Polish J. Chem., **77**, 1723–1730 (2003) **INORGANIC CHEMISTRY**

New Reactions of Tetrathiocyanatobismuthates(III) with Organic Compounds. I. Reactions of Caesium Tetrathiocyanatobismuthate(III) with Monocarboxylic Acid Salts

by M. Cichecka and A. Cygański

Institute of General and Ecological Chemistry, Technical University of Łódź, Żwirki 36, 90-924 Łódź, Poland

(Received December 23rd, 2002; revised manuscript July 14th, 2003)

Reactions of $Cs[Bi(SCN)_4]$ with solutions of sodium formate, acetate, propionate and valerate were examined. Chemical, XRD and IR analyses were carried out. Two bismuth compounds are formed in the solid phase: caesium sodium hexathiocyanatobismuthate(III) $Cs_2Na[Bi(SCN)_6]$ and BiX_3 or BiOX (X – organic anion). The composition of the precipitate depends on the kind of the ligand and its concentration. When NaX is used in excess of BiX_3, the compound forms a double salt $mBiX_3 \cdot nNaX$ or $mBiOX \cdot nNaX$. Within a certain range of sodium salt concentration it remains unchanged. When the precipitate is separated, as least soluble $Cs_2Na[Bi(SCN)_6]$ crystallizes from the solution. The compounds are of biological and analytical significance.

Key words: Bi(III) complexes, synthesis, biological active compounds, carboxylic (aliphatic) acid salts, X-ray analysis, IR spectra

Thiocyanatobismuthates(III) form the largest group of complex thiocyanate salts. The coordination number of bismuth in almost all thiocyanatobismuthates(III) is equal to six. Only three tetrathiocyanatobismuthates: $Rb[Bi(SCN)_4]$, $Cs[Bi(SCN)_4]$ [1] and $Tl[Bi(SCN)_4]$ [2] were obtained. In tetrathiocyanatobismuthates(III) bismuth is coordinatively unsaturated, thus, it easily reacts with thiocyanate or halide ions to form compounds of the general formula $M'_2M[Bi(SCN)_xL_{6-x}]$ (where $L = SCN^-, Cl^-, Br^-, I^-, F^-$; $M' = Cs, Rb$; $M = Na$). The conditions of the synthesis determine, whether the $M'_2M[Bi_2(SCN)_yL_{9-y}]$ complex is mononuclear or binuclear [3–5].

This study describes reactions of $Cs[Bi(SCN)_4]$ with organic ligands: formates, acetates, propionates and valerates. Therapeutic effects of bismuth compounds are commonly recognized. Derivatives of acetic and propionic acids form a group of non-steroid anti-inflammatory and antirheumatic drugs.

EXPERIMENTAL

Preparation: The compounds were obtained by treating solid $Cs[Bi(SCN)_4]$ [1] with aqueous solutions of HCOONa, CH_3COONa, C_2H_5COONa and C_4H_9COONa. The influence of the change of $Cs[Bi(SCN)_4]$ mass in the range of 1÷7 g, the volume of the sodium salt from 2 to 7 ml, and the time from 0.5 to 7 h on the composition of the product was established. The optimal conditions of synthesis were determined: $Cs[Bi(SCN)_4]$ mass – 3 g (0.005 mol), sodium salt volume – 5 ml and time of synthesis – 2 hours.

Chemical analysis: Bismuth was determined by gravimetric method as Bi_2S_3 [6], using thiourea and by complexometric titration. Thiocyanates were determined by the method of Volhard and by bromatometry. Caesium and sodium were determined by flame photometry after their extraction with water from the preparations. Carbon and nitrogen were determined using elemental analysis.

XRD analysis: Diffractometric analysis was performed using a Siemens D5000 diffractometer, using CuK_α radiation. The intensities were recorded over the range from 2° to 80°. Along with the X-ray diffraction patterns, print-outs with 2θ and d/n values and intensities of the peaks were obtained.

