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HAL Id: hal-00137939

<https://hal.science/hal-00137939v1>

Submitted on 29 Sep 2020

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Crystal structure of tris(pyridine)(salicylaldehyde semicarbazonato(2-))cobalt(III)-trichloropyridinecobaltate(II) at 293 and 120 K

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(Received 15 November 2005, revised 14 May 2006)

Abstract: The crystal structure of $[\text{Co}^{\text{III}}(\text{L})(\text{py})_3][\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]$ (H_2L = salicylaldehyde semicarbazone) was determined by X-ray analysis based on two single crystal X-ray experiments performed at 120 K and 293 K, respectively. It was found that the pyridine ligand of the complex anion is disordered over two positions. The preferential position of this pyridine found at 120 K was explained in terms of the C–H...Cl intermolecular interaction between the tetrahedral $[\text{Co}^{\text{II}}(\text{py})\text{Cl}_3]^-$ anions. The *mer*-octahedral geometry of the cation in the presented crystal structure was compared with previously published structures of similar composition, $[\text{Co}^{\text{III}}(\text{L}^1)(\text{py})_3]^+[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^- \cdot \text{EtOH}$ and $[\text{Co}^{\text{III}}(\text{L}^1)(\text{py})_3]^+\text{I}_3^-$ (H_2L^1 = salicylaldehyde S-methylisothiosemicarbazone). Although the tetrahedral $[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^-$ anions possess the same charge, they mutually form different intermolecular interactions which can be realized either by C–H...Cl hydrogen bonds or by π – π interactions between the pyridine rings.

Keywords: Co(III) complexes, salicylaldehyde semicarbazone, crystal structure, low temperature X-ray experiment, disordered crystal structure.

INTRODUCTION

Metal complexes of semicarbazones and thiosemicarbazones have been studied for many years because of their structural properties,¹ analytical applications² and biological activities.³ Salicylaldehyde thiosemicarbazone is one of the most frequently used ligand from these classes of compounds.⁴

It has been reported⁵ that, depending on the reaction conditions (pH, solvent), salicylaldehyde semicarbazone (H_2L) can stabilize both the lower (+2) and the

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doi: 10.2298/JSC0701063B

higher (+3) oxidation state of cobalt, giving octahedral bis(ligand) complexes of various types: cationic, anionic, and neutral. In this paper, we present the crystal structure, determined at 293 and 120 K, of the mixed H₂L/py cobalt(III) complex of the formula [Co^{III}(L)(py)₃][Co^{II}Cl₃(py)], which represents an analog to the previously described Co(III) complexes with salicylaldehyde S-methylisothiosemicarbazone.⁶

EXPERIMENTAL

Green single crystals of the title compound were prepared by the previously described procedure.⁷

Since the X-ray analysis carried out at room temperature suggested the presence of a disordered position of the pyridine ring in the [Co^{II}Cl₃(py)]⁻ complex anion, low-temperature X-ray data collection was performed at 120 K. As could be expected, the volume of the unit cell of the low-temperature crystal structure was smaller, showing a decrease of 135 Å³ compared to that at room temperature. The unit cell decrease was most significant in the *b* axis, whereas the *a* axis almost the same at both temperatures. As a result of the small size of the single crystal, the collected X-ray data were of poor crystallographic quality, but the geometry of the complex cation and the geometry of the Co(II)-tetrahedron in the complex anion in both crystal structures were very well defined.

For the preparation of the material for publication, WinGX,⁸ PLATON,⁹ PARST¹⁰ and ORTEP¹¹ software were used. Details on the crystal structure analysis, full tables and their respective isotropic displacement parameters, torsion angles and hydrogen bonds are available from the corresponding author upon request.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 601449 and 601450 for crystal structure at 120 and 293 K, 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>).

