Organoantimony(V) Cyanoximates: Synthesis, Spectra and Crystal Structures

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A series of 25 new organoantimony(V) cyanoximates has been synthesized and studied using IR, visible, and NMR spectroscopy and X-ray analysis. Crystal structures were determined for compounds $(C_6H_5)_4Sb\{ONC(CN)C(O)NH_2\}$ (**1**) and $(C_6H_5)_4Sb\{ONC(CN)C(O)N(CH_3)_2\}$ (**2**). Both complexes crystallized in the monoclinic space group $P2_1/c$ (Z = 4) with unit cell parameters (Å, grad) of $a = 14.921(3)$, $b = 10.165(2)$, $c = 17.571(7)$, $\beta = 113.26(6)$ for compound **1**, and $a = 16.415(4)$, $b = 10.406(3)$, $c = 17.152(3)$, $\beta = 117.79(2)$ for compound **2**. For 5438 and 5056 independent reflections the refinement yielded *R*-factors 0.022 and 0.037 for the structures of **1** and **2**, respectively. Cyanoxime anions are bound to the antimony(V) atoms in a monodentate fashion via the oxygen atoms of the oxime groups. The ligands adopt trans-anti configuration in these compounds. The coordination polyhedron in both complexes is a distorted trigonal bipyramid with the axial location of the cyanoxime ligand. A similar binding mode of other anions in synthesized organoantimony(V) complexes has been offered on the basis of the similarity of their IR spectra to those of the compounds whose structures were determined crystallographically. The exact assignment of vibrations involving the oxime group was carried out using synthesized ^{15}N (53%) isotopomers.

Introduction

The treatment of malignant formations with transition metals complexes has a long and successful history.[1,2] The vast majority of such compounds includes mixed halogen−amine or amino−carboxylate complexes of platinum(II) and palladium(II). These substances are active ingredients of traditional metallocomplex cancer chemotherapy drugs. The most fundamental limitation of the continuous use of these compounds is their high toxicity, which leads to kidney and/or liver failure. Therefore, a significant problem with the use of metal-containing chemotherapy agents is keeping the cytostatic activity high, while simultaneously reducing the toxicity.

Today, in addition to developing platinum compounds with improved therapeutic characteristics, there is a focus on synthesis and testing for antitumor properties of a large number of organometallic and traditional inorganic complexes. So far, most of the research has been concentrated on inorganic gallium[3] and organometallic tin(IV) derivatives such as $R'_2Sn\{S_2PR''_2\}$ (R′ = Ph, *n*-C_4H_9; R" = *i*-OC_3H_7, Ph).[4,5] Some of these complexes were reported to demonstrate considerably higher *in vitro* anticancer activity than cisplatin, $Pt(NH_3)_2Cl_2$.[6]

Over the last several years organoantimony derivatives have also shown significant antitumor activity. These compounds are diphenylorganoantimony(V) thiophosphates such as $Ph_2Sb\{S_2PR_2\}$ (Ph = C_6H_5, R = Ph, *i*-OC_3H_7)[7,8] and methylantimony(III) complexes such as $(CH_3)SbL$ (L = derivatives of meta-substituted salicylic acid).[9] The action of these complexes is associated with cytostatic activity[10] similar to that for cisplatin. In addition, the biological toxicity of organoantimony and organotin compounds is much less than that for Pt and Pd anticancer substances. The solubility of some of these complexes is high enough to maintain their appreciable and effective intracellular concentration.

It is known that compounds of the main group 5 elements, such as As and Bi, have extensive pharmacological applica-

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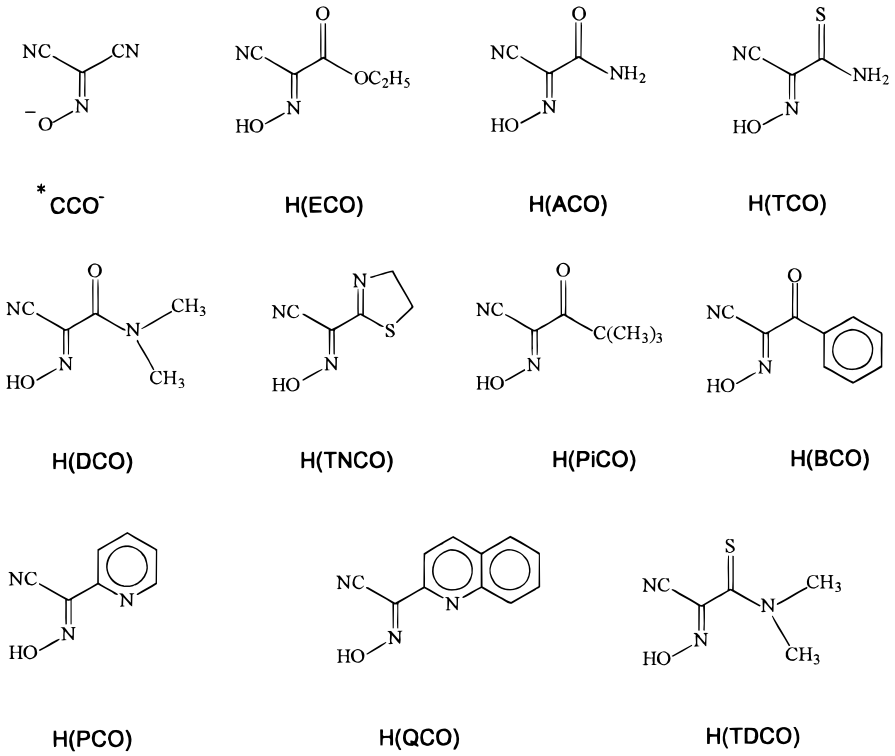
Scheme 1



*An anion; respective acid HO−N═C(CN)$_2$ is unknown.

tions,[11] as pioneered with the famous phenylarsenic derivative *salvarsan* by Paul Ehrlich. Interestingly enough, several organoantimony compounds have also exhibited antimicrobial properties.[12]

On the other hand, there is a group of multidentate organic ligands, namely, oximes, which have known biological activity such as growth regulatory, antimicrobial, and fungicidal. For example, oxime groups are present in molecules of the family of *Althiomycin* antibiotics.[13] Many oximes are weak organic acids that can easily form numerous salts and complex compounds. Some oximes, namely cyanoximes (compounds having the general formula HO−N═C(CN)−R, where R is an electron withdrawing group: Scheme 1 and ref 14), demonstrate a variety of properties as biologically active molecules with low toxicity. For instance, amide−cyanoxime HO−N═C(CN)−C(O)NH$_2$ exhibits growth regulation in plants,[15] and *N*,*N*-dimethylamide−cyanoxime, HO−N═C(CN)−C(O)N(CH$_3$)$_2$ shows antidote properties against agricultural organophosphorus pesticides.[16] The sulfur-containing thioamide−cyanoxime, HO−N═C(CN)−C(S)NH$_2$ and its Na^+, K^+, Cu^{2+}, and Ni^{2+} salts demonstrated antimicrobial and fungicidal activity,[17] etc.

It was interesting to obtain a series of organometallic antimony cyanoximates that were previously unknown. In these cases there may be an opportunity to combine useful properties both from the organometallic side of the molecule and from the acido-ligand as well. This is important for the design of a new group of organoantimony compounds with potentially useful anticancer properties. Therefore, summarizing the above, systematic studies which involve syntheses, spectroscopic, and structural characterization of the R_4SbL and $R_3Sb(Hal)L$ (R = Ph; L = monoxime anion; Hal = F^-, Cl^-, Br^-) represent the main topic of the current paper.

Experimental Part

Synthesis of Ligands. In general, α-substituted acetonitriles that have the formula NC−CH$_2$−R (R = electronwithdrawing group) are the most convenient precursors for the preparation of cyanoximes, shown with their commonly used abbreviations in Scheme 1. Meyer's reaction[18] allows the desired cyanoximes to be obtained with good yields from the above acetonitriles:

$$\mathrm{NC{-}CH_2{-}R + KNO_2(CH_3COOH) \xrightarrow{-T,\ +N_2} HO{-}N{=}C(CN){-}R} \quad (1)$$

Therefore, compounds such as H(ECO),[19] H(ACO),[20] H(TCO),[21] H(PiCO),[22] H(BCO),[14c] and H(PCO)[23] were synthesized according to reaction **1** and published procedures. These cyanoximes were then extracted by ether or CHCl$_3$ from acidified to pH = 4 aqueous solutions.

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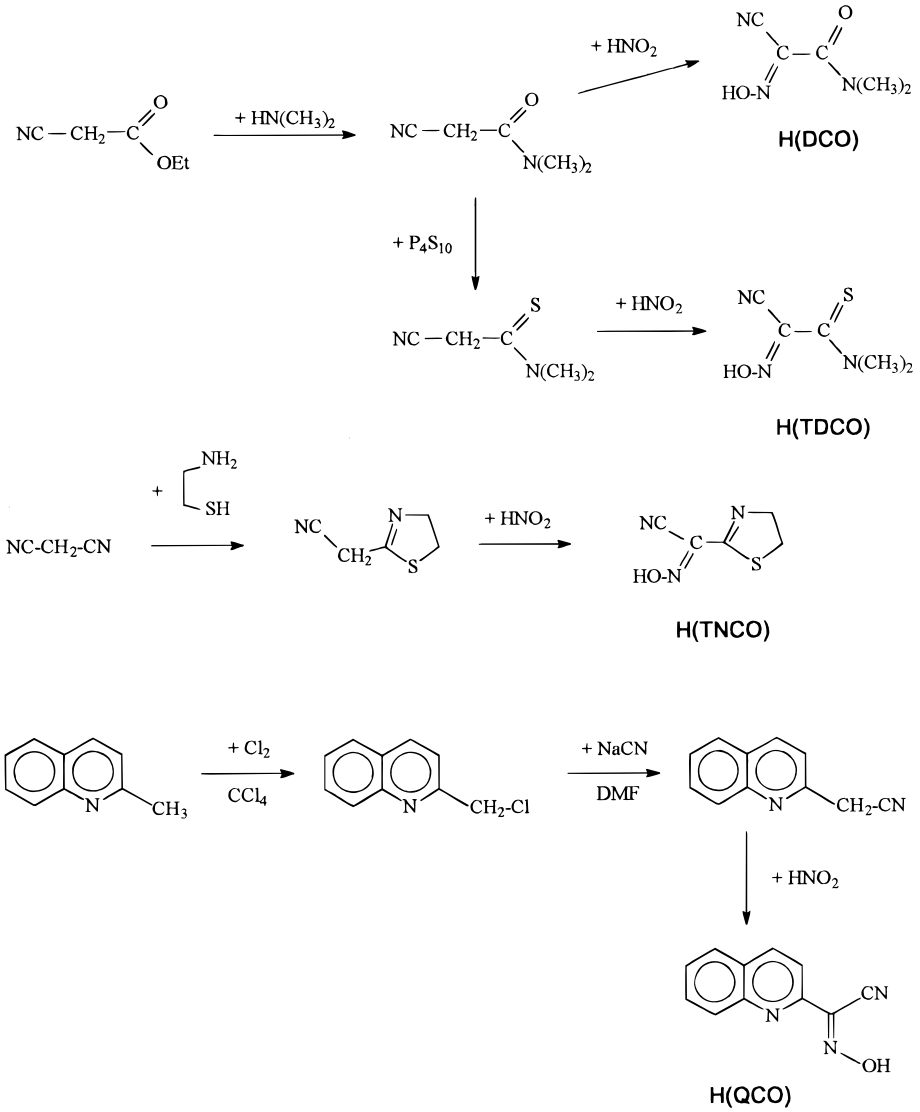
Scheme 2



The potassium salt of the malonodinitrile oxime, K(CCO), is the only source of CCO^- anion available since the respective H-oxime is unknown.[24]

Less trivial preparation of H(DCO), its thio analogue H(TDCO), and 2-hetarylcyanoximes such as H(TNCO) and H(QCO) is shown in Scheme 2 and described below.

The following procedure describes the preparation of 2-cyano-*N*,*N*-dimethylacetamide, which is a precursor for the synthesis of ligands such as H(DCO) and H(TDCO) (Scheme 2).

2-Cyano-*N*,*N*-dimethylacetamide, NC−CH_2−C(O)N$(CH_3)_2$. A 30 mL aliquot of cyanoacetic ester, NC−CH_2−C(O)OC_2H_5, was added dropwise to a 7 M solution of dimethylamine in isopropyl alcohol (200 mL). This solution was obtained by condensation of boiling dimethylamine, which was produced by reaction of $NH_2(CH_3)_2^+Cl^-$ with KOH, into *i*-PrOH. A 14 g quantity of colorless crystalline 2-cyano-*N*,*N*-dimethylacetamide precipitated from the above mixture after 12 h at −10 °C. A new portion of 30 mL of cyanoacetic ester at the same conditions gives 20.5 g more of crystalline amide. The combined precipitate was washed with cold *i*-PrOH and dried under vacuum. The compound is well soluble in H_2O and acetone; mp = 64 °C. ^{1}H NMR (200 MHz, in DMSO-d_6 (ppm)): 3.99 (2H, s, methylene), 2.93 (3H, s, methyl), 2.85 (3H, s, methyl). $^{13}C\{^1H\}$ NMR (400 MHz, in DMSO-d_6 (ppm)): 24.83 (CH_3), 35.20 (CH_3), 47.04 (CH_2), 115.61 (CN), 162.80 (amide).

2-(Oximido)(*N*,*N*-dimethylamido)acetonitrile, H(DCO). A 20 g sample of the above 2-cyano-*N*,*N*-dimethylacetamide was dissolved in 100 mL of an aqueous solution of 26.5 g of KNO_2. Then 21.8 mL of glacial acetic acid was added dropwise under stirring and inert gas protection over 3 h and the reaction mixture was cooled to −5 °C. A white precipitate of 2-(oximido)(*N*,*N*-dimethylamido)acetonitrile, 16.5 g (65%), formed after keeping the resulting solution overnight in a refrigerator at −5 °C. The microcrystalline precipitate of H(DCO) was filtered off, washed with icy water, and dried in a vacuum. The extra amount (∼6 g) of cyanoxime can be obtained from the above mother liquor by extraction of H(DCO) with ether, although the organic layer is contaminated with acetic acid. 2-(Oximido)(*N*,*N*-dimethylamido)-acetonitrile is poorly soluble in cold water but nicely soluble in ether, acetic acid, and acetone; mp = 138 °C. Anal. found (calculated) for $C_5H_7N_3O_2$, %: N, 31.76 (32.02); C, 44.59 (44.24); H, 5.64 (5.58).

2-Cyano-*N*,*N*-dimethylthioacetamide, NC−CH_2−C(S)N$(CH_3)_2$. A 22.4 g sample of 2-cyano-*N*,*N*-dimethylacetamide, NC−CH_2−C(O)N-$(CH_3)_2$, were refluxed with 28.8 g of P_4S_{10} in 200 mL of anhydrous ethyl acetate during 3 h. Control for the reaction completion was achieved by monitoring of disappearance of the starting oxo-amide on TLC. Solution was evaporated to dryness after filtration through Celite. Solid residue was twice recrystallized from iso-propyl alcohol. Yield: 14.1 g (55%). Compound represents colorless needles, poorly soluble in water, but readily dissolves in acetone, ether and *n*-PrOH; mp = 85 °C. ^{1}H NMR (200 MHz, DMSO-d_6 (ppm)): 3.98 (methylene, s, 2H),

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3.30 (methyl, s, 3H), 3.38 (methyl, s, 3H). Pos. FABMS (*m*/*z*): 128.1. Anal. For $C_5H_8N_2S$ found (calculated), %: N 21.3 (21.8), C 46.2 (46.8).