IR analysis: IR spectra in the solid phase (KBr disc technique and Nujol mull technique) were recorded on FTIR-8501 Shimadzu and Zeiss Specord M80 spectrophotometers over the range 4600–400 cm^{-1} and 4000–600 cm^{-1} respectively.

Decomposition reactions: The course of the decomposition was established. Weighted samples of the compounds (*ca.* 0.5÷1.0 g) were shaken with 150 cm^3 water or 150 cm^3 of 0.1 mol/l NaOH solution for two hours, and then filtered through a hard filter, washed with water and dried in the air at the room temperature. Chemical analysis of the soluble and insoluble fractions was carried out.

RESULTS AND DISCUSSION

Table 1 presents the postulated compositions of some products of the synthesis. Average difference between calculated and found results is for caesium – 0.77%, sodium – 0.16%, bismuth(III) – 1.25%, thiocyanates – 0.66%, carbon – 0.47% and for nitrogen – 0.38% respectively.

Table 1. Composition of the products of reaction $Cs[Bi(SCN)_4]$ with sodium formate, acetate, propionate and valerate.

Ligand and its concentration		Composition of the product	Molar ratio of the components
HCOONa	0.5 mol/l	$Cs[Bi(SCN)_4]$, $Cs_2Na[Bi(SCN)_6]$, $(HCOO)_3Bi$	4:1:2
	1.5 mol/l	$Cs_2Na[Bi(SCN)_6]$, $(HCOO)_3Bi \cdot HCOONa$	1:1
	3.0 mol/l	$Cs_2Na[Bi(SCN)_6]$, $2(HCOO)_3Bi \cdot 5HCOONa$	2:1
CH_3COONa	1.5 mol/l	$Cs_2Na[Bi(SCN)_6]$, $(CH_3COO)_3Bi$	1:1
	3.0 mol/l	$Cs_2Na[Bi(SCN)_6]$, $(CH_3COO)_3Bi$	1:1
	6.0 mol/l	$Cs_2Na[Bi(SCN)_6]$, $6(CH_3COO)_3Bi \cdot 5CH_3COONa$	3:1
CH_3CH_2COONa	0.5 mol/l	$Cs[Bi(SCN)_4]$, $Cs_2Na[Bi(SCN)_6]$, $C_3H_5O_2BiO$	2:1:1
	1.5 mol/l	$Cs_2Na[Bi(SCN)_6]$, $3C_3H_5O_2BiO \cdot 2C_3H_5O_2Na$	4:1
	2.5 mol/l	$Cs_2Na[Bi(SCN)_6]$, $6C_3H_5O_2BiO \cdot 3C_3H_5O_2Na$	4:1
$CH_3CH_2CH_2CH_2COONa$	0.5 mol/l	$Cs[Bi(SCN)_4]$, BiOOH	4:1
	1.5 mol/l	$Cs_2Na[Bi(SCN)_6]$, $C_5H_9O_2BiO$	4:5
	2.5 mol/l	$Cs_2Na[Bi(SCN)_6]$, $C_5H_9O_2BiO$	1:2

If the solution used for the synthesis contains, apart from a salt, the acid, which forms that salt, *e.g.* CH_3COOH and CH_3COONa, the composition of the precipitate remains the same over a certain composition range. If, for instance, 1.5 mol/l and 3.0 mol/l CH_3COONa is used in the presence of 3.0 mol/l or 6.0 mol/l CH_3COOH the preparations formed present a similar composition. In all XRD spectra, the most inten-

sive reflexes are those derived from the caesium sodium compound, due to its high crystallinity, its content in the preparation and molecular mass. All the other signals related to the organic bismuth salt are not so evident and sometimes overlap those attributed to $Cs_2Na[Bi(SCN)_6]$. Therefore, the presence of BiX_3 in precipitates is difficult to prove by XRD spectra.