RESULTS

Room-temperature X-ray data

Room-temperature data were collected on an Enraf-Nonius CAD-4 diffractometer,¹² using Mo K α radiation ($\lambda = 0.71069$ Å) and $\omega/2\theta$ scans in the 1.56–27.98° θ range. Cell constants and orientation matrix for data collection, obtained from 23 centered reflections in the range of 13.33–16.72°, corresponded to a monoclinic cell, the dimensions of which are given in Table I. The data were corrected for Lorentz and polarization factors.¹³

TABLE I. Crystallographic data for [Co^{III}(HL)(py)₃]⁺[Co^{II}(py)]⁻ at 293 and 120 K

	293 K	120 K
Empirical formula	C ₂₈ H ₂₇ Cl ₃ Co ₂ N ₇ O ₂	
Formula weight	717.78	
Color;habit	green;prism	
Crystal system	monoclinic	
Space group	P 2 ₁ /c	

TABLE I. Continued

	293 K	120 K
Unit cell dimensions		
$a/\text{\AA}$	13.797(4)	13.7421(5)
$b/\text{\AA}$	12.103(3)	11.8929(5)
$c/\text{\AA}$	19.988(7)	19.5539(7)
$\alpha/\text{\AA}$	90	90
$\beta/\text{\AA}$	108.51(2)	108.506(2)
$\gamma/\text{\AA}$	90	90
$V/\text{\AA}^3$	3165(1)	3030.5(2)
Z		4
$D_{\text{calc}}/\text{Mg m}^{-3}$	1.506	1.573
Absorption coefficient/ mm^{-1}	1.339	1.398
Reflections collected	7818	58170
Independent reflections	7601	10015
Data for $I > 2\sigma(I)$	3881	4026

The structure was solved by the heavy atom^{14a} and difference Fourier methods, and refined on F^2 by the full-matrix least-square method.^{10b} All H atoms were placed at the calculated positions. Idealized H atoms were refined with isotropic displacement parameters set to 1.2 times the equivalent isotropic U value of the parent atom.

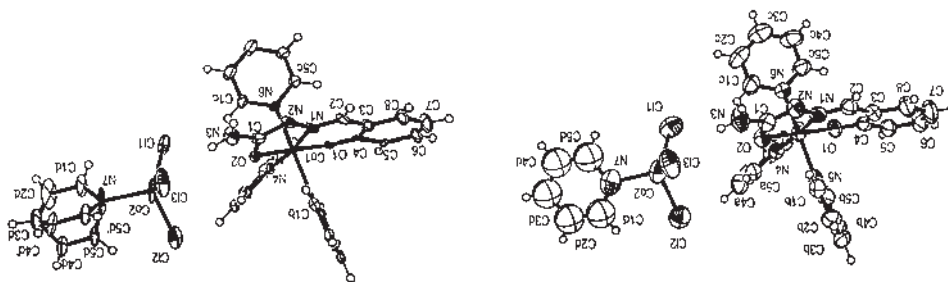


Fig. 1. An ORTEP representation of the title compound at 293 and 120 K (left and right halve, respectively). Displacement ellipsoids are drawn at the 50 % probability level for non-H atoms.

It was established that the pyridine ligand from the complex anion is in a disordered position, which could not be resolved from difference Fourier maps. Hence, the positions of the atoms in the pyridine were treated with a constrained model using the AFIX 66 command in SHELXL97,^{4b} whereby the C–C and N–C distances were fixed to 1.39 Å. The N7 atom was taken as the 'pivot atom' of a rigid group defined by the C1d–C5d atoms. The pyridine atoms were constrained to be coplanar

(Fig. 1, left) and during the refinement all atoms were with fixed isotropic *ADP* (atomic displacement parameters) of $0.15 \text{ (\AA}^2\text{)}$. The remaining non-hydrogen atoms, including the N7 atom from the disordered pyridine molecule, were successfully refined with anisotropic *ADP*. Final agreement indices for 339 parameters were: $S = 0.973$, $wR(F^2) = 0.2629$ for all data and $R1 = 0.0790$ for data with $I > 2\sigma(I)$.

Low-temperature X-ray data

Low-temperature data were collected on a Bruker SMART CCD three-circle diffractometer at $120(1) \text{ K}$, using Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The low temperature was attained by an evaporating liquid nitrogen flux over the crystal, provided by an Oxford Cryosystem device. The data collection nominally covered the full hemisphere of reciprocal space by a combination of eight sets of exposures with the CCD area detector held at three 2θ swing angles ($0, 35$ and -35°). The crystal-to-detector distance of the data collection was 5.12 cm . The reciprocal space was scanned by $0.2^\circ \omega$ steps at a different φ for each set of runs. Over 5000 frames were collected with 30 s and 60 s time of exposure for runs at 2θ swing angles of 0 and 35° . The Lorentz-polarization correction and the integration of the diffracted intensities were performed with the SAINT software package.¹⁵ Until cell parameters were obtained from 1853 selected reflections,¹⁵ and they are given in Table I.

