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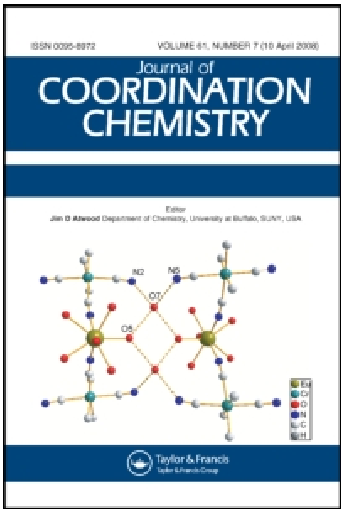

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Synthesis, Spectra, Thermal Analysis and Crystal Structure of *Trans*-Bis(2-Pyridinepropanol)Bis (Saccharinato)Cobalt(II)

Sevim Hamamci[a]; Veysel T. Yilmaz[a]; William T. A. Harrison[b]
[a] Department of Chemistry Faculty of Arts and Sciences, Ondokuz Mayis University, Kurupelit, Samsun, Turkey [b] Department of Chemistry, University of Aberdeen, Aberdeen, Scotland, UK

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SYNTHESIS, SPECTRA, THERMAL ANALYSIS AND CRYSTAL STRUCTURE OF *TRANS*-BIS(2-PYRIDINEPROPANOL)BIS (SACCHARINATO)COBALT(II)

SEVIM HAMAMCI[a], VEYSEL T. YILMAZ[a,*] and WILLIAM T.A. HARRISON[b]

[a]*Department of Chemistry, Faculty of Arts and Sciences,*
Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey;
[b]*Department of Chemistry, University of Aberdeen, Meston Walk,*
Aberdeen AB24 3UE, Scotland, UK

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The title complex, $[Co(pypr)_2(sac)_2]$ (pypr = 2-pyridinepropanol and sac = saccharinate), has been prepared and characterized by elemental analysis, electronic and FTIR spectra, magnetic susceptibility measurements, thermal analysis and X-ray diffractometry. The complex crystallizes in triclinic space group $P\bar{1}$ with $a = 8.1836(2)$, $b = 10.0062(2)$, $c = 10.4989(3)$ Å, $\alpha = 90.474(1)$, $\beta = 107.989(1)$ and $\gamma = 110.923(1)^\circ$. The cobalt(II) ion sits on a center of symmetry and is octahedrally coordinated by two pypr and two sac ligands. Both pypr and sac ligands occupy the *trans* positions of the coordination octahedron. The two pypr ligands are neutral and act as bidentate N- and O-donor ligands forming two symmetry-related seven-membered chelate rings around the cobalt(II) ion, while both sac ligands are O-coordinated through the carbonyl oxygen atoms. On heating the endothermic removal of two pypr ligands occurs in the first stages of decomposition and at higher temperatures the Co/sac intermediate decomposes to Co_3O_4 and finally to CoO.

Keywords: Cobalt(II); 2-Pyridinepropanol; Saccharinate; X-ray structure

INTRODUCTION

Metal complexes of the saccharinate anion [sac = $(C_7H_4NO_3S)^-$] have received much attention, largely because of the commercial use of its sodium salt as a non-caloric artificial sweetening agent. Sac has three donor groups, namely carbonyl, sulfonyl and the negatively charged imino nitrogen, and is able to coordinate to different metal ions rather easily through any of these moieties. Sac can act as a mono- or bidentate ligand and in some cases as a bridging ligand between two metal centers. The most common coordination mode of sac is ligation through the negatively charged nitrogen atom, usually observed in the aqua bis(saccharinato) complexes of metal(II), whereas O-bonding occurs in the case of alkaline, alkaline earth and p-block metals [1–4].

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*Corresponding author. Tel.: + 90-362-457-6020/(5116). Fax: +90-362-457 6081.
E-mail: vtyilmaz@omu.edu.tr

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In some cases, the sac ligands exhibit ambidentate coordination behavior; one is N-bonded and the other is O-bonded within the same coordination octahedron. This behavior is usually observed in transition metal–sac complexes with pyridine (py) or substituted py derivatives [5–8].

