\#2}$ $-x + 1, y, -z - 1/2$ (**I**); $^{\#1}$ $-x, y, -z + 1/2$; $^{\#2}$ $-x + 1, y, -z + 3/2$ (**II**).

Table 4. Geometric parameters of hydrogen bonds in **I**–**III**

D–H···A	Distance, Å			DHA angle, deg	Symmetry code for A
	D–H	H···A	D···A		
			I		
C(3)–H···S(2)	0.93	2.92	3.539(5)	125	x, y, z
C(4)–H···S(2)	0.93	2.90	3.534(6)	127	x, y, z
			II		
C(3)–H···S(2)	0.93	2.92	3.545(5)	125	x, y, z
C(4)–H···S(2)	0.93	2.93	3.549(5)	125	x, y, z
			III		
C(22)–H···S(4)	0.93	2.88	3.568(4)	132	$-x + 1, -y, -z + 1$
C(27)–H(B)···O(3)	0.96	2.47	3.303(5)	145	$-x + 1, -y + 1, -z + 1$

Ba coordination number is 11. In **I** and **II**, both complex components are in special positions in a twofold axis, while in **III**, the molecular complex is in a general position. The Co–N interatomic distances in the Co(II) polyhedra are in the 1.934(5)–1.976(3) Å range (Table 3) and are consistent with the data for compounds containing diacetylpyridine ligands with similar anion [28]. In the complex cations of **I** and **II** or in molecular complex **III**, three organic neutral tridentate ligands L are coordinated to Ca(II), Sr(II), and Ba(II), respectively; each of these ligands forms two coupled five-membered metallacycles. The interatomic distances in the coordination polyhedra of alkaline earth metal ions in **I**–**III** are the following: Ca–N, 2.542(2), 2.544(6); Ca–O, 2.513(3)–2.549(3) (**I**); Sr–N, 2.710(3), 2.717(7); Sr–O,

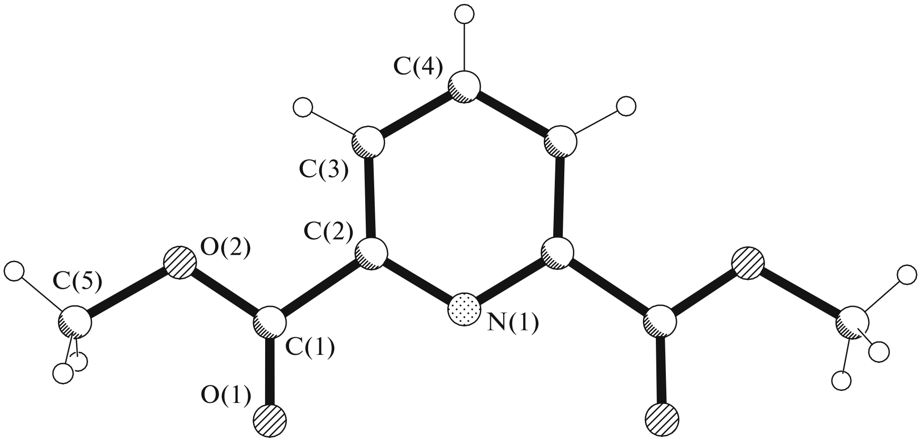

Fig. 1. Structure of compound L with indicated crystallographically independent atoms.