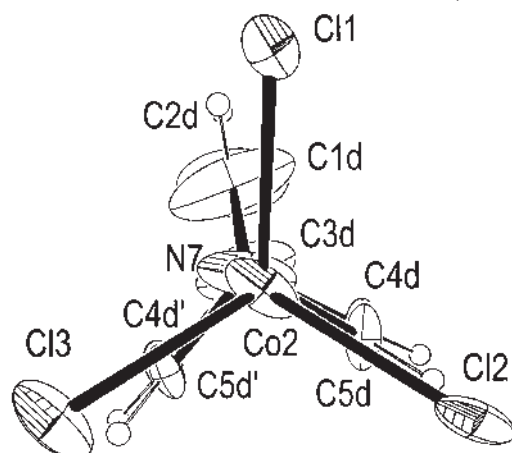


Fig. 2. Two preferential positions of N7-pyridine (N7-C1d-C2d-C3d-C4d and N7-C1-C2-C3-C4) determined from the low-temperature X-ray experiment.

During the crystal structure determination and refinement, it was observed that disordered behavior of pyridine of complex anion can be described by the model shown in Fig. 1 (right half of the Figure) and Fig. 2. The C4d and C5d atoms are presented with two positions, respectively, and occupation numbers of 0.5. This model is in very good agreement with the difference Fourier maps, and it was also proved by the refinement procedure, whereby all pyridine atoms were successfully refined with anisotropic temperature parameters without any geometrical constrain. Based on this result (established geometry and anisotropic *ADP*), it can be concluded that the pyridine ring exists (oscillates) in the two preferential posi-

tion shown in Fig. 2. The remaining atoms in the low-temperature crystal structure of $[\text{Co}^{\text{III}}(\text{HL})(\text{py})_3]^+[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^-$ are treated as described for the room-temperature data. The values of the temperature factors of non-hydrogen atoms were approximately 2.5 times smaller than those found for the room-temperature crystal structure (Fig. 1). Final agreement indices for 397 refined parameters were: $S = 1.074$, $wR(F^2) = 0.2901$ for all data and $R1 = 0.1179$ for data with $I > 2\sigma(I)$ [$R1 = 0.0836$ for data with $I > 3\sigma(I)$].

DISCUSSION

The cobalt atom has a slightly distorted octahedral coordination composed of three pyridine molecules with the tridentate ONO salicylaldehyde semicarbazone ligand L bonded to the metal atom in a *mer* configuration. L coordinates to the metal atom as a double deprotonated ligand (deprotonation of the phenolic hydroxyl and enolic form of the semicarbazide residue) with the formation of two fused chelate rings: the six-membered CoOCCCN and five-membered CoNNCO (Fig. 1). In the crystal packing, the complex cations, $[\text{Co}^{\text{III}}(\text{HL})(\text{py})_3]^+$ form a dimer through two $\text{N3-H}\dots\text{N2}$ hydrogen bonds between neighboring semicarbazone fragments (Fig. 3): $\text{N3-H} = 0.86 \text{ \AA}$, $\text{H}\dots\text{N2} = 2.21 \text{ \AA}$, $\text{N3-H}\dots\text{N2} = 174^\circ$ and $\text{N3-H} = 0.86 \text{ \AA}$, $\text{H}\dots\text{N2(i)} = 2.19 \text{ \AA}$, $\text{N3-H}\dots\text{N2} = 168^\circ$ for the structure at 293 and 120 K respectively; symmetry code: $-x+1, -y+1, -z$. Another H atom from the amine group participates in the $\text{N3-H}\dots\text{Cl3}$ hydrogen bond to the complex anion: $\text{N3-H} = 0.86 \text{ \AA}$, $\text{H}\dots\text{Cl3} = 2.49 \text{ \AA}$, $\text{N3-H}\dots\text{Cl3} = 169^\circ$ and $\text{N3-H} = 0.86 \text{ \AA}$, $\text{H}\dots\text{Cl3} = 2.40 \text{ \AA}$, $\text{N3-H}\dots\text{Cl3} = 172^\circ$ in the structure observed at 293 and 120 K, respectively. The quoted intermolecular hydrogen bonds are with an expected shorter H...acceptor distance in the crystal structure at 120 K. Selected geometric parameters for the crystal structure of $[\text{Co}^{\text{III}}(\text{HL})(\text{py})_3]^+[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^-$ at 293 and 120 K are presented in Table II.

