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Synthesis, Characterization and Crystal Structure of New Mixed-Anions of Bismuth(III) Complexes

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Complexes $[Bi(bpy)_2(NO_3)(NCS)_2]$, $[Bi(bpy)_2(NO_3)_2(NCS)]$ and $[Bi(bpy)Br_4]^-(bpyH^+)$ have been synthesized by reaction of $Bi(NO_3)_3$ and ligands using a direct synthetic method. The complexes have been isolated and characterized by CHN elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy. The structure of the $[Bi(bpy)Br_4]^-(bpyH^+)$ has been confirmed by X-ray crystallography. The single crystal X-ray data of this compound shows that the complex is monomeric and the Bi atom has an unsymmetrical six-coordinate geometry, being coordinated by four Br atoms and two nitrogen atoms of the 2,2′-bipyridine ligand. The arrangement of the 2,2′-bipyridine ligand and Br atoms exhibits a coordination gap around the Bi(III) ion, occupied possibly by a stereoactive lone pair of electrons on bismuth(III). There is one 2,2′-bipyridinium $(bpyH^+)$ cation that was not coordinated to the bismuth atom. The uncoordinated 2,2′-bipyridinium $(bpyH^+)$ cations help in forming the π-π stacking interaction between the parallel aromatic rings belonging to adjacent chains in the compound.

Key Words: Bismuth(III) complexes, Crystal structure, 2,2′-Bipyridine, Lone pair.

INTRODUCTION

Bismuth complexes are of interest in the treatment of gastric ulcer[1–4]. In relation with work on mixed-ligand complexes described earlier[5–11], it becomes a little surprise to find further examples of these complexes. Building new molecular species and addressing their architectures in order to control their physical and structural properties has been a topic for many research groups. An issue frequently discussed in considering the coordination and stereoactivity of heavy metals is that of the stereochemical activity of valence shell lone electron pairs[12–14]. Extensive recent structural studies of bismuth(III) compounds[15–17] in particular have provided a basis for a rather detailed analysis of the evidence for coordination sphere distortions which may be a consequence of the presence of such pairs. It appears that in the complexes of lead(II) and probably in those of

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related species such as Tl(I)[18–21] and Bi(III)[22–24], the nature and form of the coordination sphere is generally determined by a number of factors, possibly lone pair repulsions of comparable influence, so that seemingly minor differences in ligands or in the crystal array can have quite marked effects upon the coordination stereochemistry.

The coordination chemistry of Bismuth(III) is disproportionately sparse when compared with that of other metals[25, 26]. We want to show the nature of adducts formed between mixed-ligand bismuth(III) complexes and aromatic N,N–bidentate ligands of 2,2′-bipyridine.

EXPERIMENTAL

IR spectra were recorded as Nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-rapid analyzer.

Preparation of [Bi(bpy)$_2$(NO$_3$)(NCS)$_2$]: The complex was prepared by dissolving 0.36 g (1 mmol) bismuth(III) nitrate in distilled water and adding a mixture of alcoholic solution of 2,2′-bipyridine (bpy) (0.312 g, 2 mmol) and potassium thiocyanate (0.194 g, 2 mmol). The resulting solution was stirred for 4 h at room temperature; then it was allowed to stand for 2–3 d in a refrigerator. Yellow-white crystals of the desired product precipitated, which were filtered off and washed with acetone and ether and air dried (0.419 g, yield 60%, m.p. 218°C). Anal.: Calcd. for $C_{22}H_{16}N_7O_3S_2Bi$: C, 37.76; H, 2.28; N, 14.02%. Found: C, 37.65; H, 2.39; N, 14.31. IR (ν_{max}, cm^{-1}): 722 (s), 850 (s), 1380 (s), 1590 (s), 1648 (s), 2040 (vs), 3025 (w). ^{1}H NMR (DMSO, δ): 7.40–7.55 (t, 1H), 7.80–8.00 (t, 1H), 8.30–8.40 (d, 1H), 8.60–8.75 (d, 1H). ^{13}C ^{1}H NMR (DMSO, δ): 121.14, 124.60, 137.92, 149.36, 154.98.

