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# Polyol Metal Complexes. Part 54[1)]
# Multiply Deprotonated Purine Nucleosides as Ligands in Bismutates and Antimonates

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*Dedicated to Professor Wolfgang Beck on the Occasion of his 75th Birthday*

**Abstract.** The crystal structures of $[Co(NH_3)_6][Bi(Guo1,2',3'H_{-3})_2]\cdot 9\,H_2O$ (**1**), $Na[Sb(Ado2',3'H_{-2})_2]\cdot H_2O$ (**2**), and $Na_2[Bi(Ado2',3'H_{-2})(Ado2',3',5'H_{-3})]\cdot 13.5\,H_2O$ (**3**) were determined from single-crystal X-ray diffraction data (Guo = guanosine, Ado = Adenosine). The chelate complex anions of all structures consist of a bismuth(III) or antimony(III) center which is coordinated by the 1,2-diolato group of the ribofuranosyl moiety of the nucleosides. In **1**, two guanine moieties belonging to different complexes are linked by two hydrogen bonds of the type N2−H···N3. $^{13}C$ NMR data obtained from the mother liquors show a coordination-induced shift for the coordinating alkoxido groups of guanosine and adenosine as well as inosine.

**Keywords:** Guanosine; Adenosine; Inosine; Antimonates; Bismutates; Ribofuranoside ligands; Crystal structures

## Introduction

Nucleosides provide various metal-binding sites [1]. There is increasing evidence that, besides N-donor sites of the nucleobase, the ribose part acts as a powerful ligand towards metal centers. Specifically the deprotonated *cis*-2′,3′-diol fragment of the ribose part of a nucleoside has been found as a chelating metal-binding site in the solid state as well as in solution. The diolato(2−) coordination mode is found in several crystal structures whereas NMR spectroscopy has proved to be a useful tool to verify chelate formation in solution. In the solid state, adenosine forms a heteroleptic dinuclear complex with vanadium(V) [2] and a mononuclear one with osmium(VI) [3]. Homoleptic complexes are established with guanosine and antimony(III) [4]. $^{13}C$ NMR experiments in aqueous alkaline solution of guanosine and antimony(III) [4] on the one hand, and vanadium(V) and adenosine [5] on the other, show a significant coordination-induced shift (CIS) of the $^{13}C$ NMR signals assigned to the coordinating 2′,3′-diolato group. Herein we report on the synthesis and structural characterization of the nucleoside−metal complexes $[Co(NH_3)_6][Bi(Guo1,2',3'H_{-3})_2]\cdot 9\,H_2O$ (**1**), $Na[Sb(Ado2',3'H_{-2})_2]\cdot H_2O$ (**2**), and $Na_2[Bi(Ado2',3'H_{-2})(Ado2',3',5'H_{-3})]\cdot 13.5\,H_2O$ (**3**) and the NMR-spectroscopic characterization of the corresponding solution species.

## Results and Discussion

The crystal structure of **1** proves to be isotypical with the corresponding antimony(III) compound [3] and consists of bis(guanosinato)bismutate trianions (Fig. 1). The coordination polyhedron around the bismuth atom is best described as a distorted pseudo-trigonal bipyramid ($O_{ax}$-Bi-$O_{ax}$ 143.45(8)°, $O_{eq}$-Bi-$O_{eq}$ 100.21(8)°). The non-coordinated side of the bismuth atom is directed towards the pyrimidine ring of guanine with atomic distances between 3.569(3) Å (Bi−C22$^{iv}$, symmetry code $^{iv}$ $-x$, $-1/2+y$, $1-z$) and 3.666(3) Å (Bi−N32$^{iv}$). The two guanosine ligands are triply deprotonated, namely at the chelating alkoxido groups and at the lactam/lactim tautomer N1/O6. In accordance with the structures of free guanosine [6], one of the ribofuranosyl moieties (atomic labels of the type C*n*′1) is C2′ *endo*-puckered, the other one (atomic labels of the type C*n*′2) is C1′ *exo*-puckered [7]. The glycosidic torsion angles of 80.0(3)° and 115.3(3)° deviate significantly from those of free guanosine (−123.3° and −43.9°) and confirm the possibility that there is little restraint to rotation about the glycosidic bond in nucleosides [8]. The conformation of the complex anion is the same as in the bis(guanosinato)antimonates discussed in [4]. Moreover, all the compounds