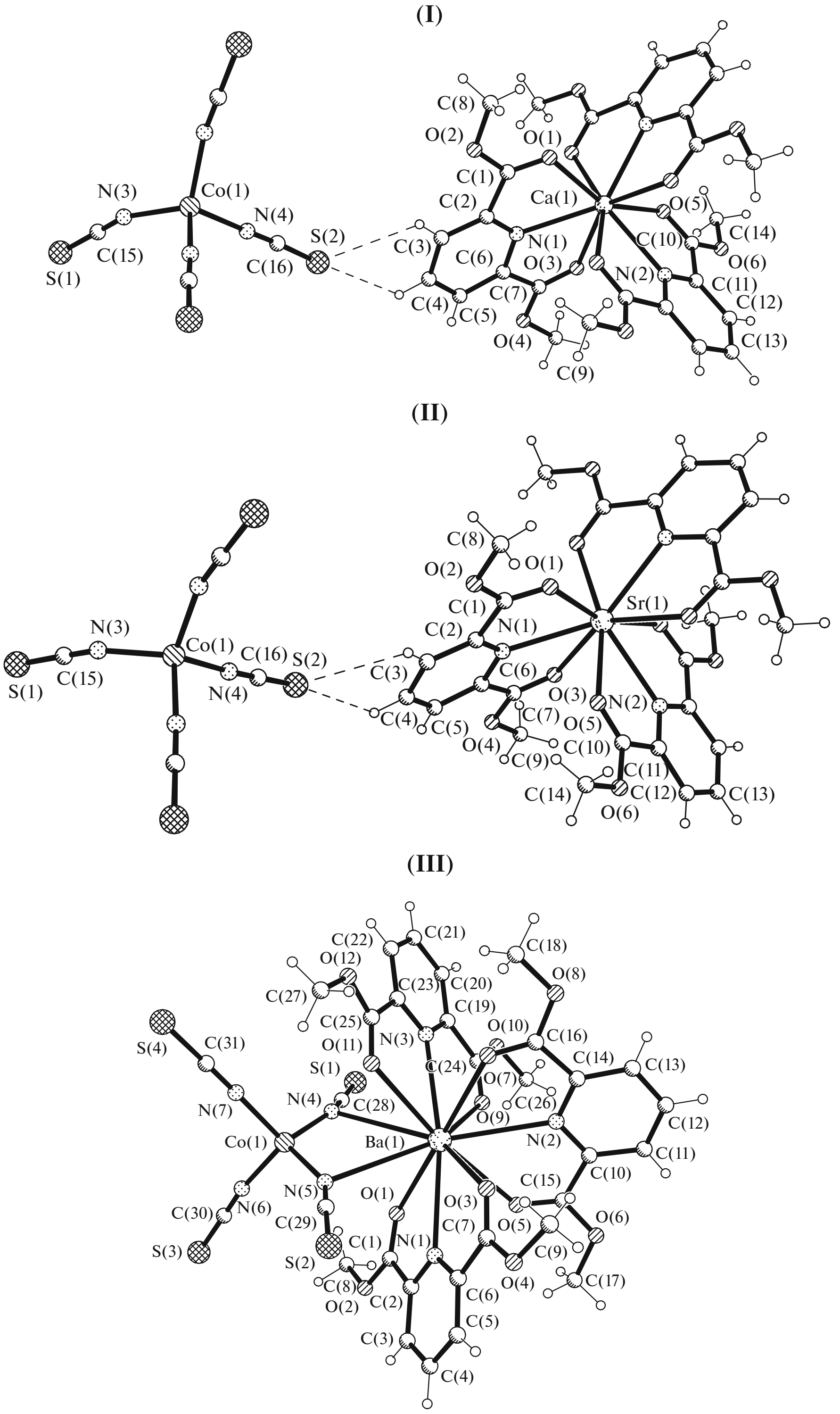

Fig. 2. Structure of compounds **I**–**III** with indicated crystallographically independent atoms.

2.23(3)–2.659(3) (**II**); Ba–N, 2.946(2)–2.984(3); Ba–O, 2.786(2)–2.877(3); Ba–N(NCS), 3.220(3), 3.325(3) Å (**III**) (Table 3). These data agree with the previously obtained distances in compounds of these metals with various similar organic ligands [29–34]. Analysis of the torsion angles in L and in **I**–**III** shows that the conformation of the coordinated L virtually does not differ from that found in the organic molecule of L.

In the crystals, the complex cations and anions in **I** and **II** and the molecular neutral complexes in **III** are