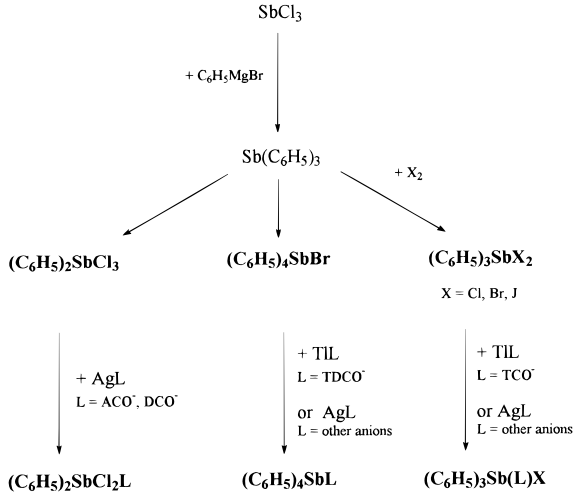
2-(Oximido)-*N*,*N*-dimethylthioamidoacetonitrile, H(TDCO). A 12.8 g sample of 2-cyano-*N*,*N*-dimethylthioacetamide and 8.3 g of $NaNO_2$ were dissolved in 800 mL of H_2O at 45 °C, and then the solution was slowly cooled to 5 °C. Hydrochloric acid (1 M, 120 mL) was dropwise added over 2 h and under inert gas protection. The reaction mixture was kept overnight at 0 °C and then filtered. Cyanoxime H(DTCO) then was extracted using three portions (50, 100, and 200 mL) of diethyl ether. The extract was dried over Na_2SO_4 and then concentrated to give an orange oil that slowly crystallized. Yield: 15.4 g (97%). The compound appears as yellow-orange crystalline material, soluble in acetone and ether and poorly soluble in water; mp = 97−99 °C. Anal. found (calculated) for $C_5H_7N_3OS$, %: N, 26.2 (26.7); S, 20.1 (20.4); C, 37.9 (38.2). Positive FABMS (*m*/*z*): 157.1.

2-(Cyanomethyl)-Δ^2-thiazolin, NC−CH_2−C_3H_4NS. The following procedure describes the preparation of 2-(cyanmethyl)-Δ^2-thiazolin, which is a precursor for the synthesis of the thiazolin−cyanoxime H(TNCO). A 23.2 g sample of 2-aminoethanethiol was added in small portions over a period 2 h to a solution prepared by dissolving 20.4 g of freshly distilled $CH_2(CN)_2$ and 17.7 mL of CH_3COOH in 150 mL of anhydrous C_2H_5OH at room temperature. The volume of the reaction mixture was reduced to a third of the original volume by slow evaporation of the solvent, which required about 5 h. The oil obtained was mixed with 150 mL of water. NC−CH_2−C_3H_4NS was extracted using three 100 mL portions of chloroform. The extract was dried over Na_2SO_4, and the solvent was removed under reduced pressure to give a red oil. This oil was quickly distilled at 80−85 °C/0.001 Hg mm to give a yellow oily product that was unstable at room temperature. Yield: 40%. The product should be stored in the refrigerator under an inert gas atmosphere. Anal. found (calculated) for $C_5H_6N_2S$, %: N, 22.43 (22.20); S, 25.08 (25.36).

2-(Oximidocyanmethyl)-Δ^2-thiazolin, H(TNCO). A 2.29 g sample of $C_5H_6N_2S$, the synthesis of which is described above, and 1.85 g of KNO_2 were dissolved in a mixture of 30 mL of water and 20 mL of ethanol. After the mixture was cooled to −3° C, 2.1 mL of concentrated HCl (∼35%) in 10 mL of H_2O was added dropwise over a period 30 min. After 3 h the resulting cyanoxime precipitate was filtered off, washed with ice water (∼5 mL), and dried. Yield: 81%. The cyanoxime obtained crystallizes as a monohydrate that is soluble in ether, methanol, and ethanol. Anal. found (calculated) for H(TNCO)·H_2O, $C_5H_7N_3O_2S$, %: N, 24.51 (24.27); S, 18.38 (18.49).

2-(Oximido)-2-quinolylacetonitrile, H(QCO). The chlorination of quinaldine was carried out in CCl_4 using gaseous Cl_2, and the disappearance of the starting compound on TLC was used as a control for the reaction completion. The introduction of a cyano group was done in hot DMF according to standard procedure. The yellowish-white waxy solid obtained was distilled in high vacuum to give pure, low melting, white crystalline 2-quinolylacetonitrile. Synthesis of the oxime was accomplished in a manner essentially the same as for the preparation of HPCO. For the oxime preparation, 1.68 g (0.01 mol) of 2-quinolyl-acetonitrile was mixed with 0.66 g (0.011 mol) of glacial acetic acid and the mixture was cooled to −50 °C. To this mixture was rapidly added 0.85 g (0.01 mol) of solid KNO_2 in an inert atmosphere. After ∼5 h of slowly warming to room temperature, the white flaky cyanoxime precipitate was filtered off, washed with 20 mL of water, and dried in a vacuum desiccator over KOH. Yield: 87%. Mp = 184 °C (H_2O), decomposition temperature = 217 °C. Anal. found (calculated) for $C_{11}H_9N_3O_2$, %: C, 61.25 (61.39); N, 19.11 (19.53); H, 4.22 (4.19). Pure H(QCO) is a white microcrystalline precipitate and is insoluble in water, hexane, and benzene but is soluble in acetone and alcohols.

Scheme 3



NMR spectra (^{1}H and other nuclei) for all shown in Scheme 1 cyanoxime ligands are presented in S1−S3 of the Supporting Information.

Coordination Compounds. All cyanoximes presented in Scheme 1 easily undergo deprotonation upon addition of base, forming yellow anions:[14b,25]

$$\underset{\text{colorless}}{HO{-}N{=}C(CN){-}R} + \text{base} = \underset{\text{yellow}}{[O{-}N{-}C(CN){-}R]^-} + \text{baseH}^+ \quad (2)$$

This is because of the several orders of magnitude increased acidity of cyanoximes in comparison with other monoximes[14c,26] or dioximes.[27] Moreover, reaction **2** is the best way of obtaining the fast crystallizable and pure Tl(I) cyanoximates if Tl_2CO_3 is used in such preparations.[14c,28] Potassium salts of the above ligands were synthesized upon reaction of K_2CO_3 with 2 equiv of cyanoximes in warm ethanol. Removal of solvent under vacuum yielded bright-yellow solid compounds that have KL formulae, as shown by elemental analyses. Potassium salts of all cyanoximates except H(TCO) and H(TDCO) have been used in the ion exchange reactions with equimolar amounts of $AgNO_3$ in aqueous solutions to form insoluble silver(I) cyanoximates. Quantitatively precipitated AgL (L = anions of ligands in Scheme 1) complexes were filtered, washed with icy water, and dried under vacuum. These silver(I) complexes then were employed for the syntheses of organoantimony(V) cyanoximates, as shown in Scheme 3. Thus, heterogeneous exchange reactions in anhydrous CH_3CN between equimolar amounts of fine powdered solid AgL and solutions of respective Sb(V) derivatives at room temperature in the dark within ∼20 min lead to a high-yield formation of organoantimony complexes.

Silver(I) complexes of thioamide-containing cyanoximes H(TCO) and H(TDCO) cannot be obtained because of their fast decomposition reactions and formation of black Ag_2S. These ligands, however, form stable and light-insensitive orange Tl{TDCO} and Tl{TCO} complexes, which have been used in a way similar to the above exchange reactions during the preparation of Sb(V) derivatives with other cyanoximates. Thallium(I) halogenides (e.g., TlBr, TlCl) are sparingly soluble in CH_3CN, and these salts at 0 °C can be quantitatively separated from solutions of organoantimony(V) cyanoximates.

Antimony trichloride (Fluka) and bromobenzene (Aldrich) were reagent grade quality and used without additional purification. $SbCl_3$ was the only precursor used for the preparation of starting materials for organoantimony(V) cyanoximates. Syntheses of $Sb(C_6H_5)_3$, $(C_6H_5)_2SbCl_3$, $(C_6H_5)_4SbBr$, and $(C_6H_5)_3Sb(halogen)_2$ were carried out according to published procedures.[29] Certainly, it is clear that any other substituted aryl derivatives of antimony(V) can be obtained in a similar manner if these functional groups do not interfere with Grignard reaction. For example, the presence of the poly(ethylene glycol)

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fragments in the phenylantimony units will provide necessary water solubility for prospective pharmacologically interesting compounds.[52]

Typical preparations of organoantimony(V) cyanoximates is described only for two compounds and shown below.

$Sb(C_6H_5)_3${PiCO}Br. To a solution of 0.513 g of triphenylantimony(V) dibromide, $Sb(C_6H_5)_3Br_2$, in 25 mL of dry acetonitrile was added 0.262 g of solid powdery Ag{PiCO} in small portions at 40 °C over ~20 min and with intensive stirring. Flaky AgBr precipitate that formed was filtered off and then, after washing with 5 mL of dry CH_3CN, discarded. Solute containing triphenylantimony(V) cyanoximate was concentrated at ambient temperature under vacuum to give a colorless microcrystalline complex.