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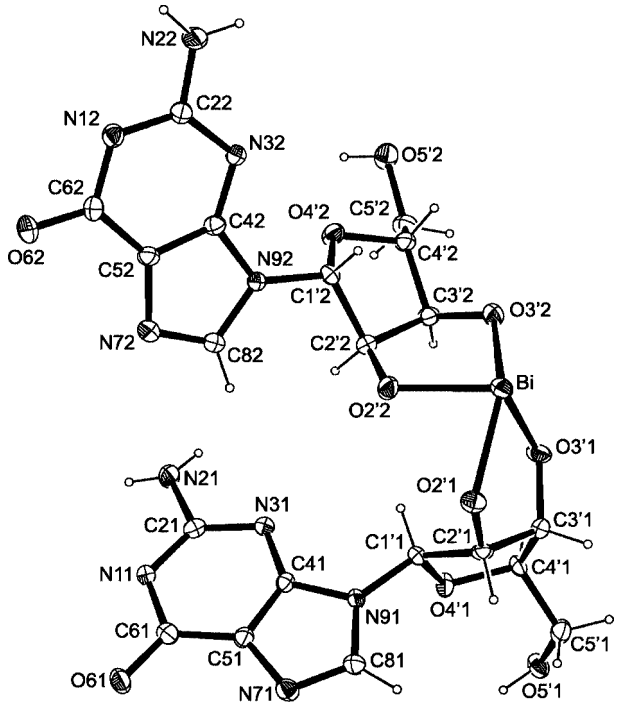



**Fig. 1** ORTEP presentation (50 % ellipsoid probability) of the complex anion in **1**. Bi-O bond lengths in Å: O3′1 2.120(2), O2′2 2.126(2), O3′2 2.177(2), O2′1 2.223(2); ring puckering parameters $Q_2$ and $\varphi_2$ [7] of the five-membered ring O4′-C1′-C2′-C3′-C4′ and glycosyl and torsion angles $\chi$ (C8-N9-C1′-O4′) and $\tau$ (O2′-C2′-C3′-O3′) of ribofuranosyl 1: $Q_2$ = 0.386(3) Å, $\varphi_2$ = 65.1(4)°, $\chi$ = 80.0(3)°, $\tau$ = −37.8(3)°; of ribofuranosyl 2: $Q_2$ = 0.433(3) Å, $\varphi_2$ = 26.8(4)°, $\chi$ = 115.3(3)°, $\tau$ = −23.0(3)°.

show similar packing of the complex anions in strands fixed by two hydrogen bonds of the type N2−H2···N3 between the exocyclic amino group bound to C2 and an endocyclic nitrogen atom forming eight-membered rings (Fig. 2, Table 2). This mode of hydrogen bonding between non-canonical guanine−guanine base pairs (GG) has also been observed in several RNA structures [9]. The importance of these hydrogen bonds in **1** may be clarified by the observation that all crystallization attempts with inosine, in which the exocylic amino group of guanosine is replaced by a hydrogen atom, failed till now. This observation is made despite the fact that in aqueous alkaline solutions containing bismuth(III) or antimony(III), inosine behaves like guanosine and forms diolato complexes, a fact which is clearly confirmed by a coordination-induced downfield shift of the involved alkoxido carbon atoms (Table 1).

**2** and **3** were prepared from aqueous sodium hydroxide solutions at pH > 13. The $^{13}$C NMR shifts of C2′ and C3′ are of about the same magnitude as those observed in guanosine- and inosine-containing solutions and indicate the presence of diolato antimonates and bismutates, respectively. There is no evidence for metal coordination by the purine nitrogen atoms for all solutions investigated in this study (Table 1).

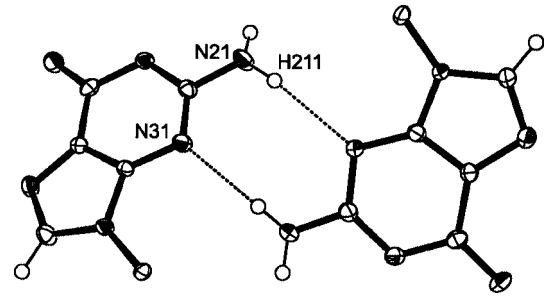



**Fig. 2** ORTEP presentation (50% ellipsoid probability) of the eight-membered ring involving two hydrogen bonds of the type N−H···N in **1**. Symmetry code and the atoms of the ribofuranosyl residues with the exception of C1′1 and C1′2 omitted for clarity, for symmetry information see Table 2.