Table 2 presents frequencies of vibrations for some of the preparations read from the IR spectra. They are also compared with the vibrations characteristic of their individual components.

Table 2. Results of IR spectra of selected synthesis products.

Substances	ν(CH)	ν(CC)	ν(OCO)	ν(CN)	ν(CS)	δ(SCN)
$Cs_2Na[Bi(SCN)_6]$	–	–	–	2075	723	461 447
Formate preparation (3.0 mol/l HCOONa)	2817	–	1560_{asym} 1404_{sym} $\Delta\upsilon = 156$	2069	746	461 447
HCOONa	2831 2715	–	1586_{asym} 1366_{sym} $\Delta\upsilon = 220$	–	–	–
Acetate preparation (3.0 mol/l CH_3COONa)	2928	936	1550_{asym} 1400_{sym} $\Delta\upsilon = 150$	2069	724	461 445
CH_3COONa	2952	928	1580_{asym} 1411_{sym} $\Delta\upsilon = 169$	–	–	–
Propionate preparation (1.5 mol/l $C_3H_5O_2Na$)	2928	976	1544_{asym} 1408_{sym} $\Delta\upsilon = 136$	2068	724	461 453 446
$C_3H_5O_2Na$	2973 2874	924	1560_{asym} 1396_{sym} $\Delta\upsilon = 164$	–	–	–
Valerate preparation (2.5 mol/l $C_5H_9O_2Na$)	2958 2929 2871	976	1540_{asym} 1402_{sym} $\Delta\upsilon = 138$	2090 2077	725	462, 447 418, 403
$C_5H_9O_2Na$	2964 2937, 2920 2858	927	1560_{asym} 1421_{sym} $\Delta\upsilon = 139$	–	–	–

The recorded IR spectra confirm the presence of SCN^- and COO^- groups as well as CH and CC bonds in the synthesized products. The frequencies are comparable with the literature data [7–12]. Vibration frequencies of the carboxylate group in the preparations differ from those observed for the sodium salt, which indicates that carboxylate bismuth complexes are formed. The type of coordination of the OCO^- group may be based on the difference of the frequencies of the symmetric and asymmetric stretching vibrations of the carboxylate group: $\Delta\nu = \nu(OCO^-)_{asym} - \nu(OCO^-)_{sym}$.

The comparison of the displacement of the bands of the sodium salt and particular preparations shows that, according to the criteria established by Nakamoto, Alcock, Deacon and Manhas [7,13–15], in all the preparations the carboxylate group is bridging bidentate [15] ($\Delta\nu < \Delta\nu_{(Na)}$ for formate, acetate and propionate preparations, which is in good agreement with literature data). For valerate preparation $\Delta\nu = \Delta\nu_{(Na)}$ and symmetric and asymmetric stretching vibration frequencies of carboxylate group are shifted towards lower values. Splitting of the absorption band ν(CN) in the valerate preparation can be caused by the existence of two non-equivalent SCN groups of different parameters and frequencies which was confirmed by crystal-structures analysis of $Cs[Bi(SCN)_4]$ and $Rb[Bi(SCN)_4]$ [16]. In valerate preparation the contents of carboxylate complex is the highest.

The hydrolysis reaction of caesium sodium hexathiocyanatobismuthate(III) is characteristic for thiocyanatobismuthates and proceeds according to:

$$Cs_2Na[Bi(SCN)_6] + H_2O \leftrightarrow BiOSCN\downarrow + 2HNCS + 2CsNCS + NaNCS$$

This reaction is reversible. When it proceeds in the solution at a higher temperature, forming HNCS dissolves BiOSCN and after cooling crystals of $Cs_2Na[Bi(SCN)_6]$ precipitate. A similar reaction proceeds in the case of hydrolysis of the obtained preparations. However, the precipitate consists of two basic bismuth(III) salts:

$$Cs_2Na[Bi(SCN)_6] + BiX_3 + 2H_2O \rightarrow BiOSCN\downarrow + BiOX\downarrow + 2HNCS +$$
$$+ 2HX + 2CsNCS + NaNCS$$

The reaction in the presence of sodium hydroxide is irreversible:

$$Cs_2Na[Bi(SCN)_6] + BiX_3 + 6NaOH \rightarrow 2BiOOH\downarrow + 2CsNCS + 4NaNCS +$$
$$+ 3NaX + 2H_2O$$

The above proposed schemes are based on the results of chemical analysis of the reaction products, present in the solution and in the precipitate.