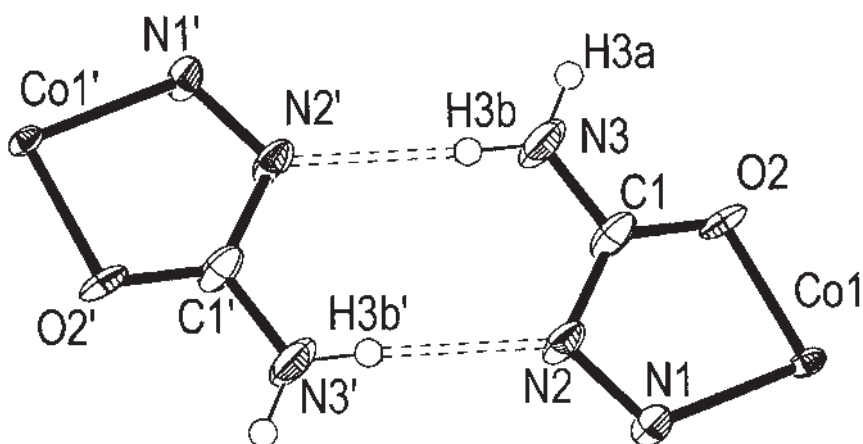


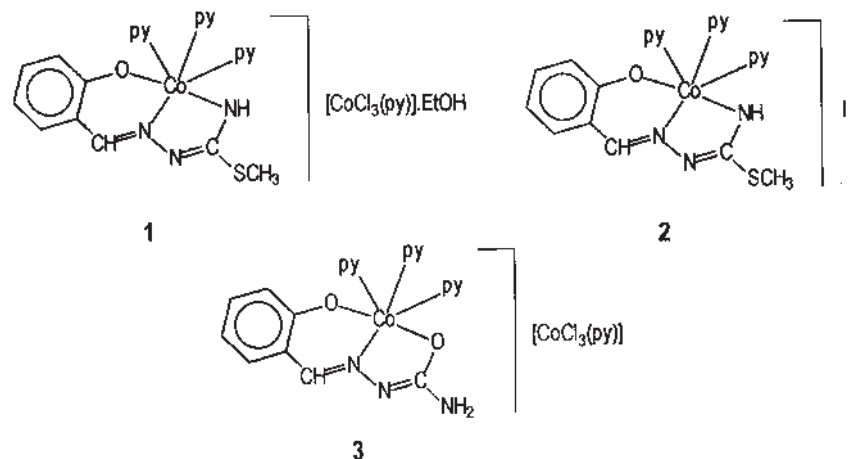
Fig. 3. Crystal lattice fragment representing the $\text{N3-H}\dots\text{N2}$ hydrogen-bonded dimer.

TABLE II. Selected geometric parameters (Å, °) for $[\text{Co}^{\text{III}}(\text{HL})(\text{py})_3]^+[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^-$ at 293 and 120 K

Bonds	293 K	120 K	Angles	293 K	120 K
Co1–O1	1.862(4)	1.844(5)	O1–Co1–O2	178.2(2)	177.9(3)
Co1–O2	1.891(4)	1.854(5)	O1–Co1–N1	95.6(2)	96.7(3)
Co1–N1	1.865(5)	1.892(8)	O1–Co1–N4	87.7(2)	87.5(2)
Co1–N4	1.978(5)	1.955(7)	O1–Co1–N5	88.4(2)	87.1(2)
Co1–N5	1.965(5)	1.962(7)	O1–Co1–N6	91.2(2)	92.6(3)
Co1–N6	1.967(5)	1.959(7)	O2–Co1–N4	94.0(2)	92.9(3)
O1–C4	1.327(7)	1.310(9)	O2–Co1–N5	90.8(2)	90.8(3)
N1–C2	1.277(8)	1.278(11)	O2–Co1–N6	89.6(2)	89.5(3)
N1–N2	1.399(7)	1.354(9)	N1–Co1–O2	82.8(2)	89.5(3)
N3–C1	1.340(8)	1.311(10)	N1–Co1–N4	176.1(2)	174.5(3)
C1–N2	1.320(8)	1.351(11)	N1–Co1–N5	90.4(2)	91.2(3)
O2–C1	1.291(7)	1.295(11)	N1–Co1–N6	90.0(2)	88.7(3)
C2–C3	1.452(9)	1.431(12)	N5–Co1–N4	91.7(2)	92.6(3)
C3–C4	1.427(9)	1.424(12)	N5–Co1–N6	170.4(2)	179.6(3)
Co2–N7	2.022(7)	2.024(8)	N6–Co1–N4	87.9(2)	87.6(3)
Co2–C11	2.258(3)	2.244(3)	N7–Co2–C11	108.6(3)	108.6(3)
Co2–C12	2.251(3)	2.234(4)	N7–Co2–C12	98.1(3)	101.6(4)
Co2–C13	2.252(2)	2.262(3)	N7–Co2–C13	113.2(3)	108.1(4)
			C12–Co2–C11	113.14(9)	114.8(1)
			C13–Co2–C11	111.0(1)	111.5(1)
			C12–Co2–C13	112.1(1)	111.7(1)