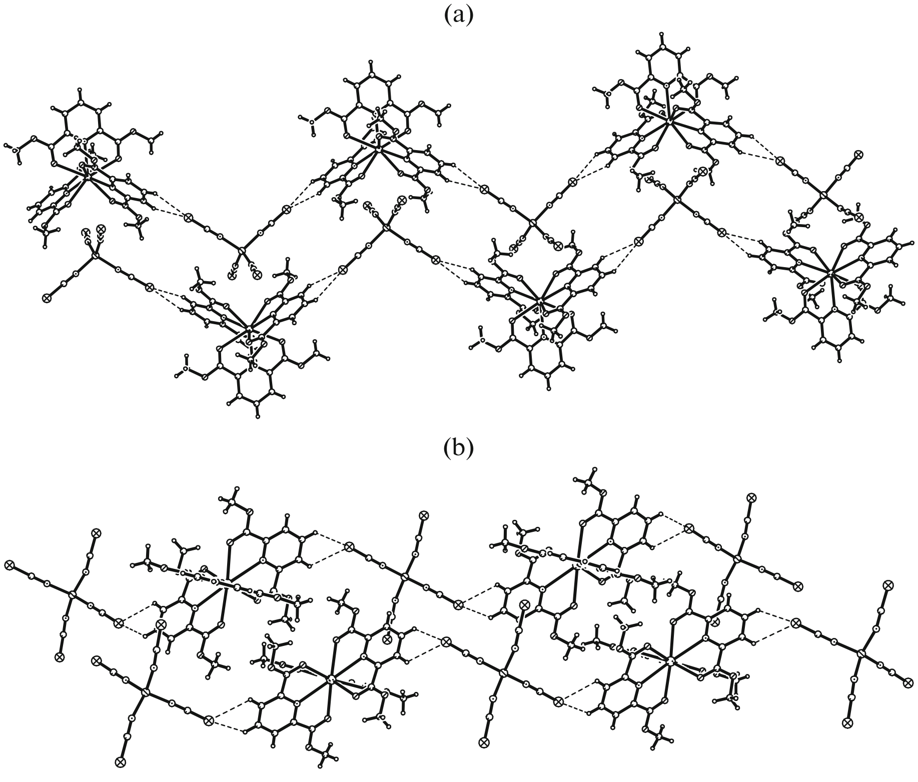

Fig. 3. Formation of chains in the crystal structures of (a) **I** and (b) **II**.

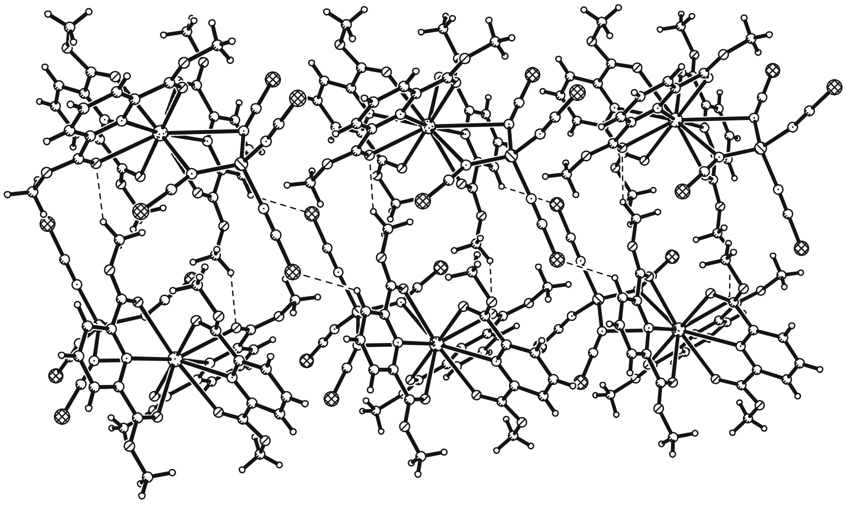

Fig. 4. Association of molecular complexes into layers in **III** by C–H···O and C–H···S hydrogen bonds.

mainly connected by weak C–H···S hydrogen bonds formed by the CH donor groups of L with the sulfur atoms of $[Co(NCS)_4]^{2-}$. In **I**–**III**, it is possible to distinguish chains composed of alternating complex cations and anions linked by C–H···S hydrogen bonds (Table 4, Figs. 3a, 3b), the parameters of which are consistent with published data [35–37]. In **III**, like in **I** and **II**, there are chains composed of molecular complexes, but they are connected by C–H···O H-bonds, which are further combined by C–H···S H-bonds (Table 4, Fig. 4).

Thus, by the reactions of various Ca(II), Sr(II), and Ba(II) salts with cobalt(II) thiocyanate and pyridine-2,6-dicarbonyl dichloride in methanol, we obtained three heterometallic complexes: $[CaL_3][Co(NCS)_4]$ (**I**), $[SrL_3][Co(NCS)_4]$ (**II**), and