We are developing our previous work on the preparation and characterization of metal complexes of the polyfunctional sac ligand in the presence of other N- and O-donor co-ligands especially with hydroxyalkyl groups. In this article, we report the synthesis, spectral, thermal and structural characterization of a new cobalt(II) complex of sac with 2-pyridinepropanol (pypr), $[Co(pypr)_2(sac)_2]$.

EXPERIMENTAL

Physical Measurements

2-Pyridinepropanol (pypr), sodium saccharinate dihydrate, and $CoSO_4 \cdot 7H_2O$ were purchased from Merck. All other analytical grade chemicals and solvents were purchased commercially and used as received.

Electronic spectra were measured on a Unicam UV2 spectrophotometer in 4×10^{-3} M methanol in the 200–900 nm range. IR spectra were recorded on a Shimadzu FTIR8900 spectrophotometer as KBr pellets. Room temperature magnetic susceptibility measurements were carried out using a Sherwood Scientific MXI model Gouy magnetic balance. The C, H, N and S contents were determined on a Vario EL Elemental Analyzer. Thermal analysis curves (TG, DTA and DTG) were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere. A sample size of 5–10 mg and a heating rate of 10° C min^{-1} were used.

Preparation of $[Co(pypr)_2(sac)_2]$

The starting complex, $[Co(sac)_2(H_2O)_4] \cdot 2H_2O$, was prepared according to the literature method [9]. $[Co(sac)_2(H_2O)_4] \cdot 2H_2O$ (1.0 mmol, 0.53 g) was dissolved in 30 mL of butanol at *ca.* 60°C and mixed with the liquid pypr ligand (2.0 mmol, 0.27 g). The resulting solution was left to stand at room temperature and allowed to evaporate slowly; pink, block-shaped, crystals formed within three days. The crystals were collected by suction filtration, washed with acetone and dried in air.

Yield 65%. Anal. Calcd. for $C_{30}H_{30}N_4O_8S_2Co$ (%): C, 51.6; H, 4.3; N, 8.0; S 9.3. Found: C, 51.2; H, 4.4; N, 7.9; S 9.8.

Crystal Structure Determination

A suitable crystal of the cobalt(II) complex was mounted on a glass fiber and X-ray diffraction data were recorded on a Enraf–Nonius Kappa CCD area detector at 120 ± 2 K. The determination of unit cell and intensity data collection were performed with Mo Kα radiation ($\lambda = 0.71073$ Å). The details of crystal data, data collection and structure refinement are listed in Table I. The structure was solved by direct methods (SHELXS97) [10] and refined by a full-matrix least-squares procedure on F^2 using SHELXL97 [11]. All non-hydrogen atoms were refined with anisotropic parameters. The O–H hydrogen atom was located from a difference map and refined by riding in its as-found position. All the H atoms bonded to C were refined by riding in idealized positions.

TABLE I Crystallographic parameters for $[Co(pypr)_2(sac)_2]$

Parameter	$[Co(pypr)_2(sac)_2]$
Empirical formula	$C_{30}H_{30}N_4O_8S_2Co$
Molecular weight	697.63
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.1836(2)
b (Å)	10.0062(2)
c (Å)	10.4989(3)
α (°)	90.474(1)
β (°)	107.989(1)
γ (°)	110.923(1)
V (Å^3)	756.94(3)
Z	1
D_{calcd} (g cm^{-3})	1.530
μ (mm^{-1})	0.763
F (000)	361
Crystal size (mm^3)	$0.14 \times 0.24 \times 0.28$
θ range (°)	3.11–27.49°
Index ranges	$-10 \leq h \leq 10$; $-12 \leq k \leq 12$; $-13 \leq l \leq 13$
Reflections collected	11247
Independent reflections	3444 [R(int) = 0.0410]
Reflections observed ($>2\sigma$)	2907
Absorption correction	multi-scan
Max. and min. transmissions	0.815 and 0.901
Data/restraints/parameters	3444/0/206
Goodness-of-fit on F^2	1.073
R [$I > 2\sigma(I)$]	$R_1 = 0.0315$, $wR_2 = 0.0719$
R (all data)	$R_1 = 0.0422$, $wR_2 = 0.0764$
Largest diff. peak and hole (e Å^{-3})	0.350 and −0.476

