

Complex compounds of cobalt(II) salts with salicylhydrazide

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Compounds $\text{Co}(\text{SH})_2\text{X}_2 \cdot n\text{H}_2\text{O}$, where SH is salicylhydrazide $\text{C}_6\text{H}_4(\text{OH})\text{CONHNH}_2$, X is Cl^- , Br^- , NCS^- , ClO_4^- , NO_3^- , and 0.5SO_4^{2-} ; n is 2, 3 or 0.5, were prepared by a reaction of cobalt(II) salts with salicylhydrazide. Isolated compounds were identified by elemental analysis and characterized on the basis of thermogravimetric analysis, conductivity and magnetic measurements, and electronic and infrared absorption spectroscopy. Based on experimental data the conclusion was drawn that coordination sites of salicylhydrazide are carbonyl oxygen and primary amino nitrogen. Stereochemistry of these compounds is also discussed.

С помощью реакций солей двухвалентного кобальта с салицилгидразидом были приготовлены соединения типа $\text{Co}(\text{SH})_2\text{X}_2 \cdot n\text{H}_2\text{O}$, где SH обозначает салицилгидразид $\text{C}_6\text{H}_4(\text{OH})\text{CONHNH}_2$, X обозначает Cl^- , Br^- , NCS^- , ClO_4^- , NO_3^- и 0.5SO_4^{2-} ; n равняется 2, 3, или 0.5. Изолированные соединения были идентифицированы с помощью элементарного анализа и характеризованы термогравиметрическим анализом, измерением электропроводности и магнетизма а также электронными и инфракрасными спектрами. На основе экспериментальных данных было показано, что координационными местами салицилгидразида являются карбонильный кислород и азот первичной аминогруппы. Обсуждается также стереохимия приведенных соединений.

In our previous communication [1] we have presented some information on compounds of bivalent metals of the first transition group with salicylhydrazide as neutral ligand. We have also identified [2] a series of compounds of Co(II), Ni(II), and Cu(II) containing deprotonated salicylhydrazide. Recently, some new data in this field have been published [3, 4]. In this paper we shall deal with the complex compounds of cobalt(II) salts with neutral salicylhydrazide in both solid state and solution.

Experimental

All reagents used for the preparation of compounds were of anal. grade (Lachema, Brno). Cobalt(II) perchlorate and bromide were prepared by reactions of cobalt(II) carbonate with perchloric and hydrobromic acid and purified by a repeated crystallization. Cobalt(II) thiocyanate was prepared by a reaction of cobalt(II) sulfate with a stoichiometric amount of barium thiocyanate. Salicylhydrazide was prepared using the method reported elsewhere [5–7].

Table 1

Analytical data, molar conductivity, and magnetic moments

Compound	Colour	Metal content		Nitrogen content		Water content		λ_M	μ_{eff} [B.M.]
		calculated	found	calculated	found	calculated	found		
$\text{Co}(\text{SH})_2(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$	Pink	9.58	9.53					83.4 ^b	
$\text{Co}(\text{SH})_2\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$	Light blue-violet	13.30	13.26	12.65	12.42	2.03	2.0		
$\text{Co}(\text{SH})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	Dark blue-violet	12.54	12.42	11.92	11.78	7.64	6.9	50.0	5.1
$\text{Co}(\text{SH})_2\text{Br}_2 \cdot 3\text{H}_2\text{O}$	Pink-violet	10.22	10.13	9.70	9.56	9.36	8.51	60.3	
$\text{Co}(\text{SH})_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	Pink	11.27	11.16	16.07	15.95	6.89	7.06	68.7	4.9
$\text{Co}(\text{SH})_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	Pink	11.90	11.83	11.31	11.19	7.27	7.31	Insoluble	
$\text{Co}(\text{SH})_2(\text{NCS})_2 \cdot 2\text{H}_2\text{O}$	Pink-violet	11.44	11.32	16.32	16.14	6.99	6.55	46.3	4.83

a) The nitrogen and water content cannot be determined by described methods since the compound decomposes explosively under heating, therefore ClO_4^- content was determined; calculated: 32.31; found: 32.16.

b) Molar conductivity λ_M of solutions in absolute ethanol [$\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$] at temperature $25 \pm 0.02^\circ\text{C}$.

The cobalt content was determined complexometrically using murexide as indicator [8]. The nitrogen content was determined by the micromethod according to Dubský. The perchlorate content was determined by the precipitation method with nitron [9]. The water content in hydrated compounds was determined by thermogravimetric analysis.

The complex compounds of cobalt(II) salts with salicylhydrazide were prepared according to [11]. The reaction of ethanol solutions (hydrate of corresponding cobalt(II) salt and salicylhydrazide) is accompanied by a colour change which can well identify the course of reaction. Only the perchlorate compound can be prepared by free crystallization. The other compounds were prepared either by evaporation of solvent in vacuum or by precipitation with ether. With respect to its lowered solubility the compound with cobalt(II) thiocyanate was isolated from the ethanol solution. Analytical data and compositions of the prepared compounds are presented in Table 1.

The prepared compounds dissolve easily in water, ethanol, methanol, pyridine, and acetic acid; they do not dissolve in chloroform, benzene, ether, and acetone. Their crystal character was studied by the powder Debye-Scherrer method. X-ray powder photographs obtained with molybdenum radiation have a diffuse character which implies that the studied compounds are amorphous.

Thermal decomposition of components was determined using a Derivatograph instrument, System Paulik, Paulik, and Erdey (MOM, Budapest). All operations were carried out with the same sample at a temperature gradient $2.5^{\circ}\text{C}/\text{min}$, using Al_2O_3 as a standard in the temperature range $20-900^{\circ}\text{C}$.

The infrared absorption spectra were recorded using the KBr technique on an Infra-scan spectrophotometer (Hilger & Watts) in the region $4000-600\text{ cm}^{-1}$.

The electronic absorption spectra were obtained using a Spektromom 202 (MOM, Budapest) spectrophotometer. A tungsten lamp with stabilized voltage 300 V was used as a source of the primary radiation. Measured solutions with concentration between 10^{-2} and 10^{-3} M obeyed the Lambert-Beer law.

The conductivity measurements were carried out using a Kondu 4 instrument (Metra, Blansko) at $25 \pm 0.02^{\circ}\text{C}$.

Magnetic susceptibility of powder samples was determined using the Gouy method in air [10] at 298 K. $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a calibrant. Magnetic scales were supplied by the Development laboratories and workshops of Palacký University. Diamagnetic corrections were estimated from Pascal constants [10].

Results and discussion

We did not study the thermal decomposition of the perchlorate compound since this compound decomposes explosively under heating. Results for other compounds are summarized in Table 2.

The dehydration of compounds shows that with the exception of thiocyanate where dehydration is characterized by an endothermal effect at 195°C which gives evidence for strongly bonded water, in all other compounds crystal water is weakly bonded.

The burning of organic parts of all but one complex compounds starts above 200°C . The compound containing a nitrate residue starts to decompose at 160°C due to low thermal stability of nitrate and the decomposition of nitrate stimulate also an earlier decomposition of organic part.

Table 2

Thermal decomposition of the complex compounds of Co(II) salts
with salicylhydrazide

Compound	Dehydration	Burning of organic part and release of residue of inorganic acid
Co(SH) ₂ Cl ₂ · 0.5H ₂ O	40–105	200–300 [290 (-)]; 300–500 [415 (+)]
Co(SH) ₂ Cl ₂ · 2H ₂ O	50–155	200–310 [290 (-)]; 320–470 [430 (+)]
Co(SH) ₂ Br ₂ · 3H ₂ O	50–160	200–315 [300 (-)]; 300–500 [470 (+)]
Co(SH) ₂ (NO ₃) ₂ · 2H ₂ O	40–140	160–320 [180 (+), 240 (+), 270 (+)]
Co(SH) ₂ SO ₄ · 2H ₂ O	50–140	190–475 [200 (+), 290 (-), 375 (+), 435 (+)]
Co(SH) ₂ (NCS) ₂ · 2H ₂ O	130–200 [195 (-)]	200–460 [295 (-), 360 (+), 390 (+), 450 (+)]

Since the decomposition was studied with samples of about 100 mg, endoeffect typical for dehydration was not observed on DTA curves with respect to the given sensitivity of instrument. Values in brackets are maxima of exo- (+) and endo- (-) effects.

