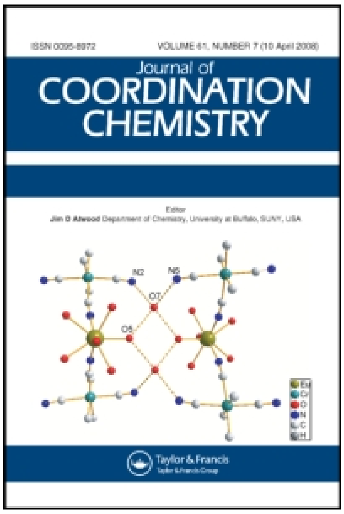

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Preparation, spectroscopic, and structural characterization of the first Co(III) cyanoxime complex: two polymorphs of *fac*-, *tris*(benzoylcyanoximato)cobalt(III), $Co(BCO)_3$

Nikolay Gerasimchuk[a]; Charles L. Barnes[b]; David Boaz[a]
[a] Department of Chemistry, Temple Hall 456, Missouri State University, Springfield, MO 65897, USA [b] Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA

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Preparation, spectroscopic, and structural characterization of the first Co(III) cyanoxime complex: two polymorphs of *fac*-, *tris*(benzoylcyanoximato)cobalt(III), Co(BCO)$_3$

NIKOLAY GERASIMCHUK*†, CHARLES L. BARNES‡
and DAVID BOAZ†

†Department of Chemistry, Temple Hall 456, Missouri State University,
Springfield, MO 65897, USA
‡Department of Chemistry, University of Missouri–Columbia, Chemistry
Building 125, Columbia, MO 65211, USA

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Coordination chemistry of cyanoximes – low molecular weight organic molecules having general formula NC–C(=NOH)–R – received attention in recent years due to their pronounced biological activity and interesting properties. The preparation, spectroscopic properties, electrochemical properties, and crystal structure of the first representative of a family of cobalt(III) *tris*-cyanoximates – Co(BCO)$_3$ (where BCO is the anion of the benzoylcyanoxime, C_6H_5–C(O)–C(NO)–CN$^-$) – are now reported. The complex crystallizes as red prisms from $CHCl_3$ solution as the *fac*-isomer in centrosymmetric R$\bar{3}$ space group with three pairs of enantiomers in the unit cell ($Z = 6$). Slow evaporation of CH_3CN solution of Co(BCO)$_3$ leads to crystallization of the same *fac*-complex without a solvent molecule in the lattice, only this time in the centrosymmetric monoclinic C2/c space group (Z = 8). Both structures have converged with final values $R_1 = 0.0462$ ($wR_2 = 0.1273$) and $R_1 = 0.0323$ ($wR_2 = 0.0809$), respectively. Therefore, two polymorphs of Co(BCO)$_3$ were observed, which is a rare case for this transition metal in Werner-type complexes. The cyanoxime anion forms a five-membered chelate ring by the nitrogen of the nitroso and the oxygen of the carbonyl, and the ligand adopts *cis-anti* configuration. The anion is bound to the metal center *via* short, covalent Co–N and Co–O bonds, and represents the second known case of very tight binding of an oxime ligand to Co(III). There is a significant degree of ligand-to-metal charge transfer reflected in an unusually low value of the redox potential Co(III) + e = Co(II) ($E_{1/2} = -0.0975$ V) as opposed to that tabulated for aqueous solutions +1.82 V, and low-field shifts of the positions of the signals in ^{13}C NMR spectrum of *fac*-Co(BCO)$_3$ compared to the free ligand.

Keywords: Benzoylcyanoxime; Cobalt(III) complex; UV-Vis spectroscopy; Polymorphs; X-ray analysis; Cyclic voltammetry

1. Introduction

Cobalt is trivalent in predominantly octahedral geometry in numerous coordination compounds [1]. With only a few exceptions (e.g. $K_3[CoF_6]$) all these complexes are low spin [2] with $3d_6$ ($^1A_1$) electronic configuration. Cobalt(III) is kinetically inert, opening

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*Corresponding author. Email: NNGerasimchuk@missouristate.edu

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the prospect for application of its *neutral* coordination compounds as delivery agents of biologically active molecules (ligands) into the cell *via* passive diffusion with subsequent intracellular reduction of the metal complex to Co(II) species that undergo fast ligand exchange reaction and release a bioactive molecule [3]. Several Co(III) complexes were recently used as DNA cleavage agents [4]. Cyanoximes with general formula NC–C(=NOH)–R, where R is an electron-withdrawing group, represent a new class of low molecular weight organic compounds that show useful properties and biological activity ranging from antimicrobial [5] and growth regulation in plants [6] to cytotoxicity [7] and agricultural herbicide antidote properties [8]. No cobalt(III) cyanoxime-based *tris*-complexes were known prior to this study, although there are several publications regarding preparation and characterization of *mono*- [9–12], *bis*- [13, 14], and *tris*-complexes [15–23] with α-ketoxime ligands. The list of those ligands is shown in "Electronic supplementary material (ESI 1)". In this work we present the synthesis, crystal structure, and spectroscopic characterization of the first neutral Co(III) complex with the benzoylcyanoxime anion, NC–C(NO)–C(O)C_6H_5, abbreviated as BCO^-.

2. Experimental

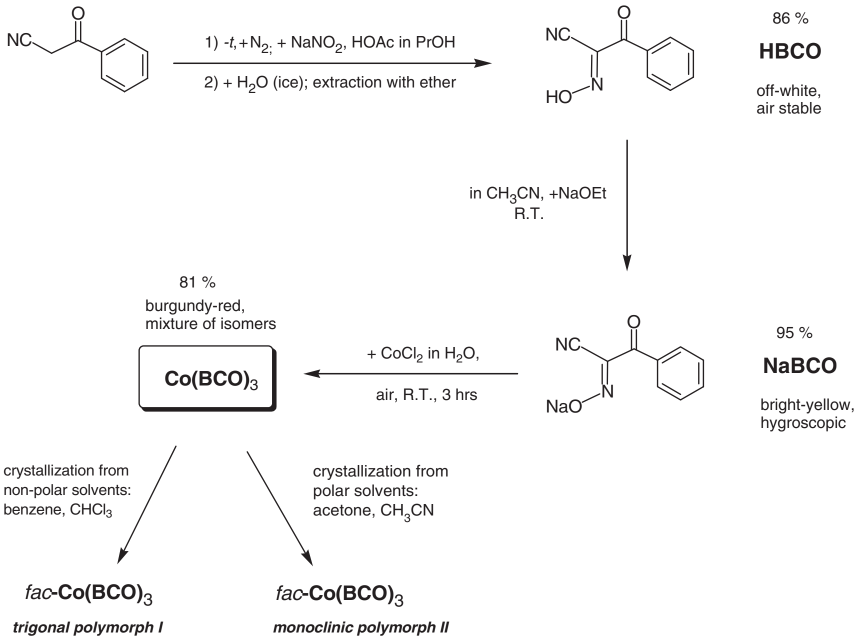
2.1. *Materials and methods*

The organic solvents from Aldrich used for the synthesis and spectroscopic measurements were all of reagent grade and dried under fresh molecular sieves. High purity $CoCl_2{\cdot}6H_2O$ was obtained from Fisher Scientific. The melting points and decomposition temperatures were determined under a vacuum in closed capillary tubes with a Thomas Hoover Uni-Melt apparatus. The C, H, N, and S elemental analyses were performed by Atlantic Microlab, Norcross, Georgia.

2.2. *Synthesis of the ligand and its Co(III) complex*

The preparation of benzoylcyanoxime, $C_9H_6N_2O_2$, HBCO, was carried out according to the published procedures [24, 25] from benzoylacetonitrile, $NCCH_2C(O)C_6H_5$, obtained from Aldrich (scheme 1). Benzoylcyanoxime is an off-white waxy solid with a melting point of 119°C. Its mass spectrum yielded a molecular mass of 174.0436 g mol^{-1} as compared with a calculated value for $C_9H_6N_2O_2$ of 174.0429 g mol^{-1}. IR spectrum (KBr), in cm^{-1}: 2232 ν(CN), 1655 ν(C=O), 1315 ν(CNO), 1060 ν(NO), 810 δ(C–CNO). NMR spectra in DMSO-d_6, δ, in ppm: ^{1}H – 15.12 (1H, oxime), 7.56 (1H, para), 7.72 (1H, meta), 7.91 (1H, ortho); $^{13}C\{^1H\}$ – 108.7 (CN-group), 185.4 (C=O), 135.2 (*ipso* carbon), 134.2 (oxime carbon), 134.1, 128.9, 130.7 (C–H).

The preparation of the cobalt(III) complex of benzoylcyanoxime, $Co(BCO)_3$, has been accomplished by using the conventional method of air oxidation of the starting Co(II) salt upon stirring at room temperature in the presence of a stoichiometric amount of the sodium salt cyanoxime (scheme 1). Burgundy-red fine precipitate was formed within ~3 h of reaction in air. It was filtered, washed with two portions of 10 mL of water and dried in a vacuum dessicator charged with concentrated H_2SO_4. For $C_{27}H_{15}CoN_6O_6 \ldots 0.5\ CHCl_3$ calculated (found), %: C – 53.11 (53.29), H – 2.50 (2.78),



Scheme 1. Preparation of the cobalt(III) complex of benzoylcyanoxime.

N – 13.59 (13.44). The mass-spectrum contained a low-intensity peak at 578.04 which corresponded to the Co(BCO)$_3^+$ molecular ion. IR spectrum (KBr), in cm^{-1}: 2221 ν(CN), 1599 ν(C=O), 1387 ν(CNO), 1295 ν(NO). NMR spectra in acetone-d$_6$, δ, in ppm: ^{1}H – 8.40 (ortho protons, 2H, doublet, $J = 8.1$ Hz), 7.73 (meta protons, 2H, triplet, $J = 8.0$ Hz), 7.92 (para proton, 1H, triplet, $J = 8.0$ Hz); ^{13}C{^{1}H} – 198.8 (carbonyl), 154.4 (oxime C), 136.7 (para carbon, Ph), 131.7 (ipso carbon, Ph), 130.1 (meta carbon, Ph), 110.1 (CN-group).

2.3. *Electrochemical measurements*

Cyclic voltammetry (CV) measurements for Co(BCO)$_3$ were carried out in dry de-aerated acetonitrile at 296 K with a CH Instruments Electrochemical Analyzer (Austin, TX, USA) equipped with a glassy carbon 3 mm working electrode and a Ag/AgCl reference electrode obtained from Cypress Systems. The electrode was standardized with a ferrocene in CH_3CN solution containing 0.2 M $LiClO_4$; the Fc/Fc$^+$ couple exhibits $E_a = 0.31$ V against saturated calomel electrode. Cobalt(III) cyanoximate was dissolved in pure CH_3CN containing 0.1 M $[N(C_4H_9)_4]PF_6$ and the voltage sweeps were carried out over the range of ±0.6 V at a 50 mV s^{-1} scan rate.

Measurements of pK_a values for synthesized benzoylcyanoxime HBCO were carried out using a Sirius Analytical Instruments automated titration station (Sussex, UK) equipped with a temperature-controlled bath. As protonated organic cyanoxime HBCO is not sufficiently soluble in water, all measurements were conducted in mixed solvent systems using methanol as solubilizing co-solvent. Atenolol^{TM} and Lidocaine^{TM} (from Aldrich) were used for calibration of the instrument [26]. Measurements consisted of the three-step multi-stage potentiometric titration in water/CH_3OH mixtures from 18.9 to 23.8 wt% content of the organic solvent with ionic strength adjusted to 0.15 with KCl. The pH ranged from 3 to 11. The values were extrapolated to "zero" CH_3OH content to obtain an aqueous pK_a value using the Yasuda–Shedlovsky procedure.

2.4. *Spectroscopic studies*

The UV-Vis spectra of Na(BCO) and $Co(BCO)_3$ have been recorded in solutions at 296 K with a diode array HP 8453 spectrophotometer from 200 to 1100 nm using a 1 cm quartz cuvette. A Bruker Vertex 70 FT IR spectrometer was used for recording the IR spectra from 365 to 4000 cm^{-1}. A 400 MHz Varian Inova NMR spectrometer has been used to record, at ambient temperature, the ^1H and $^{13}C\{^1H\}$ spectra of Na(BCO) and $Co(BCO)_3$ in acetone-d_6 with tetramethylsilane as an internal reference (figure 1). The mass spectra of the organic ligand have been obtained with Autospec Q and ZAB spectrometers with a positive FAB, under argon and with *m*-nitrobenzylic alcohol as the matrix.

2.5. *X-ray structure determination*

The crystal structure of both polymorphs of $Co(BCO)_3$ have been determined at 173 K for I and 120 K for II from a suitable prism-shaped crystal mounted on a thin glass fiber. The low-temperature experiments were conducted using the Cryostream and Kryoflex systems at an accuracy of ±1 K. Diffraction measurements were made using a Bruker APEX2 instrument working in ω scan mode and equipped with a SMART CCD area detector and with Mo-Kα 0.71073 Å radiation. The intensities were integrated from four series of 366 exposures, with each exposure covering 0.5° in ω and the total data set covering a sphere [27]. The unit cell was determined based on 272 reflections with $I \geq 20\sigma(I)$ from four series of 40 short (10 s) exposures. Multi-scan absorption corrections were applied using the Bruker AXS software [28]. The structure was solved by direct methods using SHELX-97 and refined using SHELXTL-6.10 by least squares on weighted F^2 values for all reflections [29]. All nonhydrogen atoms were refined with anisotropic displacement parameters and with no positional constraints. Because only 8 hydrogens out of 15 were found on a difference map in I, the hydrogens were attached to sp^2 hybridized carbons of the phenyl groups at C–H = 0.95 Å, and their positions were not further refined. Hydrogen atoms in the structure of polymorph II were treated similarly. The crystallographic data for both polymorphs of $Co(BCO)_3$ are presented in table 1, while selected bond and valence angles are summarized in table 2. Further details of the X-ray experiment can be found in the CIF file and the PLATON report on it provided in "Supplementary material". Pictures for figure 2 and ESI ("Electronic supporting information") describing the crystal structure of $Co(BCO)_3$ were drawn using the ORTEP-32 and the Mercury software packages [30, 31].

3. Results and discussion

Earlier we reported pK_a values for a series of disubstituted arylcyanoximes [32] and 2-heteroaryl-(cyanoximes) [33], while other representatives of this family of ligands,

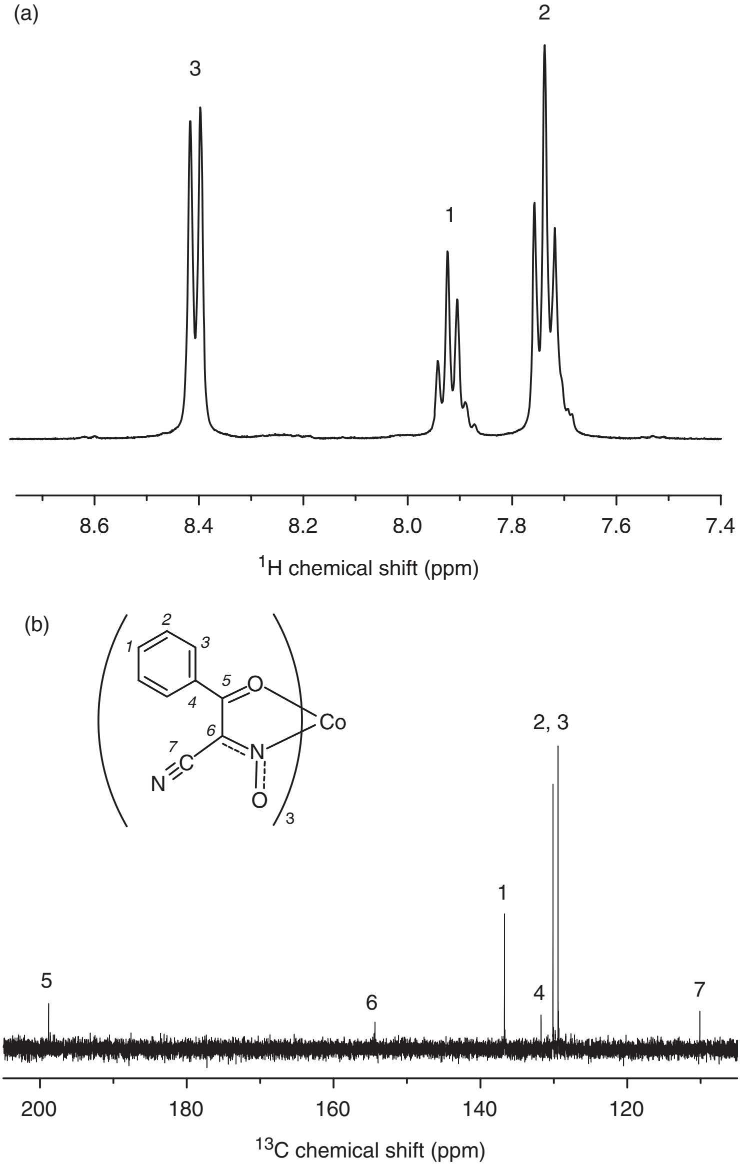


Figure 1. Fragments of proton (a) and carbon (b) NMR spectra of *fac*-Co(BCO)$_3$ in acetone-d$_6$ at room temperature showing signal assignment.

including amides and ketoximes, were not studied at all. The data from all three potentiometric titration curves for HBCO were analyzed using the RefinementPro software (provided with the Sirius Analytical Instruments multifunctional titration station) and the results indicate an organic acid of low-to-medium strength: $pK = 4.27 \pm 0.01$, comparable to aliphatic carboxylic acids [34]. Owing to the presence of the CN group, HBCO is stronger acid by a factor of ~100,000 than conventional monoximes and dioximes [35].

Table 1. Crystal data and structure refinement for two polymorphs of the *fac*-Co(BCO)$_3$.

Polymorphs	I	II
Empirical formula	$C_{27.50}$ H_{15} $Cl_{1.50}$ Co N_6 O_6	$C_{27}H_{15}CoN_6O_6$
Formula weight	637.56	578.38
Crystal size (mm^3)	$0.50 \times 0.25 \times 0.20$	$0.28 \times 0.26 \times 0.13$
Color, habit	Dark-red, prism	Light red-orange, plate
Temperature (K)	173(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Trigonal	Monoclinic, #15
Space group	R-3	C2/c
Unit cell dimensions (Å, °)		
a	13.5868(3)	17.1866(7)
b	13.5868(3)	18.4077(8)
c	25.7313(13)	15.8450(7)
α	90°	90°
β	90°	90.22°
γ	120°	90°
Volume (Å^3)	4113.6(2)	5012.8(4)
Z	6	8
Density (Calc.) (Mg/m^3)	1.544	1.533
Absorption coeff. (mm^{-1})	0.826	0.741
F(000)	1935	2352
Θ-range (°)	3.55–27.10	1.62–32.44
Index ranges	$-17 \leq h \leq 14$; $-12 \leq k \leq 17$; $-32 \leq l \leq 32$	$-25 \leq h \leq 25$; $-26 \leq k \leq 26$; $-23 \leq l \leq 23$
Reflections collected	8613	37,343
Independent reflections	2008 [R(int) = 0.0275]	8531 [R(int) = 0.0266]
Completeness to theta	27.10° (99.5%)	32.44° (94.6%)
Absorption correction	Semi-empirical (from equivalents)	Semi-empirical
$T_{\max}$ and $T_{\min}$	0.8522 and 0.6828	
Refinement method	Full-matrix least-squares on F^2	Full-matrix (LS on $F^{2)}$
Data/restraints/parameters	2008/0/133	8531/0/361
Goodness-of-fit on F^2	1.036	1.042
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0462$, $wR_2 = 0.1273$	$R_1 = 0.0323$, $wR_2 = 0.0809$
R indices (all data)	$R_1 = 0.0532$, $wR_2 = 0.1313$	$R_1 = 0.0404$, $wR_2 = 0.0855$
Largest difference peak and hole (eÅ^{-3})	0.791 and −0.650	0.570 and −0.402

The synthesis of *tris*-Co(III) benzoylcyanoximate was accomplished using the sodium salt, NaBCO, with which the reaction proceeded to a completion within ~3 h due to the higher nucleophilicity of the anion. This bright yellow sodium salt was obtained in acetonitrile but was not isolated and was used immediately after preparation to form its cobalt(III) complex. NaBCO is highly hygroscopic and we found that it is much more convenient to use a known concentration stock solution in CH_3CN, or *n*-propanol for the reaction rather than solid compound. Its UV-Vis spectrum in *n*-propanol exhibited the following transitions: $\lambda_{\max}$, in nm (ε, in $M^{-1}\,cm^{-1}$) 258 (8900) $\pi \rightarrow \pi^*$ of the CN group; 312 (14,000) $\pi \rightarrow \pi^*$; 467 (74) $n \rightarrow \pi^*$. After mixing NaBCO and $CoCl_2$, the color of the reaction mixture changes quickly from bright yellow to red due to the oxidation of Co(II) to Co(III), and after ~3 h a very fine powdery burgundy-red precipitate appears in the flask. The precipitate is a mixture of *mer*- and *fac*-geometrical isomers of Co(BCO)$_3$, but only one, the most stable *fac*-isomer, can be obtained as a crystalline product suitable for X-ray analysis.

