Tetrahedral and Octahedral Cobalt(II) in the Structure of Tris(pyridine)(salicylaldehyde *S*-methylisothiosemicarbazonato)cobalt(II) Trichloro(pyridine)cobaltate(II)

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Abstract

$[Co^{II}(C_5H_5N)_3(C_9H_{10}N_3OS)][Co^{II}(C_5H_5N)Cl_3]$, $C_{24}H_{25}CoN_6OS^+.C_5H_5Cl_3CoN^-$, $M_r = 748.9$, triclinic, $P\bar{1}$, $a = 9.005$ (1), $b = 11.832$ (7), $c = 16.864$ (8) Å, $\alpha = 100.34$ (2), $\beta = 92.38$ (2), $\gamma = 94.27$ (2)°, $V = 1760$ (1) Å^3, $D_c = 1.41$, $D_m = 1.45$ Mg m^{-3}, $Z = 2$, $\mu(Mo\,K\alpha) = 12.96$ mm^{-1}, $F(000) = 764$. The structure was refined to $R = 0.063$ for 3003 unique observed reflections. The two independent Co atoms have different coordinations: octahedral in the complex cation $[Co^{II}(HL)(py)_3]^+$ (py = pyridine) and tetrahedral in the anion $[Co^{II}Cl_3(py)]^-$, where HL is the tridentate (NNO) salicylaldehyde *S*-methylisothiosemicarbazonato ligand. Magnetic measurements (at 298 K) ($\mu_{eff} = 3.18$ BM, 1 BM $\equiv 9.27 \times 10^{-24}$ J T^{-1}) indicate that the tetrahedral and octahedral Co^{II} atoms are in high- and low-spin states respectively.

Introduction

The tridentate salicylaldehyde *S*-methylisothiosemicarbazone ligand (H$_2L$), HO—C$_6$H$_4$—CH=N—N=C(—NH$_2$)—SCH$_3$, forms complexes with some transition metals (Leovac, 1978; Leovac, Gerbeleu & Revenko, 1978; Gerbeleu, Turte, Canić, Leovac & Arion, 1980). It has been shown that this tridentate NNO ligand, by reaction with Co^{III} salts, gives octahedral bis(ligand)Co^{III} complexes of general formula $[Co(HL)_2]X.nH_2O$, where X = Cl$^-$, Br$^-$, I$^-$, (NO$_3$)$^-$, (ClO$_4$)$^-$ and HL = [O—C$_6$H$_4$—CH=N—N=C(—NH$_2$)—SCH$_3$]$^-$. All these complexes are brown in colour and diamagnetic. However, by reaction of an alcoholic solution of CoCl$_2$.6H$_2$O with H$_2L$ and pyridine, dark-green paramagnetic crystals are formed whose formula, on the basis of the elemental analysis, is Co$_2^{II}$(HL)(py)$_4$Cl$_3$.

The effective magnetic moment of this compound per one Co^{II} ion is 3.18 BM. The compound is soluble in organic solvents (methanol, ethanol, acetone, dimethylformamide) and the molar conductivity of a 10^{-3} mol dm^{-3} solution in absolute ethanol is 44 Ω^{-1} cm^2 mol^{-1} at room temperature, indicating a 1:1 electrolyte (Geary, 1971). In view of the possibly different stereochemistry of Co^{II} the above data are not sufficient to define the nature of the complex, so an X-ray analysis of its crystals has been performed.

2 cm^3 of pyridine and 10 cm^3 of ethanol were added to a mixture of 1.2 g (5 mmol) of CoCl$_2$.6H$_2$O and 1.0 g (5 mmol) of salicylaldehyde *S*-methylisothiosemicarbazone. By stirring and mild heating the reactants dissolved and dark-green, plate-like crystals were formed. After cooling to room temperature the crystals were filtered and washed out with ethanol and ether. The yield was 1.2 g. The substance is soluble in acetone, less soluble in methanol and ethanol and insoluble in ether. The results of the elemental analysis are (calculated values in parentheses): Co 15.28 (15.74), C 46.29 (46.51), H 4.13 (4.04), N 13.51 (13.09), Cl 14.28% (14.20).

Preliminary Weissenberg and oscillation photographs showed triclinic symmetry. Accurate cell dimensions were obtained by least squares from the setting angles of 25 reflections with $2\theta > 30°$. Intensities were collected on an automated Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation and the ω–2θ scan mode. Of the 4385 unique reflections recorded with $2\theta \le 50°$, 3003 were regarded as observed [$I \ge 4\sigma(I)$] and subsequently used for the structure determination and refinement. Correction for Lorentz and polarization effects was applied but not for absorption. The intensity statistics indicated the centrosymmetric space group $P\bar{1}$ as most likely. Measurements of the magnetic susceptibility were carried out at 298 K.