**Table 1** $^{13}$C NMR data of alkaline aqueous solutions of guanosine (Guo), adenosine (Ado), inosine (Ino), the mother liquors of **1**, **2**,and **3** (m.l.**1**, m.l.**2**,and m.l.**3**, respectively) and bismuth (Bi) or antimony (Sb) containing alkaline aqueous solutions of inosine. Δδ is the difference between the shifts of the free and the metal-bonded nucleosides. The spectra of the free nucleosides (Guo, Ado, Ino) were taken from separate solutions at conditions similar to the corresponding metal-containing solutions (m.l.**1**, m.l.**2**, m.l.**3**, Sb, Bi, for labelling of the nucleosides see Scheme 1).

| | C6 | C2 | C4 | C8 | C5 | C1′ | C4′ | *C3′* | *C2′* | *C5′* |
|---|---|---|---|---|---|---|---|---|---|---|
| Guo | 168.4 | 161.2 | 151.6 | 136.6 | 118.3 | 89.2 | 86.4 | 75.6 | 72.3 | 62.8 |
| m.l.**1** | 168.4 | 161.3 | 151.6 | 136.6 | 118.3 | 90.2 | 88.5 | 79.8 | 76.7 | 63.2 |
| Δδ | 0.0 | −0.1 | 0.0 | 0.0 | 0.0 | −1.0 | −2.1 | −4.2 | −4.4 | −0.4 |
| Ado | 154.5 | 151.9 | 147.9 | 139.8 | 118.0 | 89.5 | 86.4 | 76.0 | 71.7 | 62.4 |
| m.l.**2** | 154.6 | 152.0 | 147.9 | 139.9 | 118.1 | 90.3 | 87.6 | 79.2 | 75.1 | 62.5 |
| Δδ | −0.1 | −0.1 | 0.0 | −0.1 | −0.1 | −0.8 | −1.2 | −3.2 | −3.4 | −0.1 |
| Ado | 154.8 | 152.1 | 148.2 | 140.2 | 118.4 | 89.8 | 86.3 | 76.1 | 71.9 | 62.4 |
| m.l.**3** | 155.0 | 152.2 | 148.3 | 140.2 | 118.5 | 90.7 | 88.1 | 80.1 | 76.0 | 62.9 |
| Δδ | −0.2 | −0.1 | −0.1 | 0.0 | −0.1 | −0.9 | −1.8 | −4.0 | −4.1 | −0.5 |
| Ino | 167.9 | 153.8 | 149.7 | 138.8 | 123.9 | 89.6 | 86.4 | 75.7 | 72.2 | 62.6 |
| Sb | 168.0 | 154.0 | 149.7 | 138.9 | 124.0 | 90.5 | 87.7 | 78.7 | 75.2 | 62.7 |
| Δδ | −0.1 | −0.2 | 0.0 | −0.1 | −0.1 | −0.9 | −1.3 | −3.0 | −3.0 | −0.1 |
| Bi | 168.0 | 153.9 | 149.8 | 138.9 | 124.1 | 91.3 | 89.2 | 81.9 | 78.4 | 63.2 |
| Δδ | −0.1 | −0.1 | −0.1 | −0.1 | −0.2 | −1.7 | −2.8 | −6.2 | −6.2 | −0.6 |

The crystal structure of **2** contains bis(adenosinato)antimonate monoanions which are linked by sodium atoms and hydrogen bonds forming a coordination polymer along [100] (Fig. 3). Each of the symmetrically independent adenosine entities coordinates to antimony(III) as a 2′,3′-diolato ligand. The axial sites of the distorted pseudo-trigonal bipyramid are occupied by the O2′ atoms and two of the equatorial sites by the O3′ atoms ($O_{ax}$-Sb-$O_{ax}$ 149.49(8)°, $O_{eq}$-Sb-$O_{eq}$ 104.12(8)°). The increased negative charge density of the deprotonated hydroxyl groups are compensated by two methods typical for polyolato metal complexes: the O2′ atoms act as acceptors in rather short hydrogen bonds with the O5′ hydroxyls as donors (Table 2) while the O3′ atoms bind to the sodium atom. The conformations of the adenosine ligands are slightly different. One ribofuranosyl

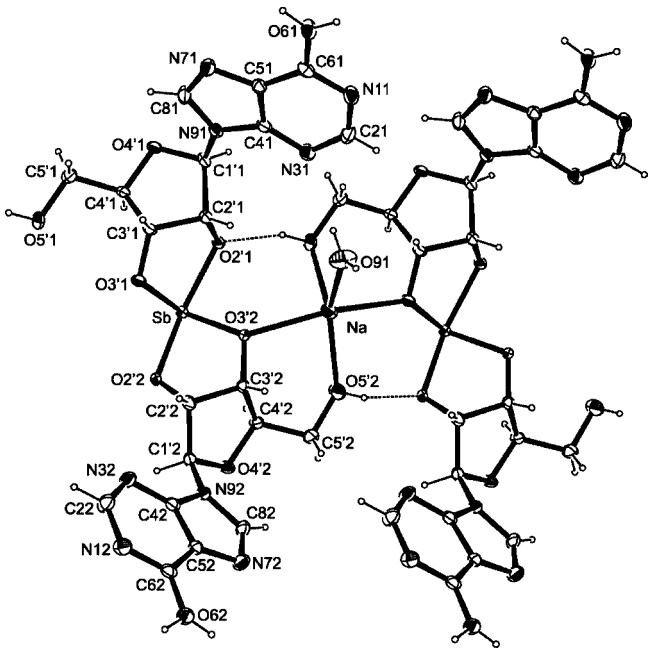
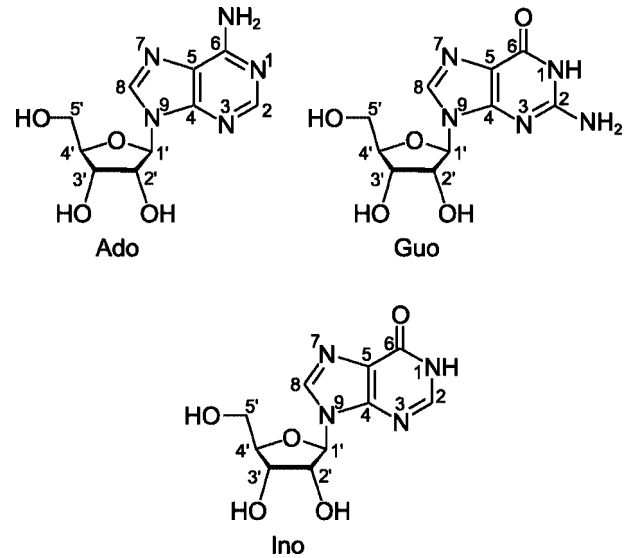



**Fig. 3** ORTEP presentation (50 % ellipsoid probability) of the coordination of the metal atoms in **2**, non-labelled non-hydrogen atoms generated by translation [i] $x-1$, $y$, $z$. Hydrogen bonds (dashed lines) see Table 2 for details. Sb-O bond lengths in Å: O3′1 2.020(2), O2′2 2.094(2), O3′2 2.018(2), O2′1 2.123(2); Na-O bond lengths in Å: O3′1 2.448(2), O3′2[i] 2.390(2), O5′1 2.360(2), O91 2.276(2), O5′2[i] 2.236(2); ring puckering parameters $Q_2$ and $\varphi_2$ [7] of the five-membered ring O4′-C1′-C2′-C3′-C4′ and glycosyl and torsion angles $\chi$ (C8-N9-C1′-O4′) and $\tau$ (O2′-C2′-C3′-O3′) of ribofuranosyl 1: $Q_2 = 0.379(3)$ Å, $\varphi_2 = 284.2(4)°$, $\chi = -1.0(3)$ °, $\tau = 41.5(3)°$; of ribofuranosyl 2: $Q_2 = 0.312(3)$ Å, $\varphi_2 = 270.0(4)°$, $\chi = -5.8(3)°$, $\tau = 38.8(2)°$.

residue (the one with C3′1 in Fig. 3) is C3′-*endo* puckered as is found for free adenosine [10]; the other one adopts a $^{C3'}T_{C2'}$ twist conformation. The torsion angles about the glycosidic bond (C8-N9-C1′-O1′) of −1.0(3)° and −5.8(2)° define the same conformer as that found for free adenosine (9.9°).