Preparation of [Bi(bpy)Br$_4$]$^-$(bpyH$^+$): The complex was prepared by dissolving bismuth(III) nitrate (0.36 g, 1 mmol) and potassium bromide (0.238 g, 2 mmol) in distilled water and adding an alcoholic solution of 2,2′-bipyridine (0.312 g, 2 mmol). The resulting solution was stirred for 5 h at room temperature, then it was allowed to stand for 2–3 d in a refrigerator (*ca.* 6°C). Yellow crystals of the desired product precipitated, which were filtered off, washed with acetone and ether and air dried (0.454 g, yield 54%, m.p.232°C). Anal.: Calcd. for $C_{20}Br_4H_{17}N_4Bi$: C, 28.50; H, 2.02; N, 6.65%. Found: C, 28.10; H, 2.11; N, 6.43. IR (ν_{max}, cm^{-1}): 759 (s), 1005 (s), 1420 (s), 1581 (s), 1610 (s), 3050 (w), 3250 (m). ^{1}H NMR (DMSO, δ): 7.40–7.50 (t, 1H), 7.85–8.00 (t, 1H), 8.30–8.40 (d, 1H), 8.60–8.80 (d, 1H). ^{13}C ^{1}H NMR (DMSO, δ): 121.20, 124.55, 137.90, 149.40, 155.00.

Preparation of [Bi(bpy)$_2$(NO$_3$)$_2$(NCS)]: The complex [Bi(bpy)$_2$(NO$_3$)$_2$(NCS)] was prepared by dissolving 0.36 g (1 mmol) bismuth(III) nitrate in distillation water and adding a mixture of alcoholic solution of 2,2′-bipyridine (0.312 g, 2 mmol) and potassium thiocyanate (0.097 g, 1 mmol). The resulting solution was stirred for 6 h at room temperature, then it was allowed to stand for 2–3 d in a refrigerator. Yellow-white crystals of the desired product precipitated, which were filtered off and washed with acetone and ether and air dried (0.463

g, yield 66%, m.p. 242°C). Anal.: Calcd. for $C_{21}H_{16}N_7O_6SBi$: C, 35.84; H, 2.27; N, 13.94%. Found: C, 35.30; H, 2.05; N, 13.85. IR (ν_{max}, cm^{-1}): 722 (s), 850 (s), 1377 (vs), 1585 (s), 1656 (s), 2035 (s), 3040 (w). ^1H NMR (DMSO, δ): 7.40–7.60 (t, 1H), 7.80–8.00 (t, 1H), 8.35–8.40 (d, 1H), 8.60–8.80 (d, 1H). ^{13}C $^1H\}$ NMR (DMSO; δ): 121.18, 124.65, 137.95, 149.35, 154.90.

Crystallography

Crystal Data and Refinement Details: $[Bi(bpy)Br_4]^-(bpyH^+)$. $C_{20}H_{17}BiBr_4N_4$, M 842.00, monoclinic, space group C2/c, $a = 15.553(2)$, $b = 9.7834(15)$, $c = 16.711(3)$ Å, $\alpha = 90.159$, $\beta = 108.373(4)$, $\gamma = 90,°$ $V = 1413.1(6)$ $Å^3$, Dc ($Z = 4$ f.u.) 2.318 mg/m^3, F (000) 1552. Specimen: $0.25 \times 0.25 \times 0.22$ mm; $T_{max, min}$ 0.932, 0.842, N 5264, N_0 6122, R 0.0504, R_w 0.0922.