$Sb(C_6H_5)_4${ECO}. Powdered silver(I) salt, Ag{ECO}, in an amount of 0.249 g was added in small portions to a solution of tetraphenylantimony(V) bromide in 25 mL of dry CH_3CN. The reaction was carried out under stirring at room temperature within ~20 min. A colorless solution of $Sb(C_6H_5)_4${ECO} was carefully filtered from AgBr and then concentrated on a rotavap at room temperature to yield white microcrystalline solid organoantimony(V) cyanoximate.

Some important properties of synthesized Sb(V) complexes such as analytical data and IR spectra are shown in Table 1 and S4 and S5 (Supporting Information). All these compounds are colorless crystalline materials with relatively low melting points.

Physical Methods. Elemental analysis for N, C, H, and S were carried out using a Carlo Erba Strumentazione C1600 apparatus. Melting points are presented without correction. Molecular weights of a series of organoantimony(V) cyanoximates were determined by cryoscopic method in benzene. This approach was used to characterize the speciation of complexes in bulk solutions since high molecular weight aggregates are rarely seen during mass-spectrometric studies. Spectroscopic and analytical data have confirmed suggested formulas for the synthesized both cyanoxime ligands and their Sb(V) complexes (Table 1 and S4 and S5).

Spectroscopy. The compounds obtained were studied by IR (400−4000 cm^{-1}) spectroscopy in KBr pellets using UR-20 (Karl Zeiss, Jena) and FT-IR Nikolet Impact 440 spectrometers. Assignments of vibrations that include the oxime group have been made using 53% enriched ^{15}N (NO group) cyanoximes and their Sb(V) complexes. IR spectroscopy data for studied organoantimony compounds are summarized in Table 1. Spectra for thallium(I) and silver(I) complexes were recorded on a Mattson 2020 Galaxy FT-IR spectrometer in Nujol mulls.

^1H, ^{13}C, and ^{14}N NMR spectra for cyanoximes and their alkali metal salts were obtained on the FT Bruker CXP-200 spectrometer using a 10 mm probe. Proton and carbon-13 spectra for organoantimony(V) cyanoximates were recorded by operating a JEOL GSX400 FT spectrometer. The same instrument has been used for variable-temperature ^1H experiments in DMSO-d_6 and $CDBr_3$.

UV−visible spectra for solutions of synthesized cyanoximes and their Sb(V) complexes were recorded on a Shimadzu SPC 2100 spectrophotometer in the range of 350−850 nm using 10 mm quartz cells. Variable-temperature experiments in a circulating thermostat were carried out for selected complexes from 291 to 358 K.

Mass spectra for several synthesized compounds were obtained using Autospec Q and ZAB spectrometers from VG-Analytical Ltd., of Manchester (England). Positive FAB technique with *m*-nitrobenzylic alcohol (NBA) as the matrix was used for characterization of different cyanoxime derivatives.

X-ray Crystallography. Single crystals suitable for X-ray diffraction experiments were obtained upon slow evaporation of acetonitrile solutions of organoantimony(V) cyanoximates at room temperature in the dark. Another successful way of growing single crystals of these complexes was found to be in slow cooling of saturated at 348 K solutions of the compounds in 50% aqueous ethanol to room temperature in a thermostat (~2 days). For the X-ray diffraction experiment, colorless crystals of prismatic habit with linear dimensions not exceeding 0.5 mm were selected. The X-ray experiment for a monocrystal of Ph_4Sb{ACO} was carried out on an Enraf Nonius CAD-4 diffractometer, while for a monocrystal of Ph_4Sb{DCO} a Syntex $P2_1$ apparatus was used for data collection. In both cases Mo Kα (λ = 0.710 73 Å) radiation and a graphite monochromator have been used for the diffraction experiment. The crystal structure of Ph_4Sb{ACO} was solved by the heavy atom technique and refined by the least-squares method in the full matrix anisotropic approximation. The reflections with $I > 3\sigma(I)$ have been used in the refinement procedure. Solution of the structure of Ph_4Sb{DCO} was carried out using the direct method and refined in the full matrix anisotropic approximation by the least-squares mode. The reflections with $I > 5\sigma(I)$ were allowed

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Table 1. Most Important Vibrational Frequencies in IR Spectra of the Synthesized Organoantimony(V)−Oxime Derivatives

	vibrations in cyanoxime group					C_6H_5− group and Sb−Ph vibrations		
compound	ν(C≡N)	ν(C═X)[a]	ν(C═N)[b]	ν(N−O)[b]	ρ(NH_2)	ν_{as}(C−H)	y(ν'_{19})	v(ν_8)
$Ph_2Sb\{ACO\}Cl_2$	2230	1668	1575	1067	1595	3180	447	682
$Ph_2Sb\{DCO\}Cl_2$	2230	1625	1585	1035		3090	447	682
$Ph_3Sb\{ACO\}F$[c]	2235	1675	1577	1062	1580	3065	454	685
$Ph_3Sb\{DCO\}F$[c]	2225	1627	1585	1020		3060	455	687
$Ph_3Sb\{ACO\}Cl$	2225	1680	1515	1030	1575	3060	452	682
$Ph_3Sb\{DCO\}Cl$	2220	1638	1570	1015		3050	453	685
$Ph_3Sb\{BCO\}Cl$	2220	1640	1565	1055		3050	455	685
$Ph_3Sb\{PiCO\}Cl$	2222	1680	1572	1029		3060	445, 456	687
$Ph_3Sb\{TCO\}Cl$	2227	882	1595	1045	1612	3050	430, 445, 455	687
$Ph_3Sb\{TNCO\}Cl$	2225	1605	1520	1050		3065	457	690
$Ph_3Sb\{ACO\}Br$	2227	1680	1520	1027	1573	3050	452	682
$Ph_3Sb\{DCO\}Br$	2220	1642	1570	1015		3055	455	677
$Ph_3Sb\{ECO\}Br$	2225	1710	1505	1028		3055	456	677
$Ph_3Sb\{PiCO\}Br$	2222	1662	1505	1025		3055	452	675
$Ph_3Sb\{ACO\}J$	2225	1700	1535	1045	1585	3060	455	692
$Ph_4Sb\{CCO\}$	2220		1565	1170		3060	415, 446	689
$Ph_4Sb\{ACO\}$	2217	1682	1480	1095	1580	3050, 3065	443, 452	695
$Ph_4Sb\{DCO\}$	2218	1635	1567	1050		3020, 3055	445, 455	692
$Ph_4Sb\{ECO\}$	2210	1730	1475	1065		3060	456	692
$Ph_4Sb\{PiCO\}$	2212	1662	1475	1130		3060	445	
$Ph_4Sb\{BCO\}$	2210	1628	1480	1132		3050	457	690
$Ph_4Sb\{TDCO\}$	2210	970	1520	1060		3050	444, 452	687
$Ph_4Sb\{PCO\}$	2212	1580	1480	1020		3060	460, 450	693
$Ph_4Sb\{QCO\}$	2215	1595	1485	1035		3060	448	694

[a] X = sulfur atom (for TCO^- and $TDCO^-$), oxygen atom (for ACO^-, DCO^-, BCO^-, $PiCO^-$, ECO^-), or nitrogen atom (PCO^-, $TNCO^-$, QCO^-). [b] The exact assignment for these vibrations was carried out using ^{15}N isotopomers and was also based on the force-field calculations.[51] [c] IR spectra also contained ν(Sb−F) vibrations at 507 (for ACO^-) and 509 (for DCO^-) cm^{-1}.

Table 2. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{27}H_{22}O_2N_3Sb$	$C_{29}H_{26}N_3O_2Sb$
molecular weight	542.2	570.2
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a	14.921(3)	16.415(4)
b	10.165(2)	10.406(3)
c	17.571(7)	17.152(3)
α, deg	90	90
β, deg	113.26(6)	117.79(2)
γ, deg	90	90
volume, $Å^3$	2339.4(2)	2591.9(2)
Z	4	4
density (calc), g/cm^3	1.480	1.461
exp temp	293	190
R_1[a]	0.022	0.037
wR_2[b]	0.031	0.043

[a] For 5972 total reflections, $F(000) = 4250$, 386 refined parameters, and weighting scheme $w = (\sigma^2F + 0.0016F^2)^{-1}$. [b] For 5271 total reflections, $F(000) = 1152$, 334 refined parameters and weighting scheme $w = (\sigma^2F + 99.0000F^2)^{-1}$.

Table 3. Selected Bond Lengths and Angles in the Structure of $(C_6H_5)_4Sb\{ACO\}$

bond	length, Å	valence angles,	grad
Sb−O(1)	2.259(1)	O(1)−Sb−C(4)	84.76(7)
Sb−C(4)	2.124(3)	O(1)−Sb−C(10)	80.59(7)
Sb−C(10)	2.122(2)	O(1)−Sb−C(16)	175.92(7)
Sb−C(16)	2.163(3)	O(1)−Sb−C(22)	83.62(7)
Sb−C(22)	2.117(3)	C(4)−Sb−C(10)	119.00(8)
O(1)−N(1)	1.342(2)	C(4)−Sb−C(16)	97.98(8)
O(2)−C(2)	1.218(3)	C(4)−Sb−C(22)	116.60(8)
N(1)−C(1)	1.282(3)	C(10)−Sb−C(16)	95.42(8)
N(2)−C(2)	1.329(4)	C(10)−Sb−C(22)	119.97(8)
N(3)−C(3)	1.134(4)	C(16)−Sb−C(22)	97.76(9)
C(1)−C(2)	1.496(3)	Sb−O(1)−N(1)	110.3(1)
C(1)−C(3)	1.434(4)	O(1)−N(1)−C(1)	115.9(2)
		N(1)−C(1)−C(2)	118.5(3)
		N(1)−C(1)−C(3)	121.6(2)
		C(2)−C(1)−C(3)	120.0(2)
		O(2)−C(2)−N(2)	124.1(3)
		O(2)−C(2)−C(1)	121.0(3)
		N(2)−C(2)−C(1)	114.9(2)
		N(3)−C(3)−C(1)	176.4(3)

in the refinement procedure. An empirical absorption correction was made by the DIFABS program, while the SHELXTL PLUS software package has been used in all calculations. The positions of hydrogen atoms were established by calculations and were refined isotropically using a riding model. Data of the X-ray experiment are shown in Table 2. The final atomic positional and thermal parameters for both structures are presented in Tables S6−S13 (Supporting Information). Selected bond lengths and angles for the structures of $Ph_4Sb\{ACO\}$ and $Ph_4Sb\{DCO\}$ are shown in Tables 3 and 4, respectively. Packing diagrams for both crystallographically characterized complexes are exhibited in S16 and S17 (Supporting Information).

Results and Discussion

Synthesized organoantimony(V) complexes with cyanoxime ligands represent monomeric species according to molecular mass measurements by the cryoscopic method (see S4, Supporting Information). Complexes form nonconducting solutions at room temperature in benzene, acetonitrile, or propanol, which evidence their molecular nature. Absence of color for these compounds in the crystal state indicates the oxime character of coordinated anions. This is opposite to the observed yellow or orange colors* for *nitroso*-anions in alkali metal,[30] ammonium,[31] phosphonium(V)[32] and arsonium(V),[33] salts of cyanoximes.[54] All these compounds form ionic bonds between cations and anions in the crystal lattice, as was shown by X-ray analysis. Nevertheless, tetraarylantimony(V) cyanoximates could have several possible structural motifs, as shown in Figure 1. These include both ionic and covalent binding of anions to the antimony atoms in complexes. Lack of the electrical conductivity of Ph_4SbL solutions in CH_3CN and the absence of high molecular weight aggregates in benzene, CH_2Cl_2 and $CHCl_3$

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(54) The color of ionic cyanoximates originates from the $n \rightarrow d\mu$ transition in the nitroso chromophore, as was observed and assigned earlier for NO_2^- and $ONC(CN)_2^-$ anions.[53] The value of molar absorptivity ϵ for anionic cyanoximes ranges between 80 and 170 M^{-1} cm^{-1} (Figures 4 and 5).

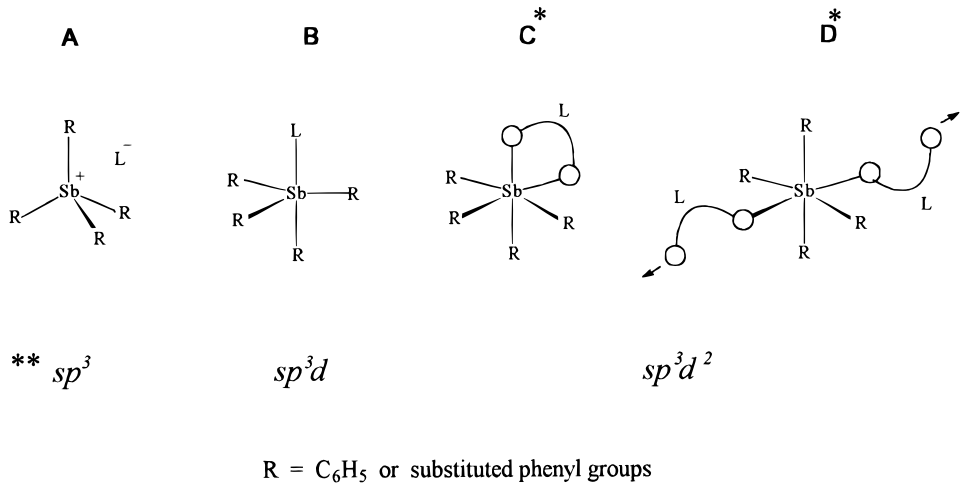


Figure 1. Possible spatial arrangements for tetraarylantimony(V) cyanoximates: (*) different bidentate coordination modes: chelate (five- or six-membered rings) and bridging; (**) idealized central atom hybridization states.

Table 4. Selected Bond Lengths and Angles in the Structure of $(C_6H_5)_4Sb\{DCO\}$

bond	length, Å	valence angles,	grad
Sb−O(1)	2.226(4)	C(11)−Sb−C(21)	94.7(2)
Sb−C(11)	2.167(6)	C(21)−Sb−C(31)	118.1(2)
Sb−C(21)	2.112(4)	C(21)−Sb−C(41)	117.7(2)
Sb−C(31)	2.122(4)	C(11)−Sb−O(1)	175.7(2)
Sb−C(41)	2.114(4)	C(31)−Sb−O(1)	82.8(2)
O(1)−N(1)	1.339(4)	C(11)−Sb−C(31)	94.7(2)
N(1)−C(1)	1.299(7)	C(11)−Sb−C(31)	94.7(2)
C(1)−C(2)	1.493(6)	C(31)−Sb−C(41)	121.3(2)
C(1)−C(3)	1.430(9)	C(21)−Sb−O(1)	83.4(2)
C(2)−O(2)	1.230(7)	C(41)−Sb−O(1)	86.6(2)
C(2)−N(2)	1.337(8)	Sb−O(1)−N(1)	104.4(3)
C(3)−N(3)	1.151(9)	N(1)−C(1)−C(2)	118.9(5)
N(2)−C(4)	1.472(10)	C(2)−C(1)−C(3)	117.8(5)
N(2)−C(5)	1.448(8)	C(1)−C(2)−N(2)	118.5(5)
		C(2)−N(2)−C(4)	124.1(4)
		C(4)−N(2)−C(5)	116.4(5)
		O(1)−N(1)−C(1)	116.2(4)
		N(1)−C(1)−C(3)	122.8(4)
		C(1)−C(2)−O(2)	118.0(5)
		O(2)−C(2)−N(2)	123.4(4)
		C(2)−N(2)−C(5)	119.0(5)
		C(1)−C(3)−N(3)	177.0(5)

(according to mass-spectrometric data and temperature depression measurements), allow us to exclude structures **A** and **D**. However, since cyanoximes themselves represent polydentate monoanionic ligands with a variety of donor atoms (Scheme 1), neither structure **B** nor **C** can be ruled out.

The question of binding modes of cyanoxime anions in synthesized complexes as well as their stability in different solvent systems and aqueous solutions is of great importance because of the possible future pharmacological applications of these compounds. Stability is particularly important for optimized drug development and biodistribution.