RESULTS AND DISCUSSION

Synthesis

The title complex was synthesized from the direct reaction of $[Co(sac)_2(H_2O)_4] \cdot 2H_2O$, with the pypr ligand in solution. The addition of the bidentate pypr ligand to the solution of the starting cobalt(II) complex resulted in the substitution of all aqua ligands. The cobalt(II) complex was obtained in a reasonable yield of 65% and the analytical data are consistent with the proposed formulation of the complex, and also confirmed by X-ray crystallography as reported in this article. The complex does not melt but decomposes at 183°C, as shown as a sharp peak in DTA curves. The title complex is soluble in water and methanol at room temperature and in warm ethanol and isopropanol.

Crystal Structure

The molecular structure of the complex is shown in Fig. 1 with the atom-numbering scheme. Selected bond lengths and angles together with hydrogen bonding geometry are listed in Table II. The structure of the complex consists of individual neutral molecules of $[Co(sac)_2(pypr)_2]$ in which the cobalt(II) ion lies on a center of symmetry and is octahedrally coordinated by two pypr and two sac ligands, forming a CoO_4N_2

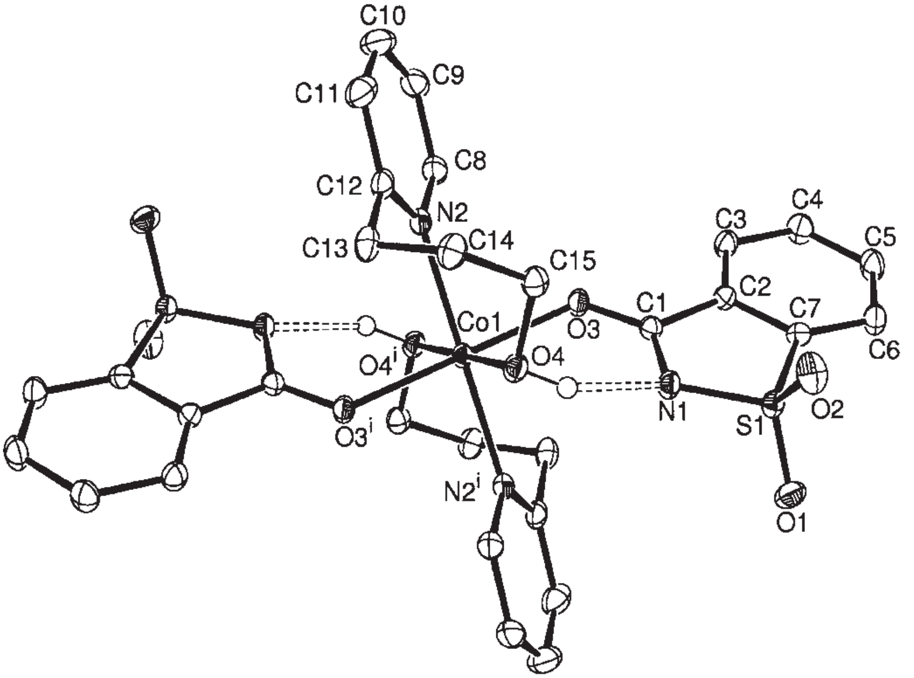

FIGURE 1 ORTEP plot of $[Co(pypr)_2(sac)_2]$ [symmetry code: (a) $-x$, $-y$,$-z$].