Determination of the structures: Crystallographic measurements were made at 293(2) K for using a Siemens R3m/V diffractometer. The intensity data were collected within the range. $2.50 \leq \theta \leq 29.01°$ for using graphite monochromataed Mo–K_α radiation (= 0.71073 Å). Accurate unit cell parameters and on orientation matrix for data collection were obtained from least-squares refinement. Intensities of 6122 unique reflections were measured, from which 1812 with $I > 2\sigma(I)$ were used in the refinement. The structures have been solved by direct methods and refined by full-matrix least-squares techniques on F^2.

The positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic thermal parameter R, R_w, with goodness of fit on F^2 0.974 are 0.0504, 0.0922. The final difference density map showed a maximum peak and hole of 2.696, –0.728 $eÅ^{-3}$. Corrections for the Lorentz and polarization effects as well as the empirical corrections for absorption using the semi-empirical from equivalent programs were applied. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package[27, 28].

Crystal data and structure refinement are given in Table-1. Selected bond lengths and angles are given in Table-2. Anisotropy thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material†. ORTEP diagrams and a perspective view of the packing in the unit cells are shown in Figs. 1 and 2.

RESULTS AND DISCUSSION

Reaction between 2,2′-bipyridine and mixture of bismuth(III) nitrate, potassium thiocyanate and potassium bromide provided crystalline material analyzing as $[Bi(bpy)_2(NO_3)(NCS)_2]$, $[Bi(bpy)_2(NO_3)_2(NCS)]$ and $[Bi(bpy)_2Br_4]^-(bpyH^+)$.

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† SUPPLEMENTARY MATERIAL

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 215233 for $[Bi(bpy)Br_4]^-(bpyH^+)$.

The IR spectra of [Bi(bpy)$_2$(NO$_3$)(NCS)$_2$] and [Bi(bpy)$_2$(NO$_3$)$_2$(NCS)] complexes show ν(NO$_3$) at *ca.* 1380 cm^{-1} and also ν(SCN) at *ca.* 2020 cm^{-1}. Attempts at isolation of mixed–ligand complexes of bromide and nitrate anions [(bpy)$_2$Bi(NO$_3$)$_n$Br$_m$] (n + m = 3) were not successful and each time the [Bi(bpy)Br$_4$]$^-$(bpyH$^+$) compound was isolated.

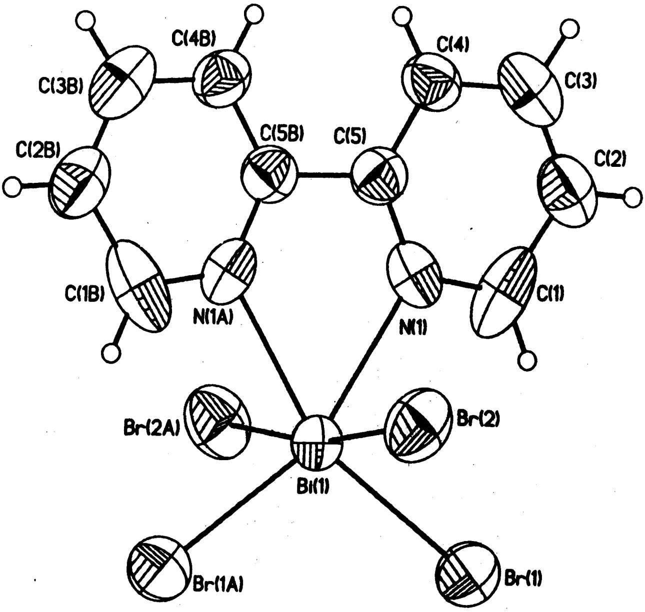

Fig 1. ORTEP diagram of [Bi(bpy)Br4]$^-$(bpyH$^+$)