While adenosine forms complex monoanions with antimony(III), dianions are built with bismuth(III) crystallizing as the sodium salt **3**. In accordance with **2**, bis(adenosinato)-bismutates are formed in **3** (Fig. 4) which crystallize as pseudo-merohedral twins in an orthorhombic, pseudo-tetragonal cell with $b \approx c$. Structure refinements in the space groups $P4_1$ (Laue class 4/*m*) and $P4_12_12$ (Laue class 4/*mmm*) are partly successful but always lead to disorder of the sodium site and the O5′ hydroxyl entity of the ribofuranosyl residue. This is avoided in a refinement in the orthorhombic space group $P2_12_12_1$ taking the twin axis [011] under consideration. Two short O5′-O5′ distances of about 2.5 Å are found indicating the existence of a strong hydrogen bond of the type O−H···O$^-$ (Table 2). By this means, dianions with the same bismuth center are linked to strands along [100]. The coordination polyhedron around the bismuth atoms is quite similar to that found for **1**




**Scheme 1** The purine nucleosides adenosine (Ado), guanosine (Guo) and inosine (Ino).

**Table 2** Selection of hydrogen bonds in **1**, **2**, and **3**. Because of the data quality, only donor-acceptor bonds are given for **3**. Bond lengths in Å, angles in °; D = donor, A = acceptor. Symmetry key: [i] $-x$, $1/2+y$, $-z$, [ii] $1+x$, $y$, $z$, [iii] $-x$, $1/2+y$, $1-z$, [iv] $-x$, $-1/2+y$, $1-z$, [v] $x-1$, $y$, $z$.

| | D | H | A | D−H | H···A | D···A | D−H···A |
|---|---|---|---|---|---|---|---|
| **1** | O5′1 | H5′1 | O2′1[i] | 0.85(2) | 1.70(2) | 2.551(3) | 177(3) |
| | O96 | H962 | O2′2[ii] | 0.85(3) | 1.92(3) | 2.760(3) | 169(4) |
| | O95 | H951 | O3′1 | 0.85(3) | 1.99(3) | 2.765(3) | 152(4) |
| | O92 | H921 | O3′2 | 0.85(3) | 1.90(3) | 2.724(3) | 163(4) |
| | N21 | H211 | N32[iii] | 0.85(2) | 2.33(2) | 3.173(3) | 173(3) |
| | N21 | H212 | O5′2[iii] | 0.85(2) | 2.31(2) | 3.143(3) | 165(2) |
| | N22 | H222 | N31[iv] | 0.87(2) | 2.11(2) | 2.974(3) | 177(1) |
| **2** | O5′1 | H5′5 | O2′1[v] | 0.82(1) | 1.91(2) | 2.685(2) | 158(3) |
| | O5′2 | H5′6 | O2′2[ii] | 0.81(1) | 1.87(1) | 2.661(2) | 165(3) |
| **3** | O5′2 | | O5′1[ii] | | | 2.53(1) | |
| | O5′4 | | O5′3[v] | | | 2.49(1) | |

($O_{ax}$-Bi-$O_{ax}$ 147.5(3)°, 144.9(3)°, $O_{eq}$-Bi-$O_{eq}$ 96.4(4)°, 97.1(3)°). Possibly as a consequence of the significantly higher water content of **3**, the sodium atoms do not coordinate to the alkoxido oxygen atoms. The acceptor functions of the latter are compensated solely by hydrogen bonds. The conformation of the adenosine ligands in **3** is clearly distinct from **2** as well as from free adenosine. The ribofuranosyl ligands are puckered between C3′ *exo* and C2′ *endo* and the glycosidic torsion angles are found to be in a range of 89 − 74°. The adenine bases are stacked parallel along [100] with an interplanar spacing of about 3.4 Å (free adenosine 3.6 Å).