Infrared absorption spectra in the region 4000–650 cm⁻¹

The wavenumbers of absorption bands of all prepared compounds and salicylhydrazide (for comparison) are presented in Table 3.

Interpretation and evaluation of spectra is similar to that of Ni(II) compounds [11].

Three absorption bands of free ligand are in the region of stretching vibrations $\nu_{as}(\text{NH}_2)$, $\nu_s(\text{NH}_2)$, and $\nu(\text{NH})$: one broad band at 3420 cm⁻¹ and two sharp bands at 3320 and 3270 cm⁻¹, the last one being the strongest. In spectra of the complexes the highest wavenumber band practically does not change, it only takes the shape of either a shoulder or a sharp peak depending on the intensity of remaining more intense bands. In connection with the bond between metal and amino nitrogen another band of the bonded NH₂ group [12] appears at about 3150–3200 cm⁻¹ in addition to the mentioned two sharp peaks $\nu(\text{NH}_2)$. The intensity of these bands decreases with decreasing wavenumber. Furthermore, a shift to lower wavenumbers, different for the different complex compounds was observed for $\nu(\text{NH}_2)$ bands. The $\nu(\text{C}=\text{O})$ band in the region 1640–1620 cm⁻¹ is also shifted to lower wavenumbers; on the contrary, deformation vibration $\delta(\text{NH}_2)$ at about 1600 cm⁻¹ is shifted to higher wavenumbers, the shift being about 20 cm⁻¹. These shifts are connected with the bond between metal and carbohydrazide group –CO NH NH₂ with carbonyl oxygen and primary amino nitrogen as donor atoms. The band at ~1250 cm⁻¹ corresponding to the free phenolic group [13–17] is present also in spectra of the complex compounds since hydrogen is not substituted. The bands at 965 and 887 cm⁻¹ of the free ligand were assigned to stretching vibration $\nu(\text{N}-\text{N})$ [11]. The shift of electron density in metal cycle manifested itself by a shift of both bands of stretching vibration $\nu(\text{N}-\text{N})$ to higher wavenumbers 1035 and 900 cm⁻¹.

Absorption bands of ClO₄⁻ and SO₄²⁻ anions in the region 1200–900 cm⁻¹ do not correspond to their purely ionic bonding [18]. On the other hand the character of splitting does not correspond to monodentate coordination (C_{3v}) either. The bands in question are: a split ν_3 band at 1112, 1093, 1035 cm⁻¹ and a weak ν_1 band at 945 cm⁻¹ of the perchlorate compound; the broad ν_{3a} band at 1100 cm⁻¹, very

Table 3
Infrared absorption spectra of the complex compounds of Co(II) salts with
salicylhydrazide in the region 400–650 cm⁻¹; KBr technique