Crystal Structures of Complexes. Although almost all synthesized organoantimony(V) cyanoximates represent microcrystalline compounds, quality single crystals suitable for X-ray analysis were obtained only for two complexes. Both complexes, $Ph_4Sb\{ACO\}$ and $Ph_4Sb\{DCO\}$, have molecular structures that are displayed in Figures 2 and 3, respectively. Packing diagrams for both structures are shown in S16 and S17 (Supporting Information), where molecules of complexes form infinite stacks held together by van der Waals forces. The antimony atoms in both complexes are five-coordinate, and their geometries are represented as distorted trigonal bipyramids (Figures 2 and 3). Coordination polyhedra in studied organoantimony(V) cyanoximates in general are similar to those determined for Ph_4-

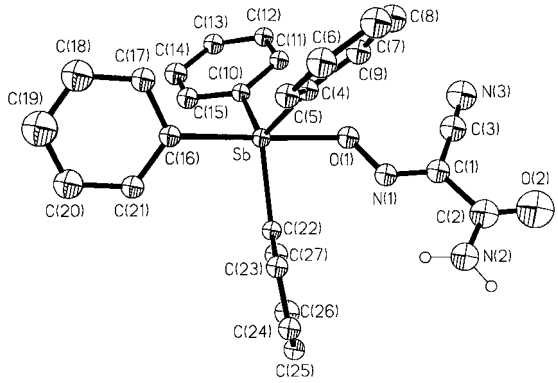


Figure 2. Molecular structure of $(C_6H_5)_4Sb\{ACO\}$ at 30% probability ellipsoids. Hydrogen atoms of phenyl groups are omitted for clarity.

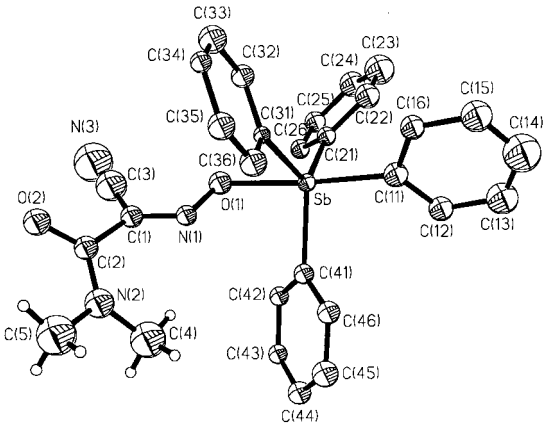


Figure 3. Molecular structure of $(C_6H_5)_4Sb\{DCO\}$: view at 30% probability ellipsoids. Shown general numbering scheme and only H atoms at methyl groups in the amide fragment.

$SbOCH_3$ and Ph_4SbOH.[29] The three equatorial positions are occupied by phenyl groups. Another phenyl group, which has slightly elongated Sb−C distances and the oxygen atom of the oxime group of the acido ligand are located in the axial positions (Tables 3 and 4). The equatorial phenyl groups adopt the most sterically favorable propeller-type configuration and are somewhat tilted toward coordinated cyanoxime ligands. Angles C_{ax}−Sb−C_{eq} in both structures are in the range between 90° and 100°. The angle C_{ax}−Sb−O_{ax} is 175.9(7)° for $Ph_4Sb\{ACO\}$ and 175.7(2)° for $Ph_4Sb\{DCO\}$ (Tables 3 and 4).

Cyanoxime anions demonstrate the monodentate binding

Table 5. Summarized Geometrical Features for ACO^- and DCO^- Cyanoxime Groups in Different Complexes

compound	ligand conformation and compound's structural feature	reference
H(ACO)	oxime is planar, trans-anti configuration	45
M{ACO} (M = Rb^+, Cs^+)	anion is planar, trans-anti configuration, nitroso-from	30a
Ni{ACO}$_2$·2H$_2$O	anion is planar, cis-anti configuration, nitroso-form in bidentate chelate trans complex	46
Pb{ACO}$_2$·H$_2$O	anion is planar, cis-anti configuration, nitroso-form in bidentate chelate cis complex	47
Tl{ACO}	nitroso-form of nonplanar anion; bridging coordination mode	48
Ph$_6$Te$_3$O$_2${ACO}$_2$ (Ph = C$_6$H$_5$)	oxime is planar, trans-anti configuration, monodentate binding via NO-group oxygen atom	49
Ph$_4$Sb{ACO}	planar oxime anion, trans-anti configuration, monodentate coordination via NO-oxygen atom	this work
(C$_2$H$_5$)$_3$Sn{ACO}	anion is planar, oxime form in trans-anti configuration; bidentate bridging coordination mode	45, 50
H(DCO)	oxime is nonplanar planar, trans-anti configuration	37
Ph$_4$Sb{DCO}	nonplanar oxime anion in trans-anti configuration, monodentate coordination via NO-oxygen atom	this work
Cu{DCO}$_2$*H$_2$O	planar anion, cis-anti configuration, nitroso-form in bidentate chelate trans complex	35d

mode via oxygen atoms of NO groups in both structures. This is a quite rare case of coordination of anions in this class of ligands.[24a,31b,34] The most common is a bidentate chelate[14c,35] or bridging mode[24b,25,28,36] observed earlier in complexes of transition metals, and p-metals such as Tl(I), Ag(I), and Sn(IV), respectively (Table 5). The distance Sb−O_{ax} is shorter in the Ph$_4$Sb{DCO} complex (2.226 Å) than for the Ph$_4$Sb{ACO} complex (2.259 Å). This fact is rather unexpected since the more bulky cyanoxime anion is closer to the central atom of Sb(V) than the less sterically hindered ACO^- anion. Moreover, the Sb−O(1)−N(1) angle of adjustment of the cyanoxime group to the tetraphenylantimony fragment is smaller in the structure of Ph$_4$Sb{DCO} (104.4°) than in the structure of Ph$_4$Sb{ACO} (110.3°) (Tables 3 and 4). These unusual structural features can be explained when examining the structures of anions in both organoantimony(V) cyanoximates. The ACO^- anion in Ph$_4$Sb{ACO} is planar, while the DCO^- ligand in Ph$_4$Sb{DCO} is not. The latter anion has two planar fragments, O(1)N(1)C(1)C(3)N(3) and O(2)C(2)N(2) with a dihedral angle between them of 47.8(1)° (Table 4). In fact, this angle is larger in Ph$_4$Sb{DCO} than in the structure of free oxime H(DCO), where it was found to be 28.2(3)°.[37] The origin of a greater dihedral angle of the cyanoxime group in the structure of Ph$_4$Sb{DCO} can be rationalized as the deviation from planarity relaxes a steric repulsion between the ligand and equatorial phenyl groups in the complex. Apparently, this also results in differences in the geometry of Sb−O(1)N(1) fragments for the two studied organoantimony(V) cyanoximates. The C(1)C(3)N(3) nitrile groups are linear; the corresponding angles equal 176.4° and 177.0° for Ph$_4$Sb{ACO} and Ph$_4$Sb{DCO}, respectively. The cyanoxime anions in structures of both complexes adopt trans-anti configuration with respect to mutual orientation of the oxime and the C═O groups. Some interesting structural peculiarities of the cyanoxime ligands for crystallographically characterized compounds are summarized in Table 5. This table contains examples that practically reflect the HSAB theory by Bassolo and Pearson. Indeed, complexes of transition metals such as Ni and Cu include cyanoximate anions that are bound in bidentate chelate fashion. Similar behavior of the ACO^- anion was found also in the Pb(II) complex (Table 5). Ligands exhibit nitroso character in the above compounds. In alkali metal ionic salts all studied to date cyanoximes are planar and also show the same nitroso character. This fact is reflected in a shorter N−O bond in comparison with the C−N bond in the C−N−O fragment. Oxophilic central atoms such as Te^{IV}, Sn^{IV}, and Sb^V prefer to form bonds with acido ligands via oxygen atoms. Anions in the later compounds are in the oxime form. Numerous examples of ampolydentate coordination of cyanoxime anions (e.g., different coordination modes for different central atoms and also often bridging function with multiple contacts) were recently reviewed.[14c,25,31b,36a]