TABLE II Selected bond and hydrogen bond geometrical data for $[Co(pypr)_2(sac)_2]$[a]

Bond distances (Å) *and angles* (°)				
Co–N(2)	2.1558(14)	O(4)–Co–N(2)	92.53(5)	
Co–O(3)	2.0946(11)	O(4)–Co–N(2)[a]	87.47(5)	
Co–O(4)	2.1626(12)	O(3)–Co–O(4)	86.53(4)	
O(3)–Co–N(2)	86.64(5)	O(3)–Co–O(4)[a]	93.47(4)	
O(3)–Co–N(2)[a]	93.36(5)			
Hydrogen bonding				
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	<DHA (°)
O(4)–H(4)···N(1)	0.87	1.86	2.685(2)	156
C(9)–H(9)···O(1)[b]	0.95	2.44	3.310(2)	152
C(5)–H(5)···π(1)[c, e]	0.95	3.01	3.83	145
C(10)–H(10)···π(2)[d, e]	0.95	3.07	3.71	125
C(11)–H(11)···π(3)[d, e]	0.95	3.02	3.89	154

Symmetry transformations used to generate equivalent atoms:

[a] $-x$, $-y$,$-z$.

[b] $1+x$, $1+y$, z;

[c] $1-x$, $-y$, $1-z$;

[d] x, $1+y$, z;

[e] π refers to the ring centroids defined by the following atoms: π(1) = N(2), C(8), C(9), C(10), C(11), C(12); π(2) = C(2), C(3), C(4), C(5), C(6), C(7); π(3) = C(1), C(2), C(7), S(1), N(1).

core. Both pypr and sac ligands occupy the trans positions of the coordination octahedron. The two pypr ligands are neutral and act as bidentate N- and O-donor ligands forming two symmetry-related seven-membered chelate rings around the cobalt(II) ion, while both sac ligands are O-coordinated through the carbonyl oxygen atoms. It is well known that sac usually interacts with transition metal ions through its deprotonated nitrogen atom and coordination *via* the carbonyl oxygen is rare.

$[V(sac)_2(py)_4]\cdot 2py$ [12] and $[Ni(sac)_2(py)_4]\cdot 2py$ [13] are the only examples, which show the same coordination behavior of sac as found in the title complex. It appears that steric hindrance of the propanol group of pypr prevents coordination of sac through the N atom.

The average Co–N bond distance is 2.1558(14) Å, while the Co–O_{pypr} and Co–O_{sac} distances are 2.11626(12) and 2.0946(11) Å, respectively. The Co–O_{sac} distance of 2.0946(11) Å is slightly longer than the values found in $[Co(sac–O)(sac–N)(mpy)_2]$ [2.0640(11) Å] [7], where mpy is 2-pyridylmethanol. The *cis* angles range from 86.53(4) to 93.47(4)° and indicate significant distortion of the coordination octahedron around the cobalt(II) ion, especially at the O(3)–Co–N(2) and O(3)–Co–O(4)^{i} angles.

Both pypr and sac rings are essentially planar, as expected. The C(13) atom is almost in the same plane as the py ring of pypr, but the C(14), C(15) and O(4) atoms ($–CH_2–CH_2–OH$ group) deviate from the plane [N(2), C(8)–C(12)] of the pypr ligand by 1.48, 2.23 and 1.48 Å, respectively.

The structure contains a number of hydrogen bonds as shown in Fig. 2 and Table II. The hydroxyl hydrogen atom of pypr forms a strong intramolecular hydrogen bond with the nitrogen atom of sac. The individual molecules of the present complex are connected by weak intermolecular C–H···O type hydrogen bonds between a ring hydrogen atom [C(9)–H(9)] of pypr and the sulfonyl O atoms of sac in the adjacent molecules. Furthermore, some ring hydrogen atoms of the pypr and sac moieties are