## Conclusion

This study confirms the fact that the nucleosides adenosine and guanosine may act as diolato ligands in homoleptic bi-

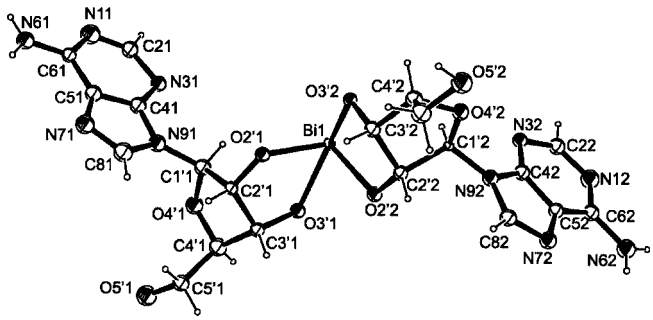



**Fig. 4** ORTEP presentation (50 % ellipsoid probability) of one of two symmetrically independent complex anions in **3**. Bi1-O bond lengths in Å: O3′1 2.234(7), O2′2 2.170(8), O3′2 2.227(6), O2′1 2.162(7); ring puckering parameters $Q_2$ and $\varphi_2$ [7] of the five-membered ring O4′-C1′-C2′-C3′-C4′ and glycosyl and torsion angles $\chi$ (C8-N9-C1′-O4′) and $\tau$ (O2′-C2′-C3′-O3′) of ribofuranosyl 1: $Q_2$ = 0.40(1) Å, $\varphi_2$ = 102(2)°, $\chi$ = 89(1)°, $\tau$ = −42(1)°; of ribofuranosyl 2: $Q_2$ = 0.38(1) Å, $\varphi_2$ = 77(2)°, $\chi$ = 74(1)°, $\tau$ = −42(1)°. Bi2-O bond lengths in Å: O3′3 2.263(7), O2′4 2.164(7), O3′4 2.254(7), O2′3 2.142(8); ribofuranosyl 3: $Q_2$ = 0.41(1) Å, $\varphi_2$ = 96(1)°, $\chi$ = 81(1)°, $\tau$ = −39(1)°; of ribofuranosyl 4: $Q_2$ = 0.39(1) Å, $\varphi_2$ = 63(2)°, $\chi$ = 76(1)°, $\tau$ = −39(1)°.

smutate(III) and antimonate(III) complexes in the solid state. Moreover, $^{13}$C NMR data indicate that these complexes are preserved in aqueous alkaline solutions. The corresponding inosine complexes can be detected in solution, however, the crystallization of the inosine complexes is possibly prevented by the absence of the exocyclic amino group which is involved in hydrogen bonds between the guanine−guanine base pair in **1**.

## Experimental Section

Hexammincobalt(III)-bis(guanosine-1,2′,3′-ato-*O2′,O3′*)bismutate(III) nonahydrate (**1**): Guanosine (0.37 g, 1.3 mmol) and sodium hydroxide (0.28 g, 7.0 mmol) are dissolved in 5 mL of water. Bismuth(III) nitrate pentahydrate (0.28 g, 0.58 mmol) is added and dissolved by slight warming. This solution is allowed to diffuse into an aqueous solution of hexammincobalttrichloride. Clusters of yellow-orange crystals of **1** form within a few days.

Sodium-bis(adenosine-2′,3′-ato-*O2′,O3′*)antimonate(III) hydrate (**2**): Antimony(III) trichloride (0.22 g, 1.0 mmol) is dissolved in a solution of adenosine (0.53 g, 2.0 mmol) and sodium hydroxide (0.24 g, 6.0 mmol) in 2 mL of water and stored at 323 K in a closed vessel. A few colorless crystals of **2** are yielded after one day.

Disodium-(adenosine-2′,3′-ato-*O2′,O3′*)-(adenosine-2′,3′,5′-ato-*O2′,O3′*)bismutate(III) 13.5 hydrate (**3**): Bismuth(III) nitrate pentahydrate (0.48 g, 1.0 mmol) is dissolved in a solution of adenosine (0.80 g, 3.0 mmol) and sodium hydroxide (0.24 g, 6 mmol) in 5 mL of water. This solution is mixed with 3.8 mL ethanol and stored at room temperature. Colorless crystals of **3** form within a few days. $^{13}$C NMR spectra of alkaline aqueous solutions containing inosine: Bismuth(III) nitrate pentahydrate (0.12 g, 0.25 mmol) or antimony(III) trichloride (0.06 g, 0.25 mmol) is dissolved in a solution of inosine (0.14 g, 0.52 mmol) and sodium hydroxide (0.08 g, 2.0 mmol) in 1 mL deuterium oxide.

