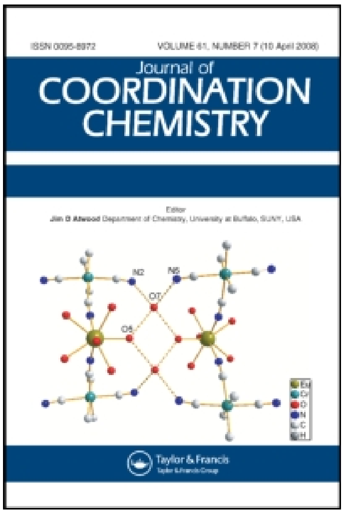

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Direct Synthesis of a Dimeric Mixed-Anions Bismuth(III) Complex: Synthesis and Structural Characterization of $[Bi_2(Phen)_4(No_3)_{4.4}I_{0.6}]I_3$ (A New Dimeric Compound)

Ali Reza Mahjoub[a]; Ali Morsali[a]
[a] Department of Chemistry School of Science, Tarbiat Modarres University, Tehran, I.R. Iran

To cite this Article Mahjoub, Ali Reza and Morsali, Ali(2003) 'Direct Synthesis of a Dimeric Mixed-Anions Bismuth(III) Complex: Synthesis and Structural Characterization of $[Bi_2(Phen)_4(No_3)_{4.4}I_{0.6}]I_3$ (A New Dimeric Compound)', Journal of Coordination Chemistry, 56: 7, 571 — 577

To link to this Article: DOI: 10.1080/0095897031000110628

URL: http://dx.doi.org/10.1080/0095897031000110628

J. Coord. Chem., Vol. 56, No. 7, