Synthesis and Structure of New Thiourea-Containing Cobalt(III)
Dioximates with the $[\text{TiF}_6]^{2–}$ Anion

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Abstract—The new Co(III) dioximates $[\text{Co(DH}_2)(\text{D})(\text{Thio})_2][\text{TiF}_6] \cdot 2\text{DMF}$ (I), $[\text{Co(NioxH}_2)(\text{Thio})_2][\text{TiF}_6] \cdot 2.25\text{H}_2\text{O}$ (II), and $[\text{Co(DpgH}_2)(\text{Thio})_2][\text{TiF}_6] \cdot 4\text{DMF} \cdot 1.5\text{H}_2\text{O}$ (III) have been synthesized and studied. The molecules and doubly charged anion; NioxH and DpgH are singly charged anions of 1,2-cyclohexanedione dioxime and diphenylglyoxime, respectively; Thio is thiourea; DMF is dimethylformamide. The composition and structure of the complexes have been studied by IR, UV, and NMR spectroscopy. The crystal structures have been determined by X-ray crystallography. The hydrogen bonds in the structures are formed by fluorine atoms of the $[\text{TiF}_6]^{2–}$ anion with Co(III) complex cations and solvent molecules of crystallization. The amino groups of coordinated thiourea molecules are also involved in the hydrogen bond system, which is responsible for their different arrangement with respect to the equatorial planes of the Co(III) complex cations.

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PHYSICAL METHODS
OF INVESTIGATION

The 3d-metal dioximates have been continuously studied owing to numerous possibilities of using these compounds as models of physiologically important substances [1, 2], as catalysts [7], etc. It has been demonstrated that the introduction of fluoro-containing Co(III) complexes into growth media of some microorganisms stimulates the enzymatic activity and increases biomass accumulation [8–11]. Studying transition metal dioximates, including Co(III) complexes, has revealed the role of the outer-sphere anion on the crystal packing and arrangement of axial ligands [12–17]. It has also been demonstrated that fluorine-containing anions have a significant effect on the position of ligands containing functional groups (thiourea, selenourea, and others) since they can be involved in hydrogen bond systems.

EXPERIMENTAL

**Synthesis of I.** To a solution of 0.33 g (1 mmol) of CoTiF$_6$ · 6H$_2$O in 30 mL of water, 0.23 g (2 mmol) of dimethylglyoxime and 0.15 g (2 mmol) of thiourea in 40 mL of methanol was added. The resulting solution was heated on a water bath for 10–15 min. Slow evaporation of the dark brown solution afforded crystals as hexagonal plates. The yield was 53%. The compound is soluble in DMSO, DMF, methanol, and ethanol and less soluble in water.

For C$_{28}$H$_{38}$Co$_2$F$_6$N$_{18}$O$_{10}$S$_4$Ti anal. calcd. (%): Co, 9.90; C, 26.22; H, 4.91; N, 21.17.

Found (%): Co, 9.59; C, 26.11; H, 4.68; N, 21.03.

**Synthesis of II.** To a solution of 0.33 g (1 mmol) of CoTiF$_6$ · 6H$_2$O in 30 mL of water, 0.28 g (2 mmol) of 1,2-cyclohexanedione dioxime and 0.15 g (2 mmol) of thiourea in 40 mL of methanol was added. The resulting solution was heated on a water bath for 7–8 min at 70°C. Within 2–3 h, needle-shaped crystals were deposited from the dark brown solution. The yield was 52%. The compound is soluble in DMSO, DMF, methanol, and ethanol and less soluble in water.

For C$_{28}$H$_{56.5}$Co$_2$F$_6$N$_{16}$O$_{10.25}$S$_4$Ti anal. calcd. (%): Co, 9.91; C, 28.28; H, 4.79; N, 18.84.

Found (%): Co, 9.62; C, 28.06; H, 4.57; N, 18.61.
Synthesis of III. A solution of 0.48 g (2 mmol) of diphenylglyoxime in 10 mL of DMF was added to 0.15 g (2 mmol) of thiourea in 50 mL of methanol. The resulting solution was heated on a water bath up to ~70°C. Then, a solution of 0.33 g (1 mmol) of CoTiF$_6$·6H$_2$O in 30 mL of water was added dropwise to the hot solution so that the temperature remained constant. The solution was heated for another 5 min, then filtered, and left for slow evaporation. Within 4–6 days, dark brown prismatic crystals were deposited from the solution. The yield was 48%. The compound is soluble in DMSO, DMF, and methanol and insoluble in water.

For C$_{72}$H$_{91}$Co$_2$F$_6$N$_2$0$_{13.5}$S$_4$Ti anal. calcld. (%): Co, 6.33; C, 46.48; H, 4.93; N, 15.06.

Found (%): Co, 6.19; C, 46.33; H, 4.71; N, 14.82.