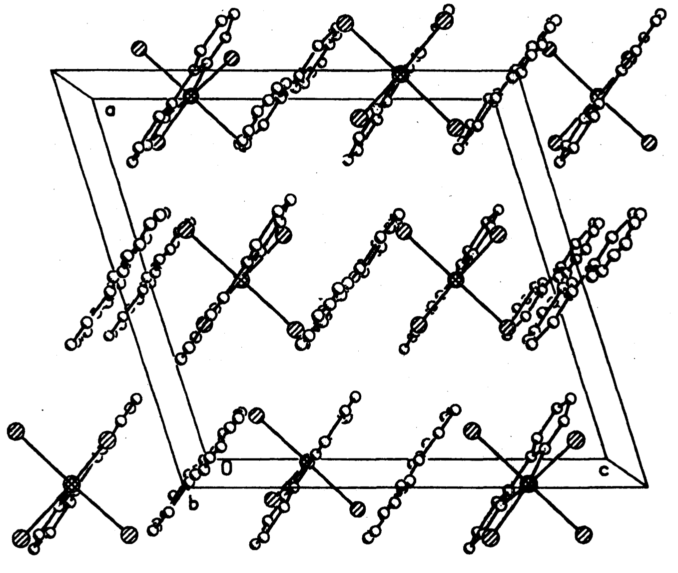

Fig 2. The unit cell and showing-stacking interaction in [Bi(bpy)Br$_4$]$^-$(bpyH$^+$)

Crystal structure of $[Bi(bpy)Br_4]^-(bpyH^+)$

Determination of the structure of the $[Bi(bpy)Br_4]^-(bpyH^+)$ by X-ray crystallography (Table-1) showed the complex in the solid state (Figs. 1, 2) to be a monomeric species with various similarities to monomeric structure $[Bi(phen)_2(NO_3)_3]$ and the environmental in bismuth atoms is six and the Bi atom is coordinated by six donor (four Br atoms and two nitrogen atoms of the

TABLE-1

CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $[Bi(bpy)Br_4]^-(bpyH^+)$

Empirical formula	$C_{20}H_{17}BiBr_4N_4$	
Formula weight	842.00	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 15.553(2) Å	$\alpha = 90°$
	b = 9.7834(15) Å	$\beta = 103.373(4)°$
	c = 16.711(3) Å	$\gamma = 90°$
Volume	2413.1(6) $Å^3$	
Z	4	
Density (calculated)	2.318 Mg/m^3	
Absorption coefficient	13.944 mm^{-1}	
F(000)	1552	
Crystal size	0.25 × 0.25 × 0.22 mm^3	
Theta range for data collection	2.50 to 29.01	
Index ranges	$-17 \leq h \leq 21, -6 \leq k \leq 13, -22 \leq l \leq 22$	
Reflections collected	6122	
Independent reflections	3071 [R(int) = 0.0407]	
Completeness to theta = 29.01	95.3%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0932 and 0.0842	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3071/0/131	
Goodness-of-fit on F^2	0.974	
Final R indices for 1812 ref. 1 $[I > 2\sigma(I)]$	$R_1 = 0.0504$, $wR_2 = 0.0922$	
R indices (all data)	$R_1 = 0.0917$, $wR_2 = 0.1005$	
Largest diff. peak, hole	2.696, –0.729 $eÅ^{-3}$	

2,2′-bipyridine ligand), the resulting geometry around the Bi atom being distorted octahedral. The arrangement of four Br^- anions and 2,2′-bipyridine ligand suggests a gap in coordination geometry around the metal ion [angle Br(1A)-Bi(1)-Br(1) is 109.67(3)° and Br(2A)-Bi(1)-Br(2) is 170.19(3)°], occupied possibly by a stereoactive lone pair of electrons on the bismuth(III)[14]. Hence, the geometry of the nearest coordination environment of every bismuth atom is likely caused by the geometrical constraints of coordinated 2,2′–bipyridyl and four Br anions and also by the influence of a stereochemically active lone pair of electrons in a hybrid orbital on the metal atom which occupies one equatorial coordination site of a pseudooctahedral.