In a previous paper,⁶ the crystal structure were presented of two metal complexes, $[\text{Co}^{\text{III}}(\text{HL}^1)(\text{py})_3]^+[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^- \cdot \text{EtOH}$ (complex 1) and $[\text{Co}^{\text{III}}(\text{HL}^1)(\text{py})_3]^+\text{I}_3^-$ (complex 2) ($\text{H}_2\text{L}^1 = \text{salicylaldehyde S-methylisothiosemicarbazone}$), with the complex cation almost identical to the one in the present crystal structure of $[\text{Co}^{\text{III}}(\text{HL})(\text{py})_3]^+[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^-$ (complex 3). The geometry of the complex cations in 1 and 2 and the mutual orientations of the pyridines were studied by quantum chemical calculations and analysis of geometrical parameter from X-ray crystal structure analysis. It was shown that the intramolecular interactions in the complex action are responsible for the orientations of the coordinated ligands, regardless of the different anions and lattice packing in 1 and 2. In complex 3, the tridentate ligand is different in its terminal part from that in complexes 1 and 2 (Scheme 1). Namely, the S–Me group from 1 and 2 is replaced by an oxygen atom, hence the coordination set is ONO instead of ONN (in 1 and 2).

Generally, the geometry of the complex cation, bond lengths, bond angles and conformation of the chelate rings in compound 3 are very similar to those for com-



Scheme 1. Structures of $[\text{Co}^{\text{III}}(\text{L})(\text{py})_3][\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]$ (1), $[\text{Co}^{\text{III}}(\text{L}^1)(\text{py})_3]^+[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^- \cdot \text{EtOH}$ (2) and $[\text{Co}^{\text{III}}(\text{L}^1)(\text{py})_3]^+\text{I}_3^-$ (3).

plexes 1 and 2, the main difference being in the complex cation, *i.e.*, in the orientation of the equatorially coordinated pyridine. This orientation can be compared by analyzing the angle between the mean planes of the pyridine ring and the equatorial coordination plane. This angle for complex 3 is $29.4(3)^\circ$, while for complexes 1 and 2 it is $35.6(2)^\circ$ and $35.4(2)^\circ$, respectively. This difference could be explained by coordination of the O2 atom in complex 3 instead of the N–H group (complexes 1 and 2). Consequently, in complex 3, two C–H...O interligand interactions exist, yielding smaller torsion angles around the Co–N4 bond (in 1 and 2, only one C–H...O interaction exists). The two quoted C–H...O interactions have H...O1 and H...O2 distances of 2.30 and 2.51 Å, respectively.

The axially coordinated pyridines have an orthogonal orientation as was observed in previous crystal structures,⁶ and they are with similar angles between the mean planes of the axial pyridines. As a result of the above difference in orientation of the equatorial pyridine, the position of the axially coordinated pyridines is somewhat different from that observed in complexes 1 and 2. The C1b–N5–N6–C1c torsion angle is $75(1)^\circ$, which is by about 9° smaller than in complexes 1 and 2, where this angle is almost the same for both crystal structures. Consequently, in complex 3, the N6-axial pyridine realizes two C–H...O interactions with H...O1 and H...O2 distances of 2.45 and 2.42 Å, respectively.