The structure was solved by the heavy-atom method. A three-dimensional Patterson function was used to locate the positions of the two symmetry-independent Co atoms. Successive cycles of Fourier and difference Fourier synthesis revealed the positions of all non-H atoms. Full-matrix least-squares refinement with isotropic temperature factors gave an R value of 0.11.

Table 1. *Final fractional coordinates* ($\times 10^4$, $\times 10^3$ *for* H) *and isotropic temperature parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}/B (Å^2)
Co(1)	136 (2)	3480 (1)	2411 (1)	2·40 (4)
Co(2)	7036 (2)	736 (1)	7034 (1)	3·63 (4)
Cl(1)	9187 (4)	566 (3)	6394 (2)	4·70 (9)
Cl(2)	7310 (4)	2190 (3)	8102 (2)	5·14 (10)
Cl(3)	5954 (4)	−899 (3)	7329 (2)	5·19 (10)
S	4593 (4)	4144 (3)	3610 (2)	3·79 (9)
O	−1829 (8)	3800 (6)	2136 (4)	2·7 (2)
N(1)	2109 (10)	3241 (7)	2725 (5)	2·9 (2)
N(2)	2247 (10)	5223 (7)	3229 (5)	2·5 (3)
N(3)	841 (10)	5049 (7)	2817 (5)	2·4 (2)
N(4)	691 (10)	3656 (7)	1330 (5)	2·7 (2)
N(5)	−441 (10)	1842 (7)	2002 (5)	2·7 (2)
N(6)	−469 (10)	3305 (7)	3490 (5)	2·7 (2)
N(7)	5521 (10)	1092 (7)	6189 (6)	3·4 (3)
C(1)	2817 (10)	4206 (10)	3151 (6)	2·7 (3)
C(2)	5214 (10)	5651 (11)	3915 (8)	4·2 (4)
C(3)	154 (10)	5926 (9)	2745 (6)	2·7 (3)
C(4)	−1330 (10)	5890 (9)	2374 (6)	2·3 (3)
C(5)	−1906 (10)	6927 (9)	2328 (7)	3·0 (4)
C(6)	−3332 (10)	6965 (9)	2018 (7)	3·2 (4)
C(7)	−4208 (10)	5961 (10)	1752 (7)	3·9 (3)
C(8)	−3687 (10)	4924 (9)	1779 (7)	3·4 (3)
C(9)	−2215 (10)	4874 (9)	2114 (6)	2·4 (3)
C(10)	1970 (10)	4249 (11)	1208 (7)	3·3 (3)
C(11)	2310 (20)	4417 (11)	448 (7)	4·5 (4)
C(12)	1363 (20)	3934 (12)	−212 (7)	4·7 (4)
C(13)	32 (20)	3307 (11)	−80 (7)	4·0 (4)
C(14)	−270 (10)	3207 (10)	687 (6)	3·1 (3)
C(15)	501 (10)	1149 (10)	1615 (7)	3·3 (3)
C(16)	118 (20)	−24 (10)	1322 (8)	4·6 (6)
C(17)	−1361 (20)	−448 (10)	1371 (9)	4·4 (7)
C(18)	−2326 (10)	228 (9)	1747 (8)	3·8 (5)
C(19)	−1843 (10)	1363 (10)	2067 (7)	3·5 (3)
C(20)	−55 (10)	2438 (9)	3845 (7)	3·3 (3)
C(21)	−410 (10)	2344 (10)	4618 (7)	3·7 (3)
C(22)	−1176 (10)	3182 (11)	5057 (7)	3·7 (3)
C(23)	−1589 (10)	4056 (10)	4703 (7)	3·5 (3)
C(24)	−1255 (10)	4118 (10)	3947 (6)	3·0 (3)
C(25)	4048 (10)	1036 (11)	6276 (7)	4·4 (4)
C(26)	3037 (20)	1281 (13)	5713 (7)	4·6 (4)
C(27)	3495 (20)	1528 (12)	5058 (8)	5·3 (4)
C(28)	4989 (20)	1605 (10)	4898 (7)	4·3 (4)
C(29)	5959 (10)	1368 (10)	5485 (7)	4·1 (4)
H(2A)	629	584	391	5·5
H(2B)	492	590	446	5·5
H(2C)	472	608	355	5·5
H(N1)	268	264	268	4·0
H(N2)	272	595	352	3·6
H(3)	65	666	295	3·7
H(5)	−129	766	252	4·0
H(6)	−372	771	197	4·3
H(7)	−522	596	154	4·8
H(8)	−432	419	157	4·2
H(10)	266	456	168	4·2
H(11)	322	485	39	5·5
H(12)	164	402	−75	5·5
H(13)	−64	295	−52	4·9
H(14)	−121	285	80	4·1
H(15)	151	148	152	4·3
H(16)	86	−51	106	5·5
H(17)	−166	−125	113	5·6
H(18)	−335	−5	181	4·9
H(19)	−257	186	234	4·1