There is one 2,2′-bipyridinium ($bpyH^+$) cation that was not coordinated to the bismuth atom. The uncoordinated 2,2′-bipyridinium ($bpyH^+$) cation ligand helps in forming the π-π stacking interaction[25, 26] between the parallel aromatic rings belonging to adjacent chain in compound in this complex, as shown in Fig. 2 as planar species in which the mean molecular planes are close to parallel and separated by a distance of *ca.* 3.5 Å, close to that of the planes in graphite. Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the "Pi-stacking" type, rather than "edge-to-face" or "vertex-to-face" types[29–32]. Projection of the structure perpendicular to the ring plane shows the overall form of the "slipped" stacking[32, 33], which is at least qualitatively understandable in terms of optimizing approaches between atoms of opposite charges[34].

TABLE-2

SELECTED BOND LENGTHS AND ANGLES FOR $[Bi(bpy)Br_4]^-(bpyH^+)$

Bond lengths (Å)		Bond angles (°)	
Bi(1)-N(1)	2.52(4)	N(1)-Bi(1)-N(1A)	64.40(2)
Bi(1)-N(1A)	2.52(4)	N(1)-Bi(1)-Br(1A)	157.24(9)
Bi(1)-Br(1)	2.81(7)	N(1A)-Bi(1)-Br(1A)	93.01(9)
Bi(1)-Br(1A)	2.81(7)	N(1)-Bi(1)-Br(1)	93.01(9)
Bi(1)-Br(2)	2.82(7)	N(1A)-Bi(1)-Br(1)	157.24(1)
Bi(1)-Br(2A)	2.82(7)	Br(1A)-Bi(1)-Br(1)	109.67(3)
		N(1)-Bi(1)-Br(2A)	88.37(1)
		N(1A)-Bi(1)-Br(2A)	83.32(1)
		Br(1A)-Bi(1)-Br(2A)	91.88(2)
		Br(1)-Bi(1)-Br(2A)	93.77(2)
		N(1)-Bi(1)-Br(2)	83.32(1)
		N(1A)-Bi(1)-Br(2)	88.37(1)
		Br(1A)-Bi(1)-Br(2)	93.77(2)
		Br(2)-Bi(1)-Br(3)	91.88(2)
		Br(2A)-Bi(1)-Br(2)	170.19(3)

#1. −x + 1, y, −z + 3/2, #2. −x, −y + 1, −z

A simple model to describe the nature of π-π interactions has been developed by Hunter *et al.*[34]. This model predicts that face-to-face stacked interactions will be disfavoured due to the dominance of π-π repulsion. However, in offset π-stacked and edge-on or T-shaped geometries, favourable π-σ attractions dominate. The polarization of aromatic systems, through the introduction of heteroatoms, electron-withdrawing groups or electron-donating groups, alters the nature of any π-π interactions. For example, although it is well known that neither benzene nor hexafluorobenzene[35] tends to form stacked arrangements, the adduct between these two molecules adopts a structure comprising inclined stacks of alternating molecules[36]. Here, the hexafluorobenzene π-system is electron-deficient with respect to benzene and this reduces the π-π repulsion, making the formation of offset π-stacked molecules more favourable. The introduction of heteroatoms can lead to a similar perturbation of aromatic interactions[31]; specifically, nitrogen atoms have been shown to remove electron density from the π-system and hence have a similar effect on electron-withdrawing groups. It has been shown that electron-poor aromatic groups interact most strongly with electron-rich aromatic groups[31]. Hence, since the molecules of this packing include equally or almost equally electron-deficient or indeed electron-rich rings, it can be expected that within the molecule discussed here model face-to-face π-stacked interactions must be disfavoured due to the dominance of π-π repulsion. This suggests that hydrogen bonding may be the most important factor and affect π-π stacking.

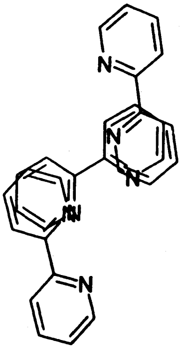

Fig. 3. Projection of nearest neighbour pairs in the π-π stacks of hetroaromatic bases in $[Bi(bpy)Br_4]^-(bpyH^+)$.

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