SH	Co(SH) ₂ Cl ₂ · 2H ₂ O	Co(SH) ₂ Cl ₂ · 0.5H ₂ O	Co(SH) ₂ Br ₂ · · 3H ₂ O	Co(SH) ₂ (ClO ₄) ₂ · · 3H ₂ O	Co(SH) ₂ (NO ₃) ₂ · 2H ₂ O	Co(SH) ₂ SO ₄ · · 2H ₂ O	Co(SH) ₂ NCS ₂ · · 2H ₂ O
3420 m	3410 s	3400 sh, s	3400 s	3420 sh, s	3100 m	3400 s	3450 b, vs 3420
3320 s	3300–3120 b, vs	3300–3130 b, vs	3300–3140 b, vs	3310–3160 b, vs	3290 b, s	3270 b, vs	3290 b, vs 3235
3270 s					3200		
3050 m					2970 w	2960	
2925 m	2940 s	2940 s	2930 m	2940 m	2930	2940 m	2940 s
2860 m	2860 m	2870 m	2860 sh, m	2870 w	2870 w	2850 m	2875 m
2760 m						2710 w	
2600 w						2590 w	
1645 s	1640 vs	1640 vs	1635 vs	1638 vs	1640 s	1640 s	2085 vs 1640 vs
1627 s	1632 vs	1630 vs	1625 vs	1625 vs	1630 s	1630 s	
1590 vs	1610 vs	1610 vs	1607 vs				
	1560 s	1565 vs	1560 s	1609 vs	1608 s	1608 vs	1612 vs
1533 vs	1534 vs	1535 vs	1530 vs	1564 s	1565 m	1563 s	1573 s
1487 vs	1495 s	1495 vs	1490 s	1530 vs	1535 m	1532 s	1540 s
1443 m	1457 m	1460 s	1455 m	1492 s	1493 m	1493 s	1500 m
	1400 w	1400 w	1400 w	1456 m	1457 w	1456 m	1460 m
	1395 w		1390 w			1395 w	1395 w
1370 s	1355 m	1355 s	1347 m	1393 w	1387 vs		
1355 s							
1305 m	1322 s	1322 s	1320 s	1349 m	1357 sh, vs	1368 m	1360 w
1256 s	1250 m	1252 s	1250 m	1321 m	1322 s	1322 m	1320 m
1242 s				1252 m	1250 m	1253 m	1255 m
1182 w	1200 s	1200 vs	1195 s	1200 s	1197 m	1200 m	1195 m
1157 w	1165 m	1167 s	1162 m	1145 vs	1165 m	1160 s	1160 w
1140 m	1131 m	1132 s	1127 m	1112 vs	1129 m		1128 m
1092 w	1103 w	1102 m	1100 w	1093 vs	1100 w	1100 b, vs	1155 w
1040 vw	1052 w	1055 w	1050 m			1055 vs	1055 w
	1036 w	1037 w	1032 m	1035 m	1036 w		1037 w
965 m				945 vw		975 w	965 vw
887 vw	902 w	903 m	900 m	902 w	903 w	903 w	900 w
	876 vw	870		867			862 vw
853 w	870						852
827 m	832 w	832 w	827 w	830 w	831 w	830 w	830 vw
798 m	795 w	798 w	792 vw	795 vw	794 w	800 w	795 vw
765 s	758 s	758 s	755 s	756 m	757 m	760 s	760 m

The values presented in Table 3 are wavenumbers of absorption maxima in cm⁻¹. Intensities of bands are denoted as follows: vs — very strong, s — strong, m — medium, w — weak, vw — very weak, sh — shoulder, b — broad band.

intense ν_{3b} bands at 1050 and 1030 cm^{-1} , and a weak ν_1 band at 970 cm^{-1} of the sulfate compound. Such splitting of bands is apparently a reflection of the semicoordination bonding of anions [19]. In the case of nitrate anion, the infrared spectrum does not give such a clear evidence for semicoordination bonding of the nitrate anions, nevertheless, the splitting of ν_3 band with a sharp maximum at 1387 cm^{-1} and a clearly visible shoulder at 1355 cm^{-1} is still apparent. The bands at 2085 cm^{-1} (ν_1 — stretching vibration CN) and 795 cm^{-1} (ν_2 — stretching vibration CS) were assigned to the thiocyanate group [20, 21]. These bands are characteristic for M—NCS type of bonding in mononuclear octahedral complex compounds [22].

The values of effective magnetic moments determined for a few compounds (see Table 1) show that in solid state the Co(II) ion has octahedral environment [10—23].

From the conductivity measurements carried out in absolute ethanol (see Table 1) it follows that the influence of the semicoordination bond, which increases with a decreasing molar conductivity from ClO_4^- to NCS^- , is manifested also in solution.

Electronic absorption spectra

As far as number, intensity, and position of absorption bands are concerned, the spectra of complex compounds of Co(II) (Table 4) are analogous to those of the corresponding Ni(II) compounds [11]. The positions and intensities of bands suggest, that the complex compounds have a deformed octahedral structure. Another evidence for lower symmetry is the magnitude of splitting of the absorption band in the near infrared region about 2500 cm^{-1} . Moreover, the sharp band in 1200 nm region is characteristic for the planar configuration of Co(II) complexes with Co— N_2O_2 arrangement [24—26]. The ν_1 absorption band was assigned to the first $d-d$ transition

Table 4

Electronic absorption spectra of solutions in absolute ethanol
in the region 350—1300 nm

Compound	ν_1^{**}				
Co(SH) ₂ (ClO ₄) ₂ · 3H ₂ O	20 000 (34.4)	13 550 (6.5)	11 000 (13.9)	9750 (19.1)	8400 (35.4)
Co(SH) ₂ Cl ₂ · 2H ₂ O	19 400 (38.9)		11 000 (22.4)	9900 (29.0)	8550 (83.5)
Co(SH) ₂ Cl ₂ · 0.5H ₂ O	19 650 (37.9)		10 850 (14.6)	9700 (19.1)	8250 (36.9)
Co(SH) ₂ Br ₂ · 3H ₂ O	20 000 (33.4)	13 700 (6.7)	11 000 (14.1)	9900 (18.2)	8550 (49.2)
Co(SH) ₂ SO ₄ · 2H ₂ O*	20 000 (24.2)	13 350 (2.7)	10 700 (5.6)	9800 (10.7)	8150 (17.9)
Co(SH) ₂ (NO ₃) ₂ · 2H ₂ O	20 000 (32.0)	13 550 (7.3)	11 000 (14.9)	9900 (19.3)	8550 (50.5)
Co(SH) ₂ (NCS) ₂ · 2H ₂ O	19 600 (99.8)	13 550 (15.8)	11 000 (30.0)	9600 (40.2)	8400 (81.2)

* Compound dissolved in mixture methanol—water 5 : 3.

** Wavenumbers ν_1' , ν_1'' , ν_1''' are maxima of the three-component absorption band corresponding to the transition ${}^4T_{2g} \leftarrow {}^4T_{1g}(F)$; ν_3 corresponds to the transition ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ in O_h symmetry [27].

of Co(II) in O_h symmetry [27]. The splitting of this band into three components is caused by a deformation of the regular octahedral field due to unequal donor atoms and influence of the axial field of anions. *trans*-Position of salicylhydrazide molecules causes apparently also the torsional deformation of Co—N₂O₂ [24]. From a correlation of the formal symmetry D_{2h} on the basis of the correlation with O_h symmetry [28, 29] and a comparison with similar effect at Ni(II) complexes [30] one can state that the ${}^4T_{2g}$ level is split in lower symmetry to three levels: $B_{1g} + B_{2g} + B_{3g}$. The position and intensity of the band in visible region corresponds to the third allowed transition (ν_3) [27] in O_h symmetry: ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$. Very weak band at $\sim 13\,500\text{ cm}^{-1}$ is very probably the spin-forbidden transition to the level from the 2G term of free ion.

If the average of ν_1 and ν_3 wavenumbers is used, the value $10 Dq = 10\,830\text{ cm}^{-1}$ for the parameter of crystal field is obtained from Lever graphs ([27], p. 393). This value is higher than the corresponding value for analogous Ni(II) complexes. With respect to the fact, that ligand field is not homogeneous, one can only conclude from this difference that the ligand field of the Co(II) complex compounds is stronger than that of analogous Ni(II) compounds.

Results of magnetic measurements (see Table 1) correspond to a high spin state of Co(II) in octahedral field [10, 23]. Values of effective magnetic moments are at upper limit of usual experimental values.

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