Table 1 (*cont.*)

	x	y	z	B (Å^2)
H(20)	52	187	354	4·4
H(21)	−13	169	485	4·7
H(22)	−144	315	560	4·4
H(23)	−214	466	499	4·5
H(24)	−150	435	343	3·9
H(25)	368	81	677	5·5
H(26)	199	126	579	5·8
H(27)	284	168	461	6·1
H(28)	540	184	440	5·6
H(29)	706	144	540	5·2

Anisotropic vibrational parameters were then assigned and further refinement lowered the R value to 0·075. The positions of all H atoms were located from a difference map and their coordinates and isotropic temperature factors were included in the calculations with all parameters fixed. After application of a weighting scheme [$w = 1/\sigma^2(F)$, where $\sigma(F)$ is the standard deviation in the observed amplitudes based on counting statistics] and a correction for extinction effects [the refined value is $g = 6·7$ (2) $\times 10^{-7}$] the final R was 0·063. Atomic scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are listed in Table 1.*

Discussion

On the basis of the X-ray crystal analysis the structural formula of the title compound can be written as [Co^{II}(HL)(py)$_3$][Co^{II}Cl$_3$(py)]. The Co atoms adopt two coordination geometries in the asymmetric unit (Fig. 1). Coordination around Co(1) is slightly distorted octahedral [right angles 81·6 (6)–95·4 (5)°] and involves five N atoms [1·889 (9)–1·963 (7) Å] from the chelate HL ligand and the pyridine groups and one O [1·893 (7) Å] from the chelate ligand. The Co(1) octahedron is weakly compressed along the O–N(1) direction and assumes *mer* configuration. Unlike Co(1), Co(2) is in a tetrahedral environment formed by three Cl atoms [2·246 (3)–2·261 (3) Å] and one pyridine N [2·052 (9) Å]. A search in the files of the Cambridge Crystallographic Data Centre showed that this is the first time this kind of coordination (3Cl + N) has been found in a complex containing Co as a central atom, though the presence in the same compound of octahedral and tetrahedral Co ions has also been found in the structures of CoCl$_2$.2½C$_2$H$_5$OH (Bkouche-Waksman & L'Haridon, 1977) and [Co(H$_2$O)$_6$]-
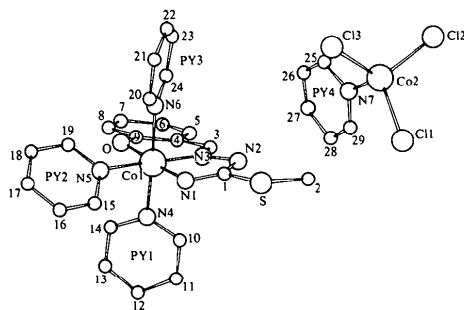
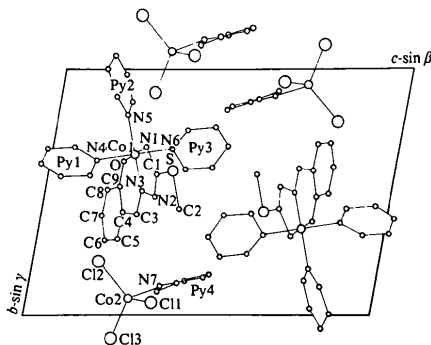Fig. 1. A perspective drawing of the complex ions.

Fig. 2. The content of a unit cell projected along **a**.