Our investigation shows that caesium tetrathiocyanatobismuthate(III) exhibits a high tendency to bind with sodium ions, present in the organic salts of the monocarboxylic acids. As a result of the reaction of caesium tetrathiocyanatobismuthate(III), caesium sodium hexathiocyanatobismuthate(III) is formed and the coordination number of bismuth increases from four to six. The structures of $Cs[Bi(SCN)_4]$ and $Cs_2Na[Bi(SCN)_6]$ are well known [16–18]. In $Cs[Bi(SCN)_4]$ and $Rb[Bi(SCN)_4]$ bi-

smuth is coordinated with the surrounding four sulfur atoms and forms a distorted double trigonal pyramid, where one corner of the base is occupied by free electron pair. In $Cs_2Na[Bi(SCN)_6]$ on the other hand bismuth is coordinated with six sulfur atoms and thus forms a distorted octahedron.

The reaction of $Cs_2Na[Bi(SCN)_6]$ formation may be probably applied as a sensitive method for microcrystalline detection of sodium in organic compounds and their determination on the basis of its content. Isostructural $Rb[Bi(SCN)_4]$, which is a more readily soluble compound, reacts like $Cs[Bi(SCN)_4]$.

In the course of the synthesis, the other compounds of bismuth is formed with the organic salt anion. It has the general formula: BiX_3 (chemical analysis and infra-red spectra confirm formation of this kind of complex). When NaX is in excess of BiX_3, the compound forms a double complex salt whose composition may be generally represented as $mBiX_3 \cdot nNaX$. Compounds with a similar composition were obtained as a result of reactions with $Bi(NO_3)_3$ and $Na_2C_2O_4$. Depending on the concentrations used, either $NaBi(C_2O_4)_2$ or $mBi_2(C_2O_4)_3 \cdot nBi(NO_3)_3$ were formed [19]. Chemical investigation and diffraction pattern analysis of Bi(III)-NaX also indicate the formation of this type of compound [20].

It is to be noted that only two structures of Bi tris-carboxylates have been determined so far: the formate $(HCOO)_3Bi$ [21] and acetate $(CH_3COO)_3Bi$ [11,22]. In bismuth(III) formate and acetate the three non-equivalent bismuth atoms are surrounded by nine oxygen atoms. In bismuth(III) formate each oxygen atom is connected to metal atom, but the Bi–O distances fall into three ranges. Considering all of them and the central atom describing as nine-coordinated, the structure seems to be in specific way polimeric, where formate groups form a three-dimensional network.

In crystal structure of bismuth(III) acetate all carboxylate groups are bidentate. Only one oxygen atom in the first, and two oxygen atoms in second acetate group are bridging, while oxygen atoms in the third acetate group are not bridging. Bi···O–Bi bridges form endless layers of $(CH_3COO)_3Bi$. The irregular shape of the coordination polyhedron can be accounted for by the stereochemically active lone electron pair in both structures.

The basic reactions proceeding in the course of the synthesis may be presented as follows:

$$Cs[Bi(SCN)_4] \xrightarrow{NaX} Cs_2Na[Bi(SCN)_6] + BiX_3 \text{ (or BiOX)}$$

where X is the formate, acetate, propionate or valerate anion. The course of the reaction depends on the kind of the organic salt and its concentration. For medium concentrations of formates (below 1.5 mol/l) and acetates (*ca.* 3.0 mol/l) it is as follows:

$$2\ Cs[Bi(SCN)_4] + 3\ NaX \rightarrow Cs_2Na[Bi(SCN)_6] + BiX_3 + 2\ NaSCN$$

$X - HCOO^-, CH_3COO^-$.

