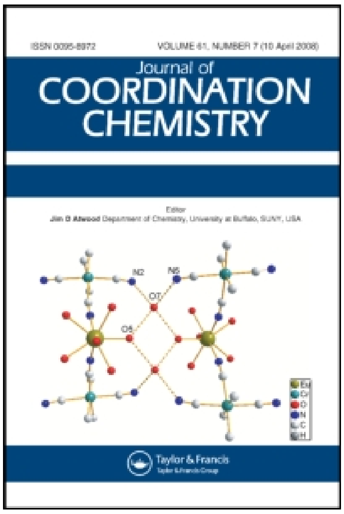

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Synthesis and Structural Characterization of the Co(III) Complex with 2'-[1-(2-Pyridinyl)-Ethylidene]-Oxamohydrazide (Hapsox): The Crystal Structure of Bis-{2'-[1-(2-Pyridinyl)-Ethylidene]-Oxamohydrazido} Cobalt(III) Perchlorate, $[Co(apsox)_2]ClO_4$

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE Co(III) COMPLEX WITH 2′-[1-(2-PYRIDINYL)-ETHYLIDENE]-OXAMOHYDRAZIDE (Hapsox): THE CRYSTAL STRUCTURE OF BIS-{2′-[1-(2-PYRIDINYL)-ETHYLIDENE]-OXAMOHYDRAZIDO} COBALT(III) PERCHLORATE, [Co(apsox)$_2$]ClO$_4$

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The synthesis of a novel ligand 2′-[1-(2-pyridinyl)-ethylidene]-oxamohydrazide (Hapsox), from a series of 2-acetylpyridine acylhydrazones, and its complex with Co(III), which is the first in this series of complexes are described. Both the ligand and the complex were characterized by elemental analysis, IR, ^{1}H-NMR, and ^{13}C-NMR spectra, and the structure of the complex [Co(apsox)$_2$]ClO$_4$ was determined by X-ray structural analysis. It was established that [Co(apsox)$_2$]ClO$_4$ has an octahedral geometry with two tridentate apsox ligands in monoanionic form. Structural characteristics, lengths of the bonds, and angles between the bonds were typical for Co(III) complexes of distorted octahedral geometry. Both direct and template synthesis afforded the same geometrical isomer of the complex with two apsox ligands meridionally bound to the central metal ion, even in the case when equimolar quantities of Co(ClO$_4$)$_2$ and Hapsox were applied.

Keywords: Co(III) complex; 2-Acetylpyridine derivative; IR spectra; NMR spectra; X-ray analysis; Crystal structure

INTRODUCTION

Our long-term studies have focused on the chemistry of complexes with hydrazone ligand systems [1–7]. Our interest in this topic is based on increasing applications of transition metal complexes with both hydrazides and hydrazones in medicine, analytical chemistry, catalysis of oxido-reduction processes, as well as in many other fields of science and technology [8,9]. Many hydrazones possess biological activity which is in

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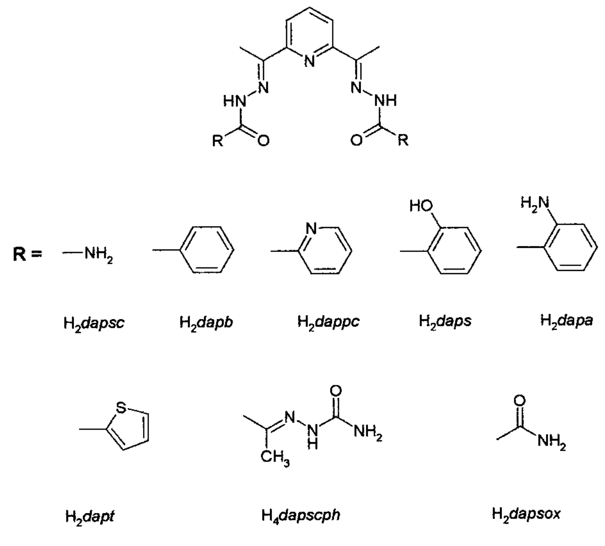
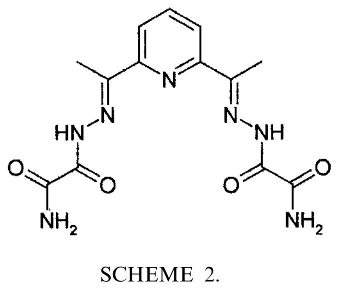
some cases much more pronounced upon complex formation with transition metals. This has prompted their application as antitumor, antiviral, bactericide, and psychotropic agents [8]. In our previous work complexes of Mo(VI), Mo(V), Cu(II), Fe(III), Co(II), Mn(II), and Zn(II) [1–7] with hydrazone ligands were investigated, as well as their biological activity [3]. Biological activity of this class of organic compounds can be intensified not only by careful choice of the metal ion, but also by condensing hydrazides with pharmacologically active carbonyl compounds.

Continuing our studies in this field [10–12] with ligands based on bis(acylhydrazone) 2,6-diacetylpyridine (Scheme 1), we synthesized $2',2'''$-(2,6-pyridindiyl-diethylidyne)-dioxamohydrazide (H_2dapsox) (Scheme 2). Our previous studies of 2,6-diacetylpyridine bis(acylhydrazones) as ligands were focused on H_2dapsox [5,6]. If a suitable central metal atom is chosen, this ligand, as well as similar ligands, coordinates in planar pentadentate fashion, forming four five-membered chelate rings around the central metal atom and imposing the relatively rare pentagonal bipyramidal (PBP) geometry. The advantage of this ligand system (Scheme 2) is in a high flexibility of the side chains of the ligand so that there is the possibility of six-membered ring formation in the equatorial plane. Taking into account the eleven potential donor atoms in the H_2dapsox ligand and the possibility of either single or double deprotonation, the total number of theoretically possible structural and geometrical isomers of the complexes is 29 [1].

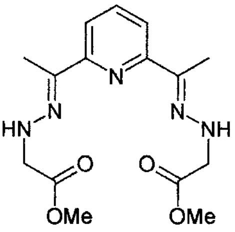


SCHEME 1.



SCHEME 2.

Further modification of ligand systems of this type was directed to the formation of 2,6-bis[1-(methoxycarbonylmethylhydrazono)ethyl]pyridine (H_2dapmeha), (Scheme 3). Replacement of one carbonyl group in the H_2dapsox ligand by a $>CH_2$ group resulted in predominantly trigonal bipyramidal (TBP) geometry, where the polydentate ligand is coordinated via the pyridine and two hydrazone nitrogen atoms, the remaining two coordination sites being occupied by solvent molecules [4].



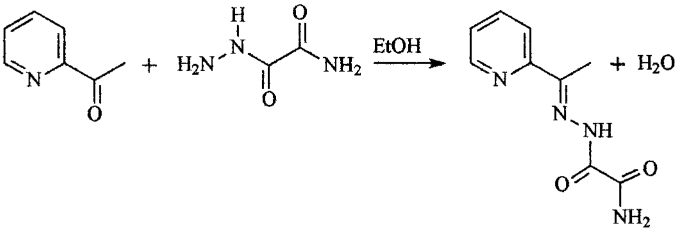
SCHEME 3.

A systematic knowledge of the complexes with H_2dapsox and H_2dapmeha ligands enabled us to study the effect of the central metal ion properties and charge of the ligand on the structure of the compounds formed. This prompted us to synthesize and characterize a novel ligand from the series of 2-acetylpyridine acylhydrazones 2′-[1-(2-pyridinyl)-ethylidene]-oxamohydrazide (Hapsox), as well as its complex with Co(III).

EXPERIMENTAL

Synthesis of 2′-[1-(2-Pyridinyl)-ethylidene]-oxamohydrazide (Hapsox)

A suspension of 1.00 g (8.25 mmol) 2-acetylpyridine and 0.85 g (8.25 mmol) semioxamazide in ethanol (200 mL) was refluxed for 4 h in the presence of several drops of conc. HCl. Upon cooling, the suspension was filtered and a pale-yellow microcrystalline product (1.61 g) was obtained (Scheme 4). Yield 95%. IR spectrum: (KBr; $\bar{\nu}$/cm^{-1}) : 3922 (w), 3868 (w), 3827 (w), 3746 (w), 3721 (w), 3677 (w), 3634 (w), 3457 (s), 3410 (s), 3344 (vs), 3289 (vs), 3148 (vs), 2860 (m), 2695 (m), 2366 (w), 1729 (vs), 1706 (vs), 1582 (s), 1562 (m), 1518 (vs), 1473 (vs), 1434 (vs), 1401 (vs), 1363 (s), 1322 (m), 1242 (m), 1186 (vs), 1115 (m), 1068 (m), 1048 (m), 981 (m), 934 (w), 904 (w), 790 (vs), 766 (s), 739 (s), 685 (s), 649 (m), 624 (m), 595 (s), 561 (s), 513 (s), 494 (m), 449 (m), 424 (m). Elemental analysis of the ligand ($C_9H_{10}N_4O_2$, Mr = 206.2) – calculated: C, 52.42; H, 4.90; N, 27.16%; found: C, 52.59; H, 4.94; N, 27.14%.



SCHEME 4.

Synthesis of [Co(apsox)$_2$]ClO$_4$

Hapsox (0.21 g; 1.0 mmol) and $Co(ClO_4)_2 \cdot 6H_2O$ (0.18 g; 0.5 mmol) were suspended in methanol (90 mL) and refluxed to clarification (Scheme 5). After 24 h, the clear solution was filtered and a dark-red monocrystalline product was obtained (0.17 g). Yield: 61%. IR spectrum: (KBr; ν/cm^{-1}) : 3927 (w), 3877 (w), 3824 (w), 3785 (w), 3755 (w), 3731 (w), 3493 (vs), 3418 (vs), 3361 (vs), 3279 (s), 3214 (m), 2361 (w), 1707 (vs), 1603 (m), 1575 (m), 1515 (vs), 1465 (vs), 1442 (m), 1399 (s), 1372 (m), 1338 (m), 1269 (s), 1151 (w), 1104 (vs), 1036 (s), 931 (w), 771 (s), 741 (w), 699 (s), 620 (s). Elemental analysis of the complex ($C_{18}H_{18}ClCoN_8O_8$, Mr = 568.78) – calculated: C, 44.96; H, 3.78; N, 11.66%; found: C, 44.92; H, 3.84; N, 11.54%.

$$Co(ClO_4)_2 \cdot 6H_2O + 2Hapsox \xrightarrow{MeOH} [Co(apsox)_2]ClO_4$$

SCHEME 5.

Template Synthesis of [Co(apsox)$_2$]ClO$_4$

2-Acetylpyridine (0.12 g; 1 mmol), semioxamazide (0.1 g; 1.0 mmol), and $Co(ClO_4)_2 \cdot 6H_2O$ (0.18 g; 0.5 mmol) were suspended in methanol (80 mL) and refluxed to clarification. After 24 h, the clear solution was filtered and dark-red monocrystalline product was obtained (0.18 g). Yield: 65%.

Physical Measurements

Elemental C, H, N analysis was performed by the standard micromethod in the Centre for Instrumental Analysis, Faculty of Chemistry, University of Belgrade. IR spectra were recorded on a Perkin Elmer FTIR 1726x spectrometer (KBr-disk technique), ^{1}H-NMR spectra were recorded on a Gemini 2000 spectrometer at 200 MHz, and ^{13}C-NMR spectra on the same instrument at 50 MHz.

X-ray Analysis

A crystal with the dimensions $0.05 \times 0.10 \times 0.20\,mm^3$ was mounted on a glass capillary using cyanoacrylate glue. The X-ray diffraction data-set was collected on a Bruker SMART APEX system with a 2K CCD detector, using Mo-$K\alpha$ radiation, at 130 K, using an Oxford Cryostream cooler. The measurements were made using 0.2° ω-scans with 30 s exposure time and 512×512 pixels resolution. The detector was fixed at $2\theta = 28°$ giving a $2\theta_{max}$ of approximately 56°. Experimental details are listed in Table I. The integration of the collected frames, data reduction and refinement of the cell parameters was done using SAINT. The cell parameters were refined in a totally unconstrained triclinic cell. The program XPREP was used for space-group determination and numerical absorption correction. In both cases the space-group was the orthorhombic non-centrosymmetric $P2_12_12_1$ and the number of formula units Z in the cell was four.

The cell axes were $a = 9.0443(5)$ Å, $b = 11.5160(6)$ Å, and $c = 20.9496(12)$ Å, determined using 4354 reflections. The agreement factor for symmetry-related reflections (R_{int}) was 4.33%. Direct methods were used to determine positional parameters for nonhydrogen atoms. All refinements were done using the program package

TABLE I Crystal data and structure refinement for $[Co(apsox)_2]ClO_4$

Empirical formula	$C_{18}H_{18}ClN_8O_8Co$
Formula weight	568.78
Temperature (K)	130
Wavelength (Å)	0.71073
Crystal system, space group	orthorhombic, $P2_1, 2_1, 2_1$
Unit cell dimensions (Å, °)	$a = 8.9460(4)$ $\alpha = 90.00$
	$b = 11.4366(5)$ $\beta = 90.00$
	$c = 20.8007(8)$ $\gamma = 90.00$
Volume ($Å^3$)	2128.16 (16)
z, Calculated density (mg/m^3)	4, 1.775
$F(000)$	1160
Reflections collected/unique	6147/4927 [$R(int) = 0.0433$]
Goodness-of-fit on F^2	0.959
Final R indices* [$I > 2\sigma(I)$]	$R1 = 0.0395$, $wR2 = 0.0654$
R indices* (all data)	$R1 = 0.0453$, $wR2 = 0.0674$
Largest ΔF maximum/minimum ($e/Å^3$)	0.849/– 0.026

*$R1 = \Sigma\ ||F_o|^2 - |F_c|^2|/\Sigma|F_o|^2$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0194\,P)^2]$, $P = [F_o^2 + 2F_c^2]/3$.

SHELXTL. The complex formed is chiral, and crystallizes in a non-centrosymmetric space group. Therefore, it was possible to determine the absolute configuration. The Flack parameter, which shows the distribution of the two enantiomers, was refined to $x = 0.23(1)$, i.e. the two forms exist roughly in a 3 : 1 ratio. The discrepancy factors after convergence were $R(F^2) = 6.14\%$ and $wR(F^2) = 7.36\%$. The oxygens in the perchlorate ion showed quite large thermal displacement ellipsoids, a known problem with a perchlorate ion.

RESULTS AND DISCUSSION

Hapsox was prepared by a condensation reaction starting with 2-acetylpyridine (ap) and semioxamazide (sox) in a molar ratio of 1 : 1 (Scheme 4). The structure of the resulting microcrystalline product (m.p. 250°C) was determined by elemental analysis, IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy.

The dark red monocrystalline product $[Co(apsox)_2]ClO_4$ is the first complex with Hapsox ligand. It was obtained in the reaction of $Co(ClO_4)_2 \cdot 6H_2O$ with Hapsox in methanol solution by refluxing (Scheme 5), during which Co(II) was air-oxidized to Co(III), as shown by diamagnetism of the product. The nature of the ligand favors tridentate coordination enabling the formation of a stable octahedral geometry around the central metal ion. As octahedral structures of Co(III) complexes are more stable than the corresponding structures of Co(II) complexes, oxidation is strongly facilitated.

Theoretically, in the case of bis(NNO-tridentate) complexes, four geometrical isomers are to be expected, one meridional (Fig. 1a) and three facial (Fig. 1b, c, and d). However, planarity of the monoanionic α-oxyazine form of apsox ligand, enables only formation of the meridional isomer.

Spectral Characterization

IR Spectrum of the Ligand

In the IR spectrum of the ligand, a sharp band at 3344 (vs) cm^{-1} and two separate bands at 3289 (vs) and 3148 (vs) cm^{-1}, originating from the secondary (–CONH–)

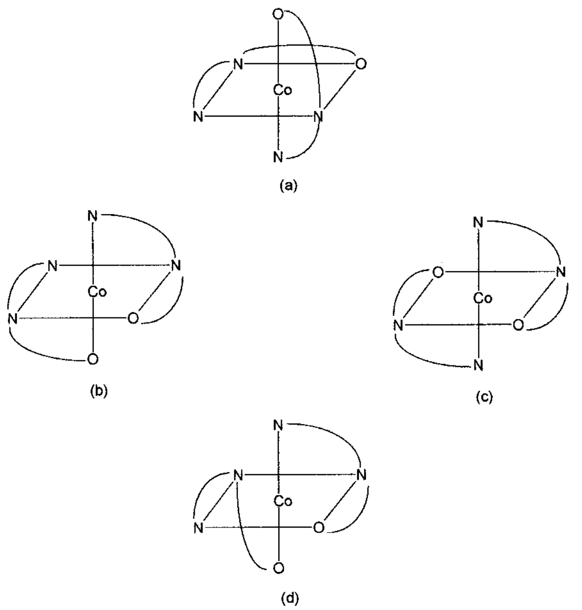


FIGURE 1 Possible geometrical isomer of $[Co(apsox)_2]ClO_4$ complex.

and primary amide ($-CONH_2$) group (ν(NH)), were seen. In the region around $1700\,cm^{-1}$, where the bands characteristic for carbonyl groups appear, two bands were detected, one at 1729 (vs) cm^{-1} originating from the carbonyl group of the primary amide (ν(C=O), amide I) and the second band at 1706 (vs) cm^{-1} originating from the carbonyl groups of the secondary amide (ν(C=O), amide I). The group of bands at 1582 (s), 1518 (vs), 1473 (vs), 1434 (vs), and 1401 (vs) cm^{-1} originates from skeletal vibrations of the pyridine ring and ν(C–N) vibrations, and the band at 1186 (vs) cm^{-1} from δ(NH) vibrations.

IR spectrum of the complex

In the IR spectrum of the complex the bands related to ν(NH) vibrations originating from the primary amide appeared (shifted to a higher frequency compared to the ligand) at 3418 (vs) and 3361 (vs) cm^{-1}. The appearance of a single band at 1707 (vs) cm^{-1} originating from the carbonyl group of the amide (ν(C=O)) is the most interesting characteristic of this spectrum, since in this region of the IR spectrum of the ligand, bands were seen. This could be explained in terms of resonance structures of the deprotonated hydrazide moiety in the ligand upon its binding in the complex $[-N^{-}-C=O \leftrightarrow -N=C-O^{-}]$. The presence of ClO_4^- ion resulted in the appearance of a very strong and broad vibration at 1104 (vs) cm^{-1}. The bands occurring between 1603 and $1399\,cm^{-1}$ can be explained by skeletal vibrations of the pyridine ring and ν(C–N) vibrations. The band at 1269 (s) cm^{-1} belongs to coordinated $-N=C-O^{-}$ group.

^{1}H-NMR and ^{13}C-NMR Spectra of the Ligand

^{1}H-NMR and ^{13}C-NMR spectra of the ligand Hapsox were recorded in DMSO-d_6 (TMS as a standard). The proton signals are listed in Table II and the ^{13}C signals are listed in Table III. The numbering of atoms is given in Scheme 6.

TABLE II ^{1}H-NMR spectral data of the ligand

Assignment (multiplicity, number of H-atoms, coupling constants in Hz)	*Chemical shift, δ* (ppm)
C1 (t, 1 × H, $J = 7.7$)	7.89
C11 (dd, 1 × H, $J = 7.7$, $J = 4.4$)	7.47
C14 (d, 1 × H, $J = 7.7$)	8.09
C16 (d, 1 × H, $J = 4.4$)	8.64
C17 (s, 3 × H)	2.44
N3 (s, 1 × H)	10.82
N4a (s, 1 × H)	8.07
N4b (s, 1 × H)	8.41

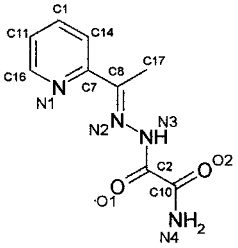
TABLE III ^{13}C-NMR spectral data of the ligand

Assignment	*Chemical shift, δ* (ppm)
C1	137.0
C2*	157.5
C7	154.7
C8	162.1
C10*	156.8
C11	124.9
C14	120.8
C16	149.0
C17	12.2

C2*, C10* – assignments can be exchanged.

^{1}H-NMR Spectrum of the Complex

The ^{1}H-NMR spectrum of the complex $[CoL_2]ClO_4$ (L = apsox) was recorded in D_2O and DMSO-d_6 using TMS as a standard. The results are shown in Tables IV and V. The atom numbering in the molecule is based on the ORTEP figure (Fig. 2). Equivalent atoms are: C1 and C13; C2 and C9; C3 and C16; C4 and C8; C5 and C10; C6 and C14; C7 and C15; C11 and C12; C17 and C18; N1 and N5; N2 and N6; N3 and N7; N4 and N8; O1 and O3; O2 and O4.



SCHEME 6.

^{13}C-NMR Spectrum of the Complex

Since the complex is sparingly soluble in water, the ^{13}C-NMR spectrum recorded in D_2O was unsatisfactory. When DMSO-d_6 was employed as a solvent, the results presented in Table VI were obtained.

TABLE IV ^{1}H-NMR spectral data of the complex in D_2O

Assignment (multiplicity, number of H-atoms, coupling constants in Hz)	*Chemical shift, δ* (ppm)
C1 (t, 1 × H, $J=7.0$)	8.20
C11 (dd, 1 × H, $J=7.0$, $J=5.2$)	7.53
C14 (d, 1 × H, $J=7.0$)	8.12
C16 (d, 1 × H, $J=5.2$)	7.83
C17 (s, 3 × H)	3.31

TABLE V ^{1}H-NMR spectral data of the complex in DMSO

Assignment (multiplicity, number of H-atoms, coupling constants in Hz)	*Chemical shift, δ* (ppm)
C1 (t, 1 × H)	Complex signal
C14 (d, 1 × H)	8.26
C11 (td, 1 × H, $J=6.4$, $J=2.6$)	7.59
C16 (d, 1 × H, $J=5.8$)	7.95
C17 (s, 3 × H)	3.25
N4a (s, 1 × H)	7.78
N4b (s, 1 × H)	7.96

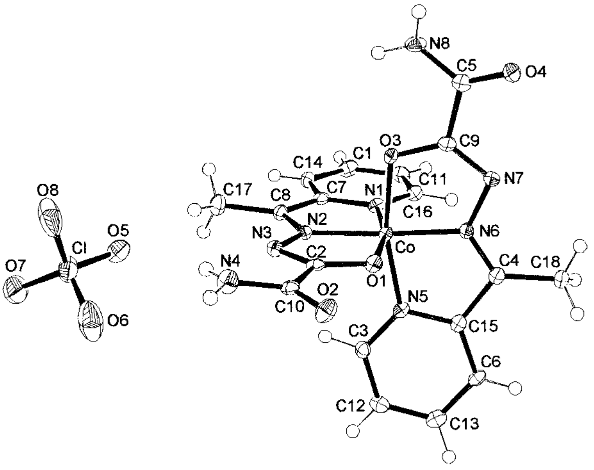


FIGURE 2 Molecular structure of $[Co(apsox)_2]ClO_4$ with numbering scheme for atoms. Thermal ellipsoids are drawn at the 50% probability level.

Comparison of the chemical shift of the C17 atom in the ^{13}C-NMR spectrum of the ligand and of the corresponding carbon atom in the ^{13}C-NMR spectrum of 2-acetyl pyridine (25.7 ppm) demonstrated the *E* configuration of the >C=N– bond [13]. Comparison of the ^{1}H-NMR and ^{13}C-NMR spectra of the ligand and the complex demonstrate complex formation since the signal shift occurred. Analysis of ^{1}H-NMR spectrum of the complex revealed loss of the N3 proton. This led to an increase of electron density at O1[$-N^{-}-C=O \leftrightarrow -N=C-O^{-}$], thus making it a better electron donor for complex formation. Also, chemical shift of the methyl group (C17) hydrogens was significantly increased, as well as that of the hydrogen on C1. This is a consequence

TABLE VI ^{13}C-NMR spectral data of the complex

Assignment	*Chemical shift*, *δ* (ppm)
C1	152.8
C2	167.1
C7	159.9
C8	176.3
C10	158.5
C11	130.0
C14	127.2
C16	142.5
C17	15.6

TABLE VII Fractional atomic coordinates and equivalent isotropic displacement parameters at 130 K (Å^2) for [Co(apsox)$_2$]ClO$_4$ $U_{eq} = (1/3)\ \Sigma_i\ \Sigma_j\ U^{ij}\ a^i a^j a_i{:}a_j$

Atom	*x*	*y*	*z*	U_{eq}
Co	0.02060(4)	0.05198(3)	0.12514(1)	0.01172(9)
C1	0.0004(4)	0.3556(2)	0.1342(1)	0.0201(7)
C2	0.1589(3)	0.2075(3)	0.1956(1)	0.0138(6)
C3	0.3069(3)	0.0386(3)	0.0572(1)	0.0154(6)
C4	0.0687(3)	0.1077(2)	0.0033(1)	0.0137(6)
C5	0.4071(3)	0.1231(2)	0.1785(1)	0.0153(6)
C6	0.1781(3)	0.1137(3)	0.0550(1)	0.0147(6)
C7	0.0813(3)	0.1685(2)	0.1701(1)	0.0139(6)
C8	0.1607(3)	0.0875(2)	0.2119(1)	0.0143(6)
C9	0.2625(3)	0.0966(2)	0.1434(1)	0.0138(6)
C10	0.2141(3)	0.3230(3)	0.2231(1)	0.0146(6)
C11	0.0823(4)	0.3015(3)	0.0866(1)	0.0179(7)
C12	0.3967(3)	0.0615(3)	0.0042(1)	0.0177(6)
C13	0.3326(4)	0.1013(3)	0.0514(1)	0.0187(7)
C14	0.0807(3)	0.2883(3)	0.1764(1)	0.0169(7)
C15	0.0937(3)	0.0902(2)	0.0013(1)	0.0136(6)
C16	0.0784(4)	0.1801(3)	0.0825(1)	0.0166(7)
C17	0.2480(4)	0.1245(3)	0.2695(1)	0.0203(7)
C18	0.1644(4)	0.1382(3)	0.0520(1)	0.0182(7)
N1	0.0011(3)	0.1153(1)	0.1224(1)	0.0135(5)
N2	0.1458(3)	0.0187(2)	0.1937(1)	0.0120(5)
N3	0.2045(3)	0.1129(1)	0.2253(1)	0.0133(5)
N4	0.2904(3)	0.3109(3)	0.2773(1)	0.0216(6)
N5	0.1587(3)	0.0555(2)	0.0547(1)	0.0135(5)
N6	0.1141(3)	0.0919(2)	0.0614(1)	0.0118(5)
N7	0.2610(3)	0.1113(2)	0.0810(1)	0.0143(5)
N8	0.4118(3)	0.0790(2)	0.2379(1)	0.0182(6)
O1	0.0722(2)	0.2107(1)	0.14622(9)	0.0144(5)
O2	0.1887(3)	0.4158(1)	0.1959(1)	0.0217(5)
O3	0.1502(2)	0.0649(1)	0.17879(9)	0.0133(4)
O4	0.5038(2)	0.1820(1)	0.15345(9)	0.0203(5)
Cl	0.5116(1)	0.21010(7)	0.40288(4)	0.0274(1)
O5	0.4294(3)	0.1300(1)	0.3622(1)	0.0272(6)
O6	0.5539(3)	0.3097(2)	0.3647(1)	0.0534(8)
O7	0.6434(3)	0.1542(2)	0.4268(1)	0.0426(7)
O8	0.4201(3)	0.2461(3)	0.4546(1)	0.063(1)

of electron withdrawal from nitrogen atoms N1 and N2 by cobalt. Electronic effects due to coordination of pyridine nitrogen N1 were less pronounced on *meta*- hydrogen atoms (C14 and C11), than in *para*- (C1) and *ortho*- (C16) positions. Because of coordination of hydrazone nitrogen (N2), the C8 atom is electron deficient, and as a result, a change in chemical shift of hydrogens on C17 takes place. The ^{13}C-NMR spectrum also confirmed coordination through nitrogen atoms N1 and N2 and oxygen O1, because changes of chemical shifts of C1, C2, and C8 atoms were the most pronounced (a somewhat less pronounced change of the signal of C17 was observed).

Analysis of the microanalysis, IR, and NMR spectra confirm the structure of the synthesized complex shown in Fig. 2.

Structural Analysis

X-ray structural analysis demonstrated that the crystal and molecular structure of the formed complex consists of $[Co(apsox)_2]^+$ cation and ClO_4^- anion, held together by Coulomb forces. Fractional coordinates of all atoms within the structure and their isotropic temperature parameters are given in Table VII. Bond lengths and angles in this structure are common for $[Co(apsox)_2]ClO_4$ complexes of octahedral geometry [14,15] (Tables VIII and IX). The ORTEP molecular structure of the racemic

TABLE VIII Bond distances at 130 K (Å, °) for $[Co(apsox)_2]ClO_4$

Atom 1	*Atom* 2	*Distance*
Co	N6	1.849(2)
Co	N2	1.854(2)
Co	O3	1.897(2)
Co	N5	1.916(2)
Co	N1	1.923(2)
Co	O1	1.923(2)
C1	C14	1.375(4)
C1	C11	1.379(4)
C2	O1	1.288(3)
C2	N3	1.311(4)
C2	N5	1.341(4)
C3	C12	1.388(4)
C4	N6	1.286(4)
C4	C15	1.470(4)
C4	C18	1.478(4)
C5	O4	1.214(3)
C5	N8	1.336(4)
C5	C9	1.516(4)
C6	C15	1.375(4)
C6	C13	1.392(4)
C7	N1	1.368(3)
C7	C14	1.377(4)
C7	C8	1.456(4)
C8	N2	1.279(3)
C8	C17	1.491(4)
C9	O3	1.297(3)
C9	N7	1.309(4)
C10	O2	1.225(3)
C10	N4	1.325(4)
C11	C16	1.391(4)
C12	C13	1.372(4)
C15	N5	1.363(3)
C16	N1	1.320(4)
N2	N3	1.368(3)
N6	N7	1.394(3)
C1	O8	1.414(3)
C1	O7	1.430(3)
C1	O6	1.438(3)
C1	O5	1.447(2)

TABLE IX Bond angles at 130 K (Å, °) for $[Co(apsox)_2]ClO_4$

Atom 1	*Atom* 2	*Atom* 3	*Angle*
N6	Co	N2	175.2(1)
N6	Co	O3	82.96(9)
N2	Co	O3	92.85(9)
N6	Co	N5	82.3(1)
N2	Co	N5	101.7(1)
O3	Co	N5	165.19(9)
N6	Co	N1	99.5(1)
N2	Co	N1	82.7(1)
O3	Co	N1	91.28(9)
N5	Co	N1	93.2(1)
N6	Co	O1	94.98(9)
N2	Co	O1	82.73(9)
O3	Co	O1	89.16(8)
N5	Co	O1	89.99(9)
N1	Co	O1	165.44(9)
C14	C1	C11	119.2(3)
O1	C2	N3	126.0(3)
O1	C2	C10	118.1(3)
N3	C2	C10	116.0(3)
N5	C3	C12	121.0(3)
N6	C4	C15	110.8(3)
N6	C4	C18	125.6(3)
C15	C4	C18	123.5(3)
O4	C5	N8	125.8(3)
O4	C5	C9	120.8(3)
N8	C5	C9	113.4(3)
C15	C6	C13	118.8(3)
N1	C7	C14	120.6(3)
N1	C7	C8	114.0(2)
C14	C7	C8	125.3(3)
N2	C8	C7	112.1(3)
N2	C8	C17	124.2(3)
C7	C8	C17	123.7(3)
O3	C9	N7	126.2(3)
O3	C9	C5	116.4(2)
N7	C9	C5	117.4(3)
O2	C10	N4	125.4(3)
O2	C10	C2	121.3(3)
N4	C10	C2	113.3(3)
C1	C11	C16	118.6(3)
C13	C12	C3	119.4(3)
C12	C13	C6	119.6(3)
C1	C14	C7	119.9(3)
N5	C15	C6	121.3(3)
N5	C15	C4	113.9(3)
C6	C15	C4	124.7(3)
N1	C16	C11	122.4(3)
C16	N1	C7	119.3(2)
C16	N1	Co	128.8(2)
C7	N1	Co	111.9(2)
C8	N2	N3	124.5(2)
C8	N2	Co	119.1(2)
N3	N2	Co	116.1(2)
C2	N3	N2	107.7(2)
C3	N5	C15	119.7(2)
C3	N5	Co	127.3(2)
C15	N5	Co	112.6(2)

(continued)

TABLE IX Continued

Atom 1	*Atom 2*	*Atom 3*	*Angle*
C4	N6	N7	123.4(2)
C4	N6	Co	120.1(2)
N7	N6	Co	116.3(2)
C9	N7	N6	106.2(2)
C2	O1	Co	107.4(2)
C9	O3	Co	108.2(2)
O8	C1	O7	110.0(2)
O8	C1	O6	109.9(2)
O7	C1	O6	109.2(2)
O8	C1	O5	109.5(2)
O7	C1	O5	109.8(2)
O6	C1	O5	108.1(1)

$[Co(apsox)_2]ClO_4$ complex shows a deformed octahedral geometry around Co(III), with two apsox ligands meridionally coordinated through pyridine nitrogen N1, hydrazone nitrogen N2, and α-oxyazine oxygen O1 (Fig. 2). Both tridentate ligands were coordinated in monoanionic form. As expected the meridional geometrical isomer of $[Co(apsox)_2]ClO_4$ was obtained (Fig. 1a). An identical product was obtained by template synthesis starting with 2-acetylpyridine (ap), semioxamazide (sox), and $Co(ClO_4)_2 \cdot 6H_2O$, as determined by elemental analysis, IR, and NMR spectroscopy.

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