### *Crystal structure determination*

**1**: $C_{20}H_{56}BiCoN_{16}O_{19}$, $M_r$ = 1092.72, monoclinic, $P2_1$, $a$ = 14.1958(2), $b$ = 9.3865(1), $c$ = 14.7620(2) Å, $\beta$ = 97.4337(7)°, $V$ = 1950.49(4) Å$^3$, $Z$ = 2, $\rho_c$ = 1.861 g cm$^{-3}$, Nonius KappaCCD, MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å), graded multilayer X-ray optics, crystal size 0.12 × 0.09 × 0.02 mm$^3$, $T$ = 200 K, $\omega/\varphi$-scans, 3.30° ≤ $\theta$ ≤ 27.51°, −18 ≤ $h$ ≤ 18, −12 ≤ $k$ ≤ 11, −19 ≤ $l$ ≤ 19, 43670 reflections measured of which 8402 were symmetrically independent (8086 reflections with $I > 2\sigma(I)$), $R_{int}$ = 0.0325, spherical absorption correction, $\mu$ = 5.025 mm$^{-1}$, nucleoside-, ammonia-, and water-hydrogen atoms with one common $U_{iso}$ each, O−H and N−H distances fixed to one common distance for each group, 645 parameters, 43 restraints, $R(F)$ = 0.0195 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.0410 (all data), $S$ = 1.036.

**2**: $C_{20}H_{24}N_{10}NaO_9Sb$, $M_r$ = 693.23, orthorhombic, $P2_12_12_1$, $a$ = 7.5237(3), $b$ = 11.2547(5), $c$ = 29.578(2) Å, $V$ = 2504.6(2) Å$^3$, $Z$ = 4, $\rho_c$ = 1.838 g cm$^{-3}$, Stoe IPDS, MoK$\alpha$ radiation ($\lambda$ = 0.71069 Å), graphite monochromator, crystal size 0.23 × 0.15 × 0.10 mm$^3$, $T$ = 200 K, $\varphi$-scans, 1.94° ≤ $\theta$ ≤ 25.73°, −8 ≤ $h$ ≤ 9, −13 ≤ $k$ ≤ 13, −36 ≤ $l$ ≤ 35, 16040 reflections measured of which 4759 were symmetrically independent (4448 reflections with $I > 2\sigma(I)$), $R_{int}$ = 0.0233, no absorption correction, $\mu$ = 1.193 mm$^{-1}$, one common $U_{iso}$ for all hydrogen atoms, O−H bond lengths fixed to one common distance, 443 parameters, 4 restraints, $R(F)$ = 0.0196 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.0424 (all data), $S$ = 1.020.

**3**: $C_{20}H_{48}BiN_{10}Na_2O_{21.5}$, $M_r$ = 1027.64, orthorhombic, $P2_12_12_1$, $a$ = 13.4775(6), $b$ = 23.216(1), $c$ = 23.270(1) Å, $V$ = 7280.9(6) Å$^3$, $Z$ = 8, $\rho_c$ = 1.875 g cm$^{-3}$, Stoe IPDS, MoK$\alpha$ radiation ($\lambda$ = 0.71069 Å), graphite monochromator, crystal size 0.50 × 0.30 × 0.10 mm$^3$, $T$ = 200 K, $\varphi$-scans, 2.31° ≤ $\theta$ ≤ 27.96°, −17 ≤ $h$ ≤ 17, −30 ≤ $k$ ≤ 30, −30 ≤ $l$ ≤ 30, 68677 reflections measured of which 17382 were symmetrically independent (14214 reflections with $I > 2\sigma(I)$), $R_{int}$ = 0.0449, numerical absorption correction, $T_{min}$ = 0.2563, $T_{max}$ = 0.5878, $\mu$ = 4.965 mm$^{-1}$, the quality of the data allows anisotropic displacement parameters only for Bi and Na, water hydrogen atoms not considered in refinement, one common $U_{iso}$ for all other hydrogen atoms, O−H bond lengths fixed to one common distance, 472 parameters, 4 restraints, $R(F)$ = 0.0356 ($I > 2\sigma(I)$), $wR(F^2)$ = 0.0824 (all data), $S$ = 0.965. All structures were solved with SHELXS-97 by direct methods and refined with SHELXL-97 [11].

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre: 634530 (**1**), 634531 (**2**), and 634532 (**3**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: file-serv@ccdc.cam.ac.uk.

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