For higher concentrations (1.5 mol/l for formates and 6.0 mol/l for acetates), assuming that m = 1, the reaction is:

$$2\ Cs[Bi(SCN)_4] + (3+n)\ NaX \rightarrow Cs_2Na[Bi(SCN)_6] + BiX_3 \cdot nNaX + 2\ NaSCN.$$

Reactions are similar in the case of propionates and valerates: only basic bismuthyl salts BiOX or BiOX·NaX are formed.
For medium concentrations of propionates:

$$2\ Cs[Bi(SCN)_4] + C_2H_5COONa + H_2O \rightarrow Cs_2Na[Bi(SCN)_6] + C_2H_5COOBiO +$$
$$+ 2\ HSCN.$$

For higher concentrations:

$$2\ Cs[Bi(SCN)_4] + (1+n)\ C_2H_5COONa + H_2O \rightarrow Cs_2Na[Bi(SCN)_6] +$$
$$+ C_2H_5COOBiO \cdot nC_2H_5COONa + 2\ HSCN.$$

Reactions for valerates (1.5 and 2.5 mol/l) lead to the formation of $Cs_2Na[Bi(SCN)_6]$ and $C_4H_9COOBiO$.

Structural analysis of basic bismuth salts of the general formula: R-COO-BiO (R = H, CH_3, C_2H_5, C_3H_7, C_4H_9) indicates that atomic configuration is similar to that found in BiOCl. The structure is of the PbFCl type and the organic anion occupies the position of the chloride ion [11,23]. The anions form double layers interleaving the layers of $Bi_2O_2^{2+}$. Because of electrostatic reasons, it can be assumed that the carboxyl groups are directed towards the $Bi_2O_2^{2+}$ layers. The formula is the best representation of structure for the formate and acetate, but the longer the organic chain, the more difficult it becomes to establish the spatial structure of the compound. The composition of the resulting precipitates in the same synthesis depends on the concentration of the organic compound (Table 1). If it is low (below 1 mol/l NaX) the precipitate usually consists of $Cs[Bi(SCN)_4]$, $Cs_2Na[Bi(SCN)_6]$ and BiX_3. At higher concentrations (1.5 mol/l NaX) unreacted $Cs[Bi(SCN)_4]$ does not occur and the product contains $Cs_2Na[Bi(SCN)_6]$ and BiX_3 – an organic bismuth compound whose content increases with the concentration of the ligand, while the content of caesium tetrathiocyanatobismuthate(III) decreases. The organic bismuth compound may occur as a single complex salt $(CH_3COO)_3Bi$ (Table 1), or more frequently, due to the excess of NaX as a double complex salt.

The investigation of bismuth compounds may be significant for pharmacological purposes. Bismuth compounds are widely known and have been used in medicine for over 200 years and the number of drugs containing bismuth is increasing, although the biological aspect of its chemical action is not fully understood [24]. Bismuth compounds are used to treat the diseases of internal organs, ears, eyes, skin, gynecological disorders, infectious, parasitic and sexually transmitted diseases. Bismuth

preparations, owing to their protective, styptic and antibacterial effects are applied in chronic gastric and duodenal ulcer disease. In the acid medium they form insoluble complexes with the proteins contained in the ulcer exudates and, thus, selectively protect the damaged mucosa from the effects of aggressive hydrochloric acid and pepsin. The derivatives of the acetic and propionic acids form an important group of analgesics, anti-inflammatory and antipyretic drugs, widely used in the treatment of rheumatic diseases and post-traumatic complications, such as diclofenac, a sodium salt of aminophenylacetic acid or ibuprofen, a sodium salt of isobutylphenylpropionic acid. It is also well known that valerate extracts have sleep-inducing and sedative effects on the central and autonomous nervous system.