[CoCl_4]–18-crown-6–acetone (Vance, Holt, Piernot & Holt, 1980). The X-ray crystal structure explains the value of the molar conductivity and the magnetic moment (3·18 BM) which corresponds well to the average of μ_{eff} for low-spin octahedral (1·80–1·85 BM) and high-spin tetrahedral (4·4–4·8 BM) Co^{II} complexes (Day & Selbin, 1969). The shortest distance between neighbouring ions is 3·37 (1) Å and it is found for the contacts N(2)···C(22) ($\bar{x}$, 1 − y, 1 − z) and N(1)···Cl(3)(1 − x, $\bar{y}$, 1 − z), the latter corresponding to a van der Waals interaction. The molecular packing is shown in Fig. 2.

The interatomic distances (Table 2) Co(2)—Cl and Co(2)—N(7) in the tetrahedral anion are in good agreement with those found in the structures of dichlorobis(4-methylpyridine)cobalt(II) (Laing & Carr, 1975), CoCl_2.2½C_2H_5OH (Bkouche-Waksman & L'Haridon, 1977) and [Co(H_2O)_6][CoCl_4]–18-crown-6–acetone (Vance et al., 1980). The bond distance Co(2)—N(7) is significantly longer (about 0·1 Å) compared to the corresponding Co(1)—N(py) bond distances of the complex cation.

Salicylaldehyde S-methylisothiosemicarbazone takes part in the coordination as a tridentate NNO ligand with the OH group deprotonated as found in the structures of chloro(salicylaldehyde S-methylisothio-semicarbazonato)copper(II) (Biyskin, Gerasimov & Belov, 1981), ammonium (salicyaldehyde S-methyliso-thiosemicarbazonato)dioxovanadate(V) monohydrate

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Octahedron

Co(1)—O	1·893 (7)	Co(1)—N(4)	1·953 (7)
Co(1)—N(1)	1·889 (9)	Co(1)—N(5)	1·960 (8)
Co(1)—N(3)	1·911 (8)	Co(1)—N(6)	1·963 (7)

N(1)—Co(1)—O	176·8 (5)	N(4)—Co(1)—N(3)	90·1 (6)
N(3)—Co(1)—N(5)	175·9 (6)	N(4)—Co(1)—N(5)	89·4 (6)
N(4)—Co(1)—N(6)	178·6 (6)	N(4)—Co(1)—O	88·9 (5)
N(1)—Co(1)—N(3)	81·6 (6)	N(6)—Co(1)—N(1)	89·1 (6)
N(1)—Co(1)—N(5)	94·4 (6)	N(6)—Co(1)—N(3)	90·2 (6)
N(3)—Co(1)—O	95·4 (5)	N(6)—Co(1)—N(5)	90·4 (6)
N(5)—Co(1)—O	88·6 (5)	N(6)—Co(1)—O	89·8 (5)
N(4)—Co(1)—N(1)	92·2 (6)		

Tetrahedron

Co(2)—Cl(1)	2·261 (4)	Co(2)—Cl(3)	2·246 (3)
Co(2)—Cl(2)	2·248 (3)	Co(2)—N(7)	2·052 (9)

Cl(1)—Co(2)—Cl(2)	110·6 (2)	Cl(2)—Co(2)—Cl(3)	113·0 (2)
Cl(1)—Co(2)—Cl(3)	115·8 (2)	Cl(2)—Co(2)—N(7)	110·2 (4)
Cl(1)—Co(2)—N(7)	104·8 (2)	Cl(3)—Co(2)—N(7)	101·5 (4)

Chelate ligand

S—C(1)	1·76 (1)	C(4)—C(5)	1·38 (1)
S—C(2)	1·80 (1)	C(4)—C(9)	1·38 (1)
C(1)—N(1)	1·34 (1)	C(5)—C(6)	1·37 (2)
C(1)—N(2)	1·33 (1)	C(6)—C(7)	1·37 (2)
N(2)—N(3)	1·40 (1)	C(7)—C(8)	1·35 (2)
N(3)—C(3)	1·27 (1)	C(8)—C(9)	1·43 (2)
C(3)—C(4)	1·45 (2)	C(9)—O	1·35 (1)

C(2)—S—C(1)	102·0 (9)	C(3)—C(4)—C(5)	118 (2)
N(1)—C(1)—N(2)	123 (2)	C(3)—C(4)—C(9)	123 (2)
N(1)—C(1)—S	119 (1)	C(5)—C(4)—C(9)	119 (2)
N(2)—C(1)—S	118 (1)	C(4)—C(5)—C(6)	121 (2)
N(3)—N(2)—C(1)	108 (1)	C(5)—C(6)—C(7)	120 (2)
Co(1)—N(1)—C(1)	111 (1)	C(6)—C(7)—C(8)	121 (2)
Co(1)—N(3)—N(2)	116 (1)	C(7)—C(8)—C(9)	120 (2)
Co(1)—N(3)—C(3)	126 (1)	C(8)—C(9)—O	115 (1)
Co(1)—O—C(9)	123 (1)	C(4)—C(9)—O	126 (2)
N(2)—N(3)—C(3)	118 (1)	C(4)—C(9)—C(8)	119 (2)
N(3)—C(3)—C(4)	125 (2)		

Pyridine(1)

N(4)—C(10)	1·35 (2)	C(12)—C(13)	1·41 (2)
C(10)—C(11)	1·38 (1)	C(13)—C(14)	1·36 (1)
C(11)—C(12)	1·38 (2)	C(14)—N(4)	1·36 (1)

mean ∠ = 120·1

Pyridine(2)

N(5)—C(15)	1·33 (1)	C(17)—C(18)	1·33 (2)
C(15)—C(16)	1·40 (2)	C(18)—C(19)	1·39 (2)
C(16)—C(17)	1·40 (2)	C(19)—N(5)	1·36 (1)

mean ∠ = 120·4

Pyridine(3)

N(6)—C(20)	1·35 (1)	C(22)—C(23)	1·35 (2)
C(20)—C(21)	1·38 (1)	C(23)—C(24)	1·34 (1)
C(21)—C(22)	1·37 (2)	C(24)—N(6)	1·38 (1)

mean ∠ = 120·4

Pyridine(4)

N(7)—C(25)	1·34 (2)	C(27)—C(28)	1·38 (2)
C(25)—C(26)	1·37 (2)	C(28)—C(29)	1·37 (2)
C(26)—C(27)	1·27 (1)	C(29)—N(7)	1·35 (1)

mean ∠ = 120·6

(Ribár, Kozmidis-Petrović & Leovac, 1980) and (o-phenanthroline)(salicylaldehyde S-methylisothiosemi-carbazonato)copper(II) nitrate (Petrović, Carić, Leovac & Canić, 1979). Bond distances and angles in the chelating ligand are in good agreement with those found in these compounds. It is worth noting that the Co(1)–N(1) distance is slightly (but not significantly, $\Delta/\sigma = 1\cdot83$) shorter than Co(1)–N(3), and the same difference has been observed for the other transition-metal complexes of S-methylisothiosemi-carbazones.

As a consequence of chelation five- and six-membered metallocycles are formed in which the displacements from the best planes do not exceed 0·08 Å. The dihedral angle between these planes is 8·0°. The angles between the benzene ring and the six- and five-membered metallocycles are 2·6 and 10·3° respectively. The py(1) and py(3) planes are approximately perpendicular to each other and to the best plane through N(1), N(3), N(5) and O. The py(2) ring forms an angle of 34·5° with this plane and it is nearly perpendicular to the plane through N(1), N(4), N(6) and O. The py(4) plane is approximately a symmetry plane for the Cl(2)–Co(2)–Cl(3) angle, while Cl(1) is located closely to this plane. The torsion angle C(29)–N(7)–Co(2)–Cl(1) is 11 (1)°.

The imido form for the thiosemicarbazide fragment [···N–N(–H)–C(–NH)–SCH₃] of the ligand, characteristic for all S-methyl derivatives of thio-semicarbazides and thiosemicarbazones (Divjaković, Ribár, Leovac & Gerbeleu, 1981), has been confirmed. The double bond is delocalized along N(1)–C(1)–N(2) as indicated by the values of the distances C(1)–N(1) and C(1)–N(2) which are practically equal and intermediate between single and double bonds. The imido

form of the ligand is also substantiated by the positions of the H atoms: in the difference Fourier map around N(1) there is only one maximum which may correspond to an H atom. Furthermore, there is a maximum at a distance of 0·97 Å from N(2) which can be ascribed to an H atom, supposedly transferred, during the complex formation, from the N(1)H₂ group to the hydrazine N(2).

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Low-Temperature Crystallization of Orthorhombic Ferrocene: Structure Analysis at 98 K

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Abstract

Single crystals of the new low-temperature modification of ferrocene, isomorphous with ruthenocene, have been obtained by crystallization at temperatures below 110 K. Once formed, the crystals can be warmed to about 275 K before transformation to the monoclinic phase occurs. The structure of orthorhombic ferrocene has been determined at 98 K: $Fe(C_5H_5)_2$, $M_r = 186\cdot0$, $a = 6\cdot987$ (6), $b = 8\cdot995$ (7), $c = 12\cdot196$ (5) Å, $U =$

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