It is interesting to compare the crystal structures of complexes 1 and 3. They possess the same complex anion, $[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^-$ and very similar complex cations (see the scheme above). Although the two compounds (1 and 3) crystallize in different crystal systems, their complex anions are oriented in a similar way (alternately to each other with respect to the Co–pyridine bond), giving rise to mutual intermolecular interactions in both crystal structures. However, the intermolecular interactions between the anions in 1 and 3 are of a completely different type. Thus,

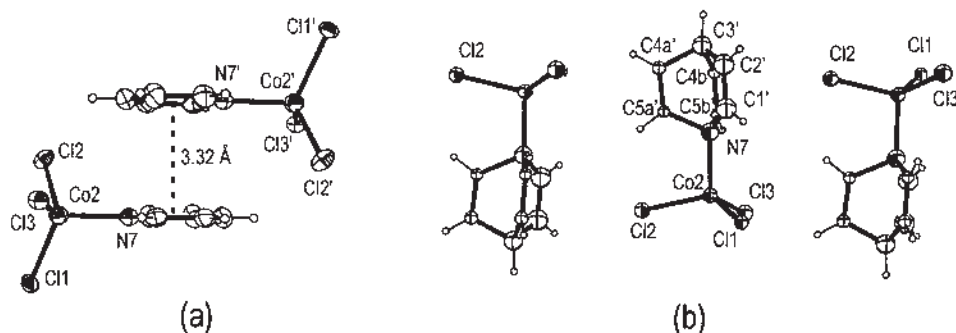


Fig. 4. (a) The π - π interaction between neighboring complex anions in the $[\text{Co}^{\text{III}}(\text{HL})(\text{py})_3]^+[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^- \cdot \text{EtOH}$ complex; (b) Crystal lattice fragment representing the mutual orientation of neighboring complex anions in the title compound.

in the crystal lattice of complex 1, the pyridines from the neighboring complex anions are parallel to each other, forming π - π interactions with a short distance of 3.32 Å between the ring planes (Fig. 4a). On the contrary, in the crystal packing of complex 3, the orientation of the same pyridines is not parallel, forming intermolecular hydrogen bonds with the neighboring complex anions (Fig. 4b). Hence, these intermolecular hydrogen bonds could be responsible for the disordered position of the pyridine from the complex anion. The low-temperature X-ray experiment showed that the N7-pyridine exists in the two preferential positions presented in Fig. 2. Both positions enable intermolecular and intramolecular H...Cl interactions.

Acknowledgement: This work was financially supported by the Ministry of Science and Environmental Protection of the Republic of Serbia (Project No. 142028B – 'Synthesis, physical, structural and biological characteristics of new complex compounds').

ИЗВОД

КРИСТАЛНА СТРУКТУРА

ТРИС(ПИРИДИН)(СЕМИКАРБАЗОНСАЛИЦИЛАЛДЕХИДАТО(2-))КО- БАЛТ(III)ТРИХЛОРО-ПИРИДИНКОБАЛТАТА(II)

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Рендгенском структурном анализом одређена је кристална структура комплекса $[\text{Co}^{\text{III}}(\text{L})(\text{py})_3][\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]$ (H_2L = семикарбазон салицилалдехида) на 293 и 120 К. Нађена је неуређеност положаја пиридинског лиганда у комплексном аниону. Два преферентна положаја овог пиридина, идентификована на 120 К, објашњена су постојањем молекуларних интеракција између тетраедарских $[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^-$ аниона. Геометрија катјона

у овој структури упоређена је са раније публикованим кристалним структурама сличног састава $[\text{Co}^{\text{III}}(\text{L}^1)(\text{py})_3]^+[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^- \cdot \text{EtOH}$ и $[\text{Co}^{\text{III}}(\text{L}^1)(\text{py})_3]^+\text{I}_3^-$ ($\text{H}_2\text{L}^1 = \text{S}$ -метилизотиосемикарбазон салицилалдехид). Иако $[\text{Co}^{\text{II}}\text{Cl}_3(\text{py})]^-$ анјони имају исто наелектрисање, они узајамно ступају у молекулске интеракције које могу да се реализују преко C–H...Cl водоничних веза или π – π интеракција између пиридинских прстенова.

(Примљено 15. новембра 2005, ревидирано 14. маја 2006)

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