Spectroscopic Studies. IR Spectra. The assignments of vibrations with participation of the −CNO group of the cyanoxime ligand were carried out using ^{15}N isotopomeric compounds. There were observed splitting and shifts in IR bands associated with vibrations of the oxime group in comparison with spectra of nonlabeled compounds. Previously it was found that the positions of ν(NO) and ν(CNO) vibrations in IR spectra are dependent to a great extent on the oxime or nitroso character of this group in a particular compound.[24a,36a,38] Moreover, the coordination mode of the cyanoxime ligand was found to be reflected in the IR spectrum.[39,40] The respective spectral−structural correlation based on comparison of data of X-ray analysis and vibrational spectroscopy were well established.[41] The most pronounced feature of IR spectra of organoantimony(V) cyanoximates is in their very low frequencies of ν(NO) vibrations in comparison with 3d metal complexes or alkali metal salts (Table 1). The positions of these bands are close to those found in IR spectra of free cyanoximes HL. This is unambiguous evidence of monodentate coordination of cyanoxime anions to Sb(V) by means of the oxygen atom of the oxime group. There were no significant changes observed for vibrational frequencies of other functional groups of anions in the IR spectra of organoantimony(V) cyanoximates that might be associated with additional coordination of these ligands to Sb(V) atoms. Since all complexes synthesized and discussed

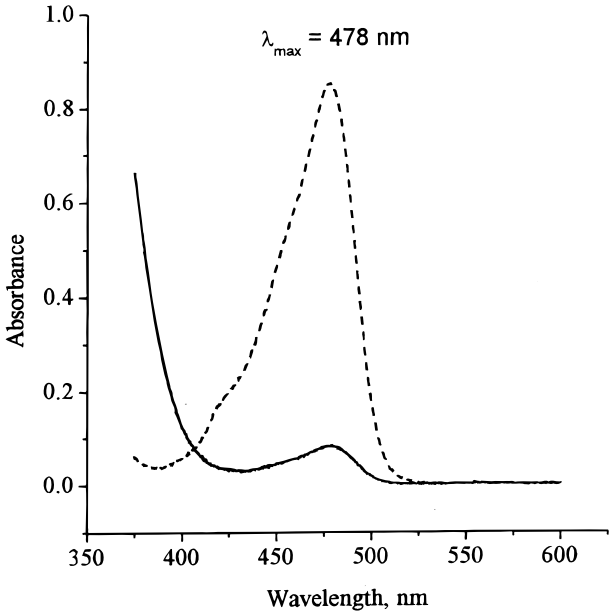


Figure 4. UV−visible spectra of fully dissociated $As(C_6H_5)_4^+(ACO)^-$ (7.6×10^{-3} M solution, dotted line) and $[Sb(C_6H_5)_4\{ACO\}]$ in DMF after heating at 100 °C within 5 min (6.2×10^{-3} M solution, solid line).

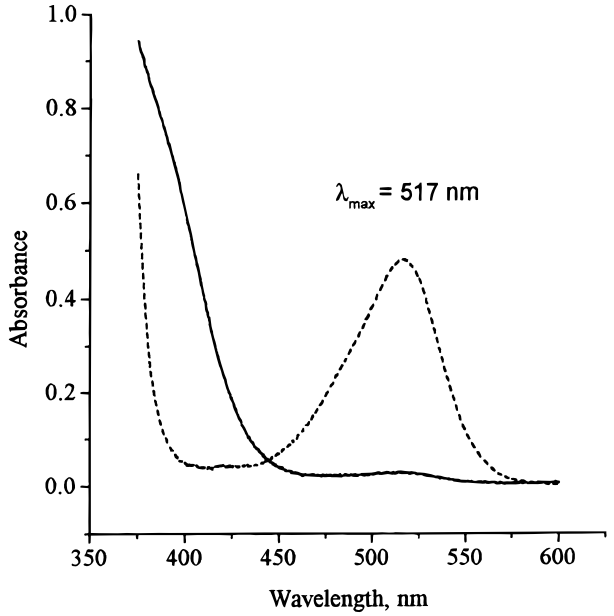
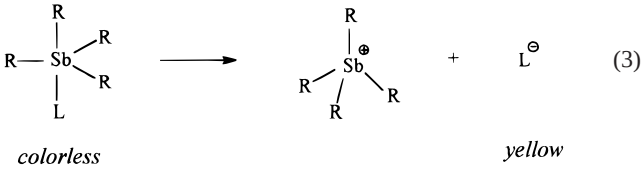


Figure 5. UV−visible spectra of ionic solution of $As(C_6H_5)_4^+(BCO)^-$ (5.4×10^{-3} M) in pyridine (dashed line) and molecular solution of $[Sb(C_6H_5)_4\{BCO\}]$ (4.8×10^{-3} M) in pyridine (solid line).

here demonstrate very similar IR spectra, an assumption about the analogous structures of tetraarylantimony(V) cyanoximates to those determined by X-ray analysis has been made (Table 1). This observation means all other Ph_4SbL compounds obtained likely contain monodentate anions bound to the antimony atoms in a fashion similar to that found in the structures of $Ph_4Sb\{ACO\}$ and $Ph_4Sb\{DCO\}$. Therefore, structure **B** in Figure 1 clearly reflects this binding mode.

Monohalogenated trisphenylantimony(V) cyanoximates probably also have a trigonal bipyramidal structural motif where the phenyl groups are located in the equatorial plane while monodentate cyanoxime anions and atoms of halogens occupied axial positions. However, to this date there is no direct structural confirmation to that suggestion.

UV−Visible Stability Studies of Tetraarylantimony(V) Cyanoximates. Tetraalkylammonium cyanoximates $R_4N^+L^-$ and compounds with the general formula Ph_4EL (E = P, As; L = cyanoxime anions) represent ionic substances that readily dissociate in solutions. Increasing the metallic character of antimony upon transition in the 5A group down from N to Sb leads to formation of more stable covalent organoantimony cyanoximates described in this paper.[55] However, it was possible to suggest that temperature and donor solvents such as pyridine, ethanol, ethanol/water mixtures, DMF, and DMSO will initiate the dissociation of tetraarylantimony(V) complexes according to the equation below.

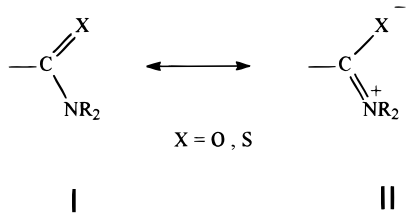


(3)

(55) Generally, it would be interesting to observe the binding mode and its strength in organobismuth cyanoximates. Comparison of the organoantimony with similar organobismuth complexes should be interesting as well. Unfortunately, Bi(III)−cyanoximes have not been synthesized yet.

Temperature and/or solvent dependent color change could be used for monitoring of reaction **3** using UV−visible spectroscopy if such a reaction would occur. Variable-temperature spectroscopic measurements in the above donor solvents in the range +18° to +85 °C revealed that there are no significant changes in absorbance between 350 and 850 nm. After heating in test tubes to above 100 °C, solutions of several organoantimony(V) cyanoximates in pure DMF gradually change color and became slightly yellow, but no quantitative information was drawn from these observations (Figures 4 and 5; S18 (Supporting Information)). Therefore, at ambient temperatures in solvents of potential biological interest, the Sb(V) complexes synthesized and discussed in the present paper are stable.

NMR Spectroscopic Studies of Rotational Barriers in Some Compounds. Two cyanoxime ligands such as H(ACO) and H(DCO) and their tetraphenylantimony(V) complexes were examined using variable-temperature ^1H NMR experiments. Amides contain the C(O)−N group in which bonds have partially double character due to significant contribution of the form **II** into the overall electronic structure:



(4)

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This leads to restricted rotation around the C−N bond, which requires some activation energy to overcome the barrier. Room-temperature ^1H NMR spectra of both ligands and their complexes consist of well-resolved singlet lines corresponding to individual signals of protons in the absence of rotation. Increasing the temperature leads to acceleration of exchange between two individual states due to rotation around the C−N bond (Figures 6 and 7). Observation of the coalescence temperature ($t_{coal.}$) is required for estimation of the process activation energy. Therefore, values of $\Delta G^{\neq}$ were calculated

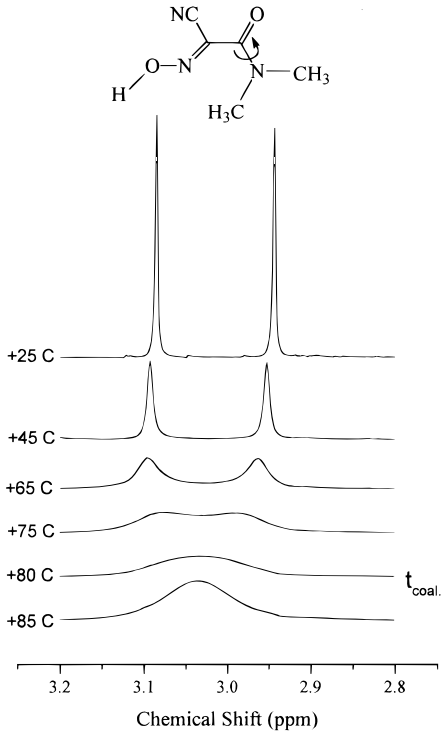

Figure 6. Fragments of selected proton NMR spectra for H(DCO) at different temperatures. Solution of cyanoxime ligand in DMSO-d_6 ($C_M = 1.2 \times 10^{-3}$) and each spectrum obtained after 64 scans.