$[BaCoL_3(\mu\text{-}NCS)_2(NCS\text{-}\kappa N)_2]$ (**III**) (L = dimethyl pyridine-2,6-dicarboxylate). Although in any of **I**–**III**, three tridentate ligands L are coordinated to the alkaline earth metal atoms in the same fashion, compounds **I** and **II** are ionic and are formed by the $[CaL_3]^{2+}$ or $[SrL_3]^{2+}$ complex cations, respectively, and $[Co(NCS)_4]^{2-}$ complex anions, whereas **III** is a molecular complex in which $[BaL_3]^{2+}$ and $[Co(NCS)_4]^{2-}$ components are linked by two bridging NCS^- ligands of the $[Co(NCS)_4]$ moiety.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Larson, S.B. and Dalley, N.K., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, vol. 36, p. 1201.
2. Newkome, G.R., Fronczek, A.L., Slebodnick, C., et al., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1981, vol. 37, p. 2114.
3. Huang, F., Rheingold, F.R., and Kohli, D.K., *Tetrahedron*, 2005, vol. 61, p. 10242.
4. Kumar, S., Hundal, G., Kaur, N., et al., *Tetrahedron Lett.*, 1997, vol. 38, p. 131.
5. Kumar, S., Hundal, M.S., Hundal, G., et al., *Tetrahedron*, 1997, vol. 53, p. 10841.
6. Brown, A.M., Mennie, K.M., Mason, O., et al., *Dalton Trans.*, 2017, vol. 46, p. 13376.
7. Boudalis, A.K., Raptopoulou, C.P., Psycharis, V., et al., *Eur. J. Inorg. Chem.*, 2008, p. 3796.
8. Kaboub, L., Fabre, J.-M., Vendier, L., and Legros, J.-P., *Acta Crystallogr., Sect. C: Cryst Struct. Commun.*, 2010, vol. 66, p. 2010.
9. Renaud, F., Piguet, C., Bernardinelli, G., et al., *Chem. Eur. J.*, 1997, vol. 3, p. 1660.
10. Banfi, S., Carlucci, L., Caruso, E., et al., *Dalton Trans.*, 2002, p. 2714.
11. Georgopoulou, A.N., Adam, R., Raptopoulou, C.P., et al., *Dalton Trans.*, 2010, vol. 39, p. 5020.
12. Georgopoulou, A.N., Raptopoulou, C.P., Psycharis, V., et al., *Inorg. Chem.*, 2009, vol. 48, p. 3167.
13. Hakimi, M., Moeini, K., Mardani, Z., et al., *J. Coord. Chem.*, 2013, vol. 66, p. 1129.
14. Hakimi, M., Mardani, Z., Moeini, K., and Mohr, F., *Polyhedron*, 2015, vol. 102, p. 569.
15. Pointillart, F., Bourdolle, A., Cauchy, T., et al., *Inorg. Chem.*, 2012, vol. 51, p. 978.
16. Bazhina, E.S., Gogoleva, N.V., Zorina-Tikhonova, E.N., et al., *J. Struct. Chem.*, 2019, vol. 60, no. 6, p. 855. https://doi.org/10.1134/S0022476619060015
17. Sidorov, A.A., Gogoleva, N.V., Bazhina, E.S., et al., *Pure Appl. Chem.*, 2020, vol. 92, p. 1093.
18. Allen, F.H., *Acta Crystallogr., Sect. B: Srruct. Sci.*, 2002, vol. 58, p. 380.
19. Ranganathan, D., Haridas, V., Gilardi, R., and Karle, I.L., *J. Am. Chem. Soc.*, 1998, vol. 120, p. 10793.
20. Grossel, M.C., Golden, Ch.A., Gomm, J.R., et al., *CrystEngComm*, 2001, vol. 42, p. 1.
21. Huang, J.-Yi. and Xu, W., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, vol. 62, vol. 62, p. o2653.
22. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Cryst.*, 2008, no. 1, p. 112.
23. Nakamoto, K., *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
24. Bellamy, L.J., *The Infrared Spectra of Complex Molecules*, New York: Wiley, 1958.
25. Tarasevich, B.N., *IK-spektry osnovnykh klassov organicheskikh soedinenii: spravochnye materialy* (IR Spectra of Main Classess of Inorganic Compounds. Reference Materials), Moscow: MGU, 2012.
26. Nakanishi, K., *Infrared Absorption Spectroscopy*, Tokyo: Holden-Day, 1963.
27. Adams, D.M., *Metal-Ligand and Related Vibrations: A Critical Survey of the Infrared and Raman Spectra of Metallic and Oganometallic Compounds*, London: Edward Arnold, 1967.
28. Bulhac, I., Danilescu, O., Rija, A., et al., *Russ. J. Coord. Chem.*, 2017, vol. 43, no. 1, p. 21. https://doi.org/10.1134/S1070328417010018
29. Ghadermazi, M., Derikvand, Z., Mahmouidiazar, Z., et al., *J. Coord. Chem.*, 2015, vol. 68, p. 3982.
30. Aghabozorg, H., Daneshvar, S., and Nemati, A., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2008, vol. 64, p. m1063.
31. Le, C.D., Pham, Ch.Th., and Nguyen, H.H., *Polyhedron*, 2019, vol. 173, p. 114143.
32. Soleimannejad, J., Aghabozorg, H., Hooshmand, S., and Adams, H., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, vol. 63, p. m3089.
33. Zhong, W.W., Di You-Ying, and Dou, J.M., *J. Therm. Anal. Calorim.*, 2014, vol. 115, p. 2527.
34. Saalfrank, R.W., Seitz, V., Heinemann, F.W., et al., *Dalton Trans.*, 2001, p. 599.
35. Han, S., Dai Shu-L., Chen, W.-Q., et al., *J. Coord. Chem.*, vol. 65, no. 15, p. 2751.
36. Semenaka, V.V., Nesterova, O.V., Kokozay, V.N., et al., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2011, vol. 67, p. m1021.
37. Laachir, A., Rhoufal, F., Guesmi, S., et al., *J. Mol. Struct.*, 2020, vol. 1208, p. 127892.

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