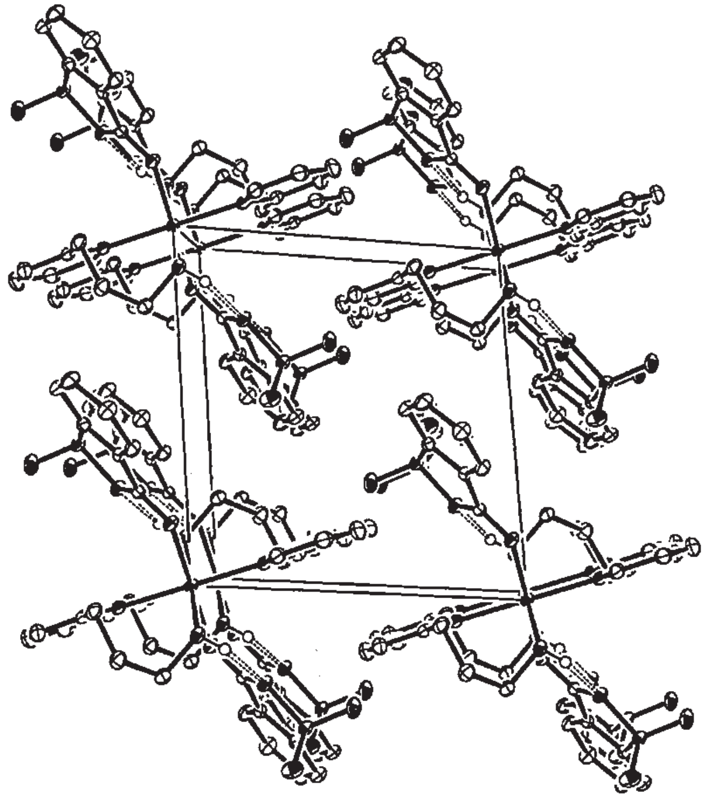

FIGURE 2 Packing diagram of $[Co(pypr)_2(sac)_2]$ viewed down the [100] direction.

also involved in weak interactions of the C–H$\cdots\pi$ type (Table II). These hydrogen bonds and interactions result in a packing of the molecules in a three-dimensional network.

Spectroscopic and Magnetic Properties

The broad absorption bands between 3550 and 3300 cm^{-1} are attributed to the ν(OH) vibrations of both the hydroxyl groups involved in coordination and hydrogen bonding. The comparatively weak bands in the range 2800 and 3000 cm^{-1} are due to the vibrations of the CH_2 groups of the pypr ligand. The stretching vibration of C=N of the pyridine ring at *ca.* 1600 cm^{-1} was not clearly observed because of the overlap of the ν(C=O) vibration of the sac ions. The ν(C=O) vibration of sac appears at 1608 cm^{-1} as a very strong band. The absorption bands of $Na(sac) \cdot H_2O$ and $[Co(sac)_2(H_2O)_4] \cdot 2H_2O$ are observed at 1642 and 1626 cm^{-1}, respectively. The significant shift in the carbonyl frequency of the present complex clearly indicates coordination of sac through the carbonyl group. The stretching vibrations of $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$ occur at *ca.* 1305 and 1167 cm^{-1}, respectively. The bands for the SO_2 moiety of the title complex are comparable to those of the corresponding saccharinate complex with mpy [7].

In the electronic spectrum of the title compound, the intense peaks between 220 and 300 nm are assigned to π–π* transitions of the pypr and sac ligands, respectively. The broad band at 510 nm is assigned to d–d transitions for the octahedral cobalt(II) species.

The room temperature magnetic moment of the title complex of 4.2 BM is somewhat higher than the calculated spin-only value of 3.87 BM, suggesting an orbital contribution for the high-spin d^7 octahedral configuration.

Thermal Analysis

Thermal properties of the cobalt(II) complex were followed up to 1000°C in a static air atmosphere. The complex begins to decompose at 130°C. The elimination of two pypr ligands takes place in two stages in the temperature range 130–220°C and 250–360°C with three endothermic DTA peaks at 183, 325 and 345°C. The experimental mass loss value of *ca.* 19.5% for each stage is consistent with the calculated value of 19.6%. The intermediate, probably $Co(sac)_2$, formed at around 350°C, is unstable and undergoes further decomposition in two stages. The stage between 365 and 450°C is endothermic and corresponds to the degradation of one sac ion with a mass loss of 25.4% (calcd. 26.1%). The decomposition of the residue is violently exothermic and mass-loss calculations suggest that the product formed at 550°C is Co_3O_4, which further decomposes to the end product CoO at 900°C.

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Supplementary Data

Crystallographic data (atomic coordinates, atomic displacement parameters and bond geometries) for the structure reported in the article have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary material with a deposition number CCDC 203163. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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