using the Eyring equation:[42]

$$k_c = \chi\left(\frac{k_B T_c}{h}\right)\exp\left(\frac{-\Delta G^{\neq}}{RT_c}\right) \quad (5)$$

where k_c is the exchange rate constant at coalescence temperature T_c (K), k_B is Bolzmann's constant, h is Plank's constant, and χ is the transmission coefficient, which in this case equals 1. Since rotation around the amide bond is carried between two equally populated states, eq 6 was used to determine the rate constant k_c with good approximation.[43]

$$k_c = \pi\frac{\sqrt{2}}{2}(\nu_a - \nu_b) \quad (6)$$

The NMR frequencies for individual states in the absence of exchange are marked as ν_a and ν_b. Fragments of overlaid proton NMR spectra at different temperatures for the H(ACO) ligand and graphic determination of $t_{coal.}$ for $Ph_4Sb\{ACO\}$ are shown in S14 and S15 (Supporting Information). Experimentally determined values of $\Delta\nu$, $t_{coal.}$ and therefore calculated values of $\Delta G^{\neq}$ are presented in Table 6. This table also contains bond distances C−N in amide group for all compounds examined here. Commonly observed[44] activation energies of amides are in the range of 12 to 16 kcal/mol. Hence, thermodynamic data obtained for amides, some ligands, and their organoantimony(V) complexes studied in this paper are not significantly different from those reported previously. Unexpectedly, there was no correlation observed between values of rotational activation energy $\Delta G^{\neq}$ and bond lengths C−N in the amide group (Table 6). However, a small difference in $\Delta G^{\neq}$ and $t_{coal.}$ between $Ph_4Sb\{ACO\}$ and $Ph_4Sb\{DCO\}$ complexes can be attributed to the kinematic factor that is a weight difference between the hydrogen atom and CH_3 group in these ligands.

Interestingly, the amide-containing cyanoxime anions $TDCO^-$ and DCO^- in their Cs^+ salts exhibit only one signal in proton NMR spectra at room temperature. Two equivalent methyl groups in Cs{DCO} appeared as a sharp singlet at 3.05 ppm, while in Cs{TDCO}, they are at 3.42 ppm. Values of chemical shifts for both salts were measured in DMSO-d_6 solutions at 291 K. The bright-yellow color of Cs{DCO} and Cs{TDCO} indicates the nitroso character of the CNO group in the compounds ($\lambda_{max} = 384-455$ nm).[24a,30] The observation of the singlet line from two methyl groups in ^{1}H NMR spectra at room temperature suggests a low rotational barrier in these compounds, which is associated with decreased electron density on C−N amide bonds. This is contrary to quite significant values of $\Delta G^{\neq}$ found for both protonated amide−cyanoximes HL and their organoantimony(V) derivatives described in present paper.

Results of these variable-temperature NMR experiments have confirmed data of UV−visible spectroscopy that in the studied temperature region in DMSO organoantimony(V) cyanoximates are stable compounds. Therefore, monodentate coordination of

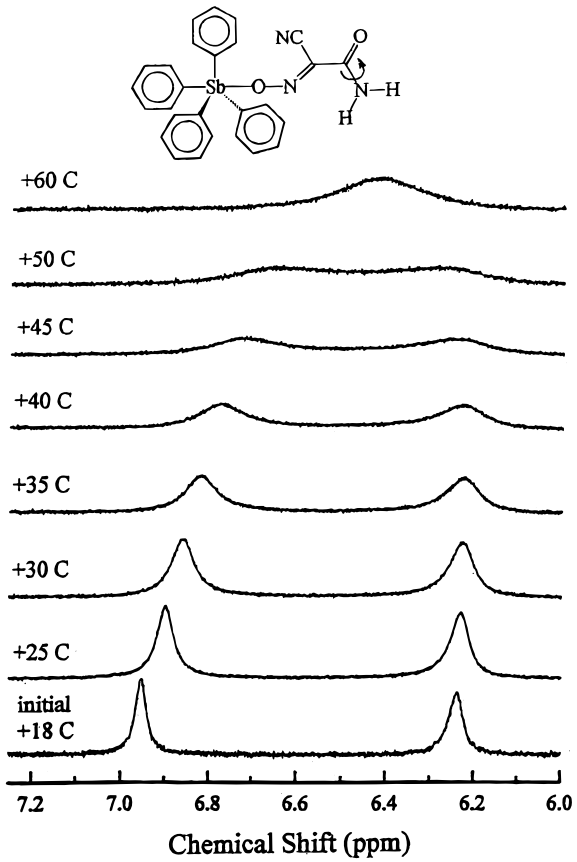

Figure 7. Fragments of selected ^{1}H NMR spectra of $(C_6H_5)_4Sb\{ACO\}$ in the region of amide protons at different temperatures. Solution of the complex in DMSO-d_6 (1.7×10^{-3} M). Each spectrum recorded after 32 scans.

Table 6. Data of Dynamic NMR Experiments for Amide-Containing Cyanoximes and Their Tetraphenylantimony(V) Complexes

compound	$\Delta\delta$, Hz[a]	$t_{coal.}$, °C (K)	$k_{coal.}$, c^{-1}	$\Delta G^{\neq}$, kcal/mol (kJ/mol)[b]	bond length C−N (Å)
HACO	32.4	50 (323)	72	16.2 (67.7)	1.331(5)[c]
$Ph_4Sb\{ACO\}$	285.9	57 (330)	635	15.1 (63.1)	1.329(4)[d]
HDCO	56.7	80 (353)	126	17.4 (72.6)	1.328(6)[e]
$Ph_4Sb\{DCO\}$	43.2	88 (361)	96	18.0 (75.2)	1.337(8)[d]

[a] Distance between two signals in the absence of rotation. [b] Accuracy of determination is ±0.1 kcal/mol. [c] Data from ref 45. [d] This work. [e] Data from ref 37. Accepted values for C−N single bond: 1.472 Å, for C=N double bond: 1.320 Å, for C≡N triple bond: 1.157 Å (data from ref 27).

anions in complexes as well as their chemical integrity is unchanged in a variety of different solvents and temperatures. This is an important factor for prospective pharmacological applications of new coordination compounds described in this paper.

Conclusion

A total of 25 different organoantimony(V) cyanoximates have been synthesized and characterized using different spectroscopic methods. All compounds obtained are monomeric, both in solution and in the solid state. Crystal structures were determined for two complexes in which anions demonstrate a monodentate binding mode to Ph_4Sb^+ units via the oxygen atom of the oxime group. Coordination polyhedra of Sb(V) atoms in both compounds are distorted trigonal pyramids with the axial binding of cyanoxime anions. Analogous IR spectra of other obtained organoantimony(V) complexes to those characterized by X-ray analysis suggest a similar coordination mode of anions in these compounds. All synthesized complexes have shown significant stability toward dissociation in several solvent systems and at different temperatures. Values of activation energies for rotational barriers for some amide−cyanoximes and their tetraphenylantimony(V) compounds have been measured.

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Supporting Information Available: Data of the NMR spectroscopy for all synthesized ligands are presented in S1−S3, while analytical data for all obtained organoantimony(V) cyanoximates are given in Table S4 and S5. Tables S6−S13 contain crystallographic details such as thermal displacement parameters and hydrogen atoms coordinates; Figures S16 and S17 show packing diagrams for $Ph_4Sb\{ACO\}$ and $Ph_4Sb\{DCO\}$; Figures S14 and S15 exhibit variable temperature ^1H NMR data for H(ACO) and $Ph_4Sb\{ACO\}$; Figure S18 contains variable-temperature UV−visible spectra for a $Ph_4Sb\{ACO\}$ solution in DMF. This material is available free of charge via the Internet at http://pubs.acs.org.

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