The synthesis and examination of the compounds, which combine the pharmacological properties of bismuth with the effects of selected biologically active organic compounds, may bring about important results for both the fundamental research and practice.

CONCLUSIONS

1. Aqueous solutions of organic aliphatic monocarboxylic sodium salts (formate, acetate, propionate and valerate) react with solid $Cs[Bi(SCN)_4]$.
2. The composition of the reaction products depends on nature and concentration of organic salts.
3. At medium concentrations of organic salts, $Cs_2Na[Bi(SCN)_6]$ and BiX_3 or BiOX are formed.
4. At higher concentrations of organic salts, $Cs_2Na[Bi(SCN)_6]$ and double salt $mBiX_3 \cdot nNaX$ or $mBiOX \cdot nNaX$ are formed.
5. Synthesized preparations contain inorganic and organic complex bismuth(III) salts. In organic complex salts ligands are of therapeutic use.

REFERENCES

1. Cygański A., *Roczn. Chem*., **39**, 193 (1965).
2. Pociello A. and Foa N., *Gazz. Chim. Ital*., **53**, 526 (1923).
3. Cygański A. and Turek A., *Polish J. Chem*., **65**, 169, 1497 (1991).
4. Bukowska-Strzyżewska M., Cygański A., Turek A. and Zagajewska K., *ibid*., **69**, 19 (1995).
5. Turek A. and Cygański A., *Thermochim. Acta*, **197**, 225 (1992).
6. Sołoniewicz R., *Chem. Anal. (Warsaw)*, **10**, 311 (1965).
7. Nakamoto K., Infrared Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, NY 1970, pp. 187, 220.
8. Donaldson J.D., Knifton J.F. and Ross S.D., *Spectrochim. Acta*, **20**, 847 (1964).
9. Gattow G. and Sarter K., *Z. anorg. allg. Chem.*, **463**, 163 (1980).
10. Donaldson J.D., Knifton J.F. and Ross S.D., *Spectrochim. Acta*, **21**, 275 (1965).
11. Gattow G. and Schwank H., *Z. anorg. allg. Chem*., **382**, 49 (1971).
12. Pisarevsky A.P., Martynenko L.I. and Dzjubenko N.G., *Zh. Neorg. Khim*., **35**, 1498 (1990).
13. Alcock N.W., Tracy V.M. and Waddington T.C., *J. Chem. Soc. Dalton Trans*., **21**, 2243 (1976).
14. Deacon G.B. and Phillips R.J., *Coord. Chem. Rev*., **33**, 227 (1980).

15. Manhas B.S. and Trikha A.K., *J. Indian Chem. Soc*., **LIX**, 315 (1982).
16. Gałdecki Z., Główka M.L. and Goliński B., *Acta Cryst*., **B32**, 2319 (1976).
17. Bukowska-Strzyżewska M., Cygański A., Maniukiewicz W., Turek A. and Zagajewska K., *J. Chem. Cryst.*, **24**, 425 (1994).
18. Sieroń L., Bukowska-Strzyżewska M., Cygański A. and Turek A., *Polyhedron*, **15**, 3923 (1996).
19. Orylska K. and Basińska H., *Stud. Soc. Sci. Torun, Sect. B*, **6(4)**, 21 (1967).
20. Unpublished results.
21. Stalhandske C.I., *Acta Chem. Scand.*, **23**, 1525 (1969).
22. Troyanov S.I. and Pisarevsky A.P., *Koord. Khim*., **17**, 909 (1991).
23. Aurivillius B., *Acta Chem. Scand.*, **9**, 1213 (1955).
24. Sun H. and Sadler P.J., *Top. Biol. Inorg. Chem*., **2(Metallopharmaceuticals II)**, 159 (1999).