Physical methods. The composition and structure of the complexes were determined on the basis of elemental analysis, IR and UV spectroscopy, NMR, and X-ray crystallography data. The IR spectra were recorded on Perkin–Elmer Spectrum 100 (mineral oil mulls, 400–4000 cm$^{-1}$) and ATP (650–4000 cm$^{-1}$) FT-IR spectrophotometers; the UV spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer (aqueous solutions, concentration 0.5 $\times$ 10$^{-4}$ mol/L); the $^1$H and $^{13}$C NMR spectra were recorded on Bruker AC-200 and AC-400 (operating at 400.13 MHz for $^1$H and 100.61 MHz for $^{13}$C, DMSO-d$_6$ solutions, TMS as the internal reference) spectrometers. Chemical shifts were given in ppm.

X-ray crystallography. Structural data for I were collected at room temperature on an Oxford Diffraction Xcalibur CCD diffractometer; for II and III, data were collected at 213 and 100 K on STOE IPDS and Nonius Kappa CCD, diffractometers, respectively (MoK$_{α}$ radiation, $λ=0.71073$ Å, graphite monochromator, $ω$ scan). The unit cell parameters were refined over the entire array of experimental data. Intensity integration and reduction to the common scale for III were performed with the DENZO and SCALEPACK programs [20]. Correction for absorption was made using the XEMP program [21]. The crystal structures were solved by direct methods and refined by least-squares calculation in the anisotropic full-matrix approximation for non-hydrogen atoms (SHELX-97) [22]. In all three structures, solvent molecules of crystallization (DMF, H$_2$O) were found, which occupied two positions or were disordered over two positions. The hydrogen atoms of the oxime groups and water were located from difference Fourier synthesis, and the other hydrogen atoms were introduced into the geometrically calculated positions and refined isotropically using the rigid body model. The crystal data and experimental details for I–III are summarized in Table 1, bond lengths and bond angles are given in Table 2, and the geometric parameters of hydrogen bonds are listed in Table 3. The positional and thermal parameters for I–III were deposited with the Cambridge Crystallographic Data Centre (CCDC 866936, 866937, and 866938, respectively).

RESULTS AND DISCUSSION

On the basis of elemental analysis of I–III, we assumed that these compounds are Co(III) trans-dioximates formed by metal complex cations containing two chelating dioxime residues (DioxH is monodeprotonated dioxime anion) and two monodentate thiourea molecules bound to outer-sphere [TiF$_6$]$_2$– anions and solvent molecules of crystallization.

The UV spectra of the complexes show two absorption bands. One of them at 234 (I), 237 (II), and 245 nm (III) is assigned to the π→π* transfer in the Co(DioxH)$_2$ group, and the other band at ~337 nm characterizes the coordinated thiourea molecule. The intensity of the latter decreases with time, which can be explained by the substitution of solvent molecules for the coordinated thiourea molecules resulting in aqua and dioxia complexes.

The absorption bands ν(CN) at 1658 cm$^{-1}$, ν(NO)$_{b_{1g}}$ at 1233 and 1086 cm$^{-1}$, δ(CNO) at 713 cm$^{-1}$, ν$_{a}$(Co–N) at 542 cm$^{-1}$, and ν$_{c}$(Co–N) at 492 cm$^{-1}$ in the IR spectrum of complex I and the bands ν(CN) at 1642 cm$^{-1}$, ν(NO)$_{b_{1g}}$ at 1222 and 1059 cm$^{-1}$, δ(CNO) at 730 cm$^{-1}$, ν$_{a}$(Co–N) at 538 cm$^{-1}$, and ν$_{c}$(Co–N) at 422 cm$^{-1}$ in the IR spectrum of complex II are evidence that the dioximes are coordinated to the central atom. The IR spectrum of complex III shows the bands ν(CN) at 1639 cm$^{-1}$ and ν(NO) at 1255 and 1075 cm$^{-1}$, as well as the bands at 736 and 691 cm$^{-1}$ due to bending out-of-plane vibrations δ(C–H) of the monosubstituted aromatic ring. The bands ν$_{a}$(NH) at 3288–3301 cm$^{-1}$, ν$_{c}$(NH) at 3210–3240 cm$^{-1}$, δ(NH$_2$) at 1627–1633 cm$^{-1}$, and ν(CN) + ν(CS) + δ(HNC) at 1057–1066 cm$^{-1}$ point to presence of coordinated thiourea molecules in the dioximates. The corresponding stretching and bending vibration frequencies differ slightly from the values characteristic of free thiourea.

In the $^1$H NMR spectrum of complex I, the signal of methyl groups is shifted downfield to 2.14 ppm (1.91 ppm for the free ligand). In the $^1$H NMR spectrum of complex II, there are two singlets characterizing the CH$_2$ groups of 1,2-cyclohexanedione dioxime. One singlet at 1.69 ppm is assigned to the CH$_2$ groups more distant from the oxime groups, and the other singlet at 2.85 ppm is due the CH$_2$ groups neighboring to quaternary carbon atoms. In the spectrum of III, the signals at 7.12–7.35 ppm are due to the phenyl rings of the dioxime.

The signals at ~17.10–18.02 ppm in the spectra of I–III correspond to the OH protons and are strongly shifted downfield as compared with the uncoordinated dioxime, which proves the formation of intramolecular hydrogen bonds in the equatorial plane of the cation.