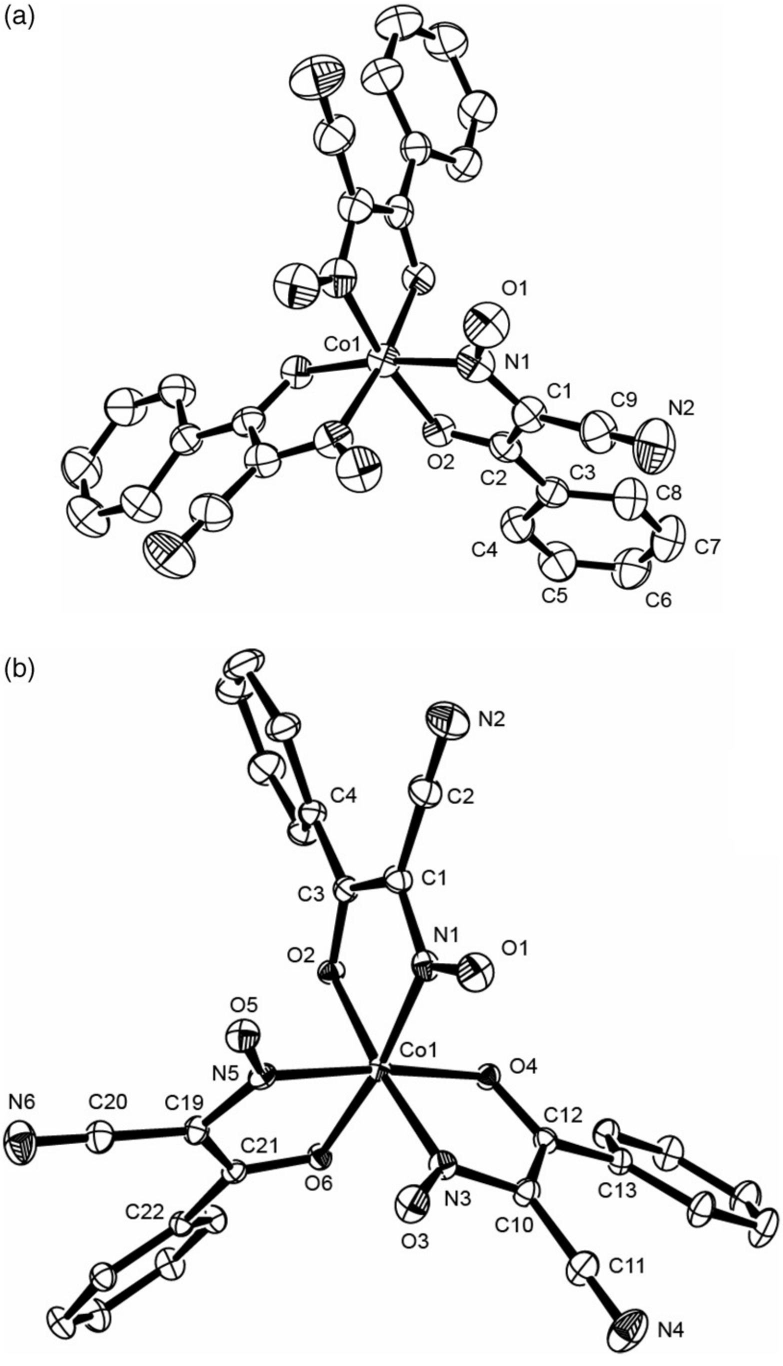


Figure 2. Molecular structure and numbering scheme for the trigonal polymorph (a) and monoclinic polymorph (b) of *fac*-isomer of *tris*(benzoylcyanoximato)cobalt(III); shown Δ and Λ enantiomers respectively. An ORTEP drawing at 50% thermal ellipsoids probability level. Hydrogen atoms and disordered chloroform solvent molecules are not shown for clarity.

Statistically, the amount of low-symmetry *mer*-isomer (C_1 point group) should be greater, but slow crystallization affords only crystals of more symmetrical *fac*-isomer (D_3 point group). All our attempts to obtain a crystalline sample for the *mer*-isomer were unsuccessful.

The NMR spectra of *fac*-$Co(BCO)_3$ are shown in figure 1 and contain one set of narrow signals indicating the low-spin $3d_6$ configuration of the central atom and high symmetry (C_3) of the complex with all three coordinated cyanoxime ligands being magnetically equivalent. This burgundy-red complex on dissolution in organic solvents forms bright-yellow solutions with one intense charge-transfer band in the UV-Vis spectrum (Supplementary material). The position of this band migrates in the range ~12–380 nm depending on the solvent, which confirms its charge-transfer origin.

A small quantity of pure, crystalline *fac*-$Co(BCO)_3$ was used for recording CV data in degassed CH_3CN solution. The results of CV measurements evidenced a reproducible and reversible transition between Co(III) and Co(II) oxidation states with $E_{1/2} = -0.0975\,V$ (Supplementary material). The value of redox potential is very low for Co(III) reduction [34, 35], indicating a very significant charge transfer from the cyanoxime anion to cobalt. Therefore, an intense band at 382 nm in the UV–Vis spectrum of *fac*-$Co(BCO)_3$ is assigned to the ligand-to-metal charge transfer. Moreover, when comparing values of $^{13}C\{^1H\}$ chemical shifts for the HBCO and *fac*-$Co(BCO)_3$, it is apparent that all carbons, except *ipso*-carbon, underwent a low-field shift supporting their deshielding in agreement with the localization of electron density from cyanoxime ligands on metal. For instance, $\Delta\delta$ (for carbonyl atom C5) = 13.4 ppm, $\Delta\delta$ (for oxime atom C6) = 20.2 ppm, and $\Delta\delta$ (for cyano group carbon C7) = 1.4 ppm. Similarly, the overall depletion of electron density in the coordinated cyanoxime ligand as compared to nonbound, free HBCO is also evident from the low-field shift of signals of all C–H bound carbon atoms C1, C2, and C3 in the phenyl group. Furthermore, the IR spectrum of the *fac*-$Co(BCO)_3$ has a value of $\nu(C\equiv N)$ at 2221 cm^{-1} compared to 2232 cm^{-1} in HBCO, which also indicates the decrease of electron density in the group and correlates well with the NMR data.

The crystal structure of *fac*-$Co(BCO)_3$ in polymorph I contains a disordered $CHCl_3$ solvent molecule which, unfortunately, was only partially resolved. Although thermal ellipsoids for assigned Cl and C atoms have reasonable values, complete modeling of the disorder was rather difficult. No hydrogen atoms were assigned to carbon of the solvent. We did not use the SQUEEZE program from the PLATON software package to eliminate electron density for the disordered solvent molecule because this action would alter the original data set, and that is not fully endorsed by the crystallographic community. A solvent disorder that was not completely resolved led to some warnings from the checkCIF program and PLATON report (Supplementary material). Certainly, disordered solvent did not compromise the quality of data for the structure of $Co(BCO)_3$ whose geometry was reliably determined. The complex has a slightly distorted octahedral geometry around the metal center (Supplementary material). The Co(III) atom occupies a special position in the crystal and sits on a threefold axis which leads to an elegant, symmetrical structure (figure 2(a); Supplementary material). The cyanoxime ligand forms a five-membered chelate ring Co1–N1–C1–C2–O2 with the "bite" angle of 83.76° (Supplementary material). As *fac*-$Co(BCO)_3$ crystallizes in a centrosymmetric rhombohedral space group $R\bar{3}$, these chelate rings are arranged around the metal center to form the two optical isomers Δ and Λ. The structure of one is displayed in figure 2(a), while both the enantiomers are shown in Supplementary material. The cyanoxime anion BCO^- is in the nitroso form and adopts favorable for metal chelating *cis-anti* geometry contrary to the *trans-anti* geometry found in the tetraphenyl antimony complex $SbPh_4BCO$ [36]. The distance N1–O1 in *fac*-$Co(BCO)_3$ is 1.247 Å, which corresponds to a double bond –N=O with the distance of 1.22±0.02 Å found in organic nitrites [34]. In the *tris*-oximato Co(III) complex with similar ligand, such as benzoyl-acetoneoxime, average N–O and C–N distances are 1.253 and 1.348 Å, respectively [16]. The anion in the structure of *fac*-$Co(BCO)_3$ in polymorph I is nonplanar with three planes N2–C9–C1–N1–O1, O1–N1–C1–C2–O2, and the phenyl group C3–C4–C5–C6–C7–C8. The first plane defines the cyano-group connected to the nitroso group, while the second plane defines a conjugated fragment between the nitroso and carbonyl groups. The dihedral angle between those mean planes is 6.96° and indicates the deviation of the CN group from co-planarity with the conjugated nitroso/carbonyl core. The phenyl group has dihedral angles between the two mean planes O1–N1–C1–C2–O2 and N2–C9–C1–N1 equal to 15.17° and 22.06°, respectively. Angles less than 30° are considered to be the limit for conjugation in nonplanar systems such as, for example, biphenyl. Crystallization of the complex in centrosymmetric C2/c space group in polymorph II affords two enantiomers related to each other *via* the inversion center (ESI 7,8). The molecular structure of the *fac*-$Co(BCO)_3$ complex in the monoclinic form II is essentially the same (figure 2b). The only difference is that all three anions in the complex are not identical. Also, similarly to the trigonal polymorph I, the BCO^- anion is not planar, and its structure defined with two distinct planes, for example: the cyano-nitroso group O1–N1–C1–C2–N2, and the phenyl group C4–C5–C6–C7–C8–C9 with dihedral angle 28.94°. Analogous angles for other two anions are 21.70° and 26.57°. Therefore, based on the data of the crystal structure we conclude that the cyanoxime anion in *fac*-$Co(BCO)_3$ is conjugated, in agreement with the NMR spectroscopic and electrochemical data discussed above. A small value of the sum of the metal-to-ligand distances (for instance Fe–N and Fe–O [37] or Co–N and Co–O in our case) may serve as an indication of the "tightness" of binding in a complex. By this parameter, *fac*-$Co(BCO)_3$ I and II represent the second and third known cases of a very strong coordination of the oxime ligand: $Co1{-}N1 = 1.883$ Å, $Co1{-}O2 = 1.909$ Å ($\Sigma = 3.792(2)$ Å) (for trigonal polymorph I), and $Co{-}N = 1.8879$ Å, $Co{-}O = 1.9128$ Å (for monoclinic polymorph II, both average of three) with $\Sigma = 3.8007(9)$ Å (table in Supplementary material), following after $Co{-}N = 1.858$ Å (average of three) and $Co{-}O = 1.896$ Å (average of three) ($\Sigma = 3.754(5)$ Å) reported earlier by Tiekink [21].

4. Conclusions

The first complex of Co(III) with the cyanoxime ligand *fac*-$Co(BCO)_3$ was synthesized and characterized using CV, UV-Vis, IR, ^1H, ^{13}C NMR, spectroscopy, and X-ray analysis. Depending on a solvent used for crystallization of the complex – $CHCl_3$ or CH_3CN – two polymorphs were obtained: trigonal, I with included disordered chloroform molecule, and solventless monoclinic II. The low-spin Co(III) has unusually low value of the redox potential ($E_{1/2} = -0.0975$ V), evidence of a significant ligand-to-metal charge transfer. This conclusion is in agreement with results of the spectroscopic studies of *fac*-Co(BCO)$_3$. The cyanoxime anion in the complex in the nitroso form adopts *cis*-*anti* configuration and exhibits very tight binding to Co(III).

Supplementary material

Pages of this material such as: the list of ligands previously used for the preparation of mono-, bis-, and *tris*-oximato complexes (ESI 1), a view of an enantiomeric pair of *fac*-Co(BCO)$_3$ molecules in the unit cell of trigonal polymorph I (ESI 2), the unit cell content in the structure of trigonal polymorph I (ESI 3), a view of an enantiomeric pair of *fac*-Co(BCO)$_3$ molecules in the unit cell of monoclinic polymorph II (ESI 7), the unit cell content in the structure of monoclinic polymorph II (ESI 8), the check CIF/Platon report for both crystal structures (ESI 4–6 and 9, 10), geometry of coordination polyhedron of Co(III) center (ESI 11), and the CV curve for the complex (ESI 12) are available online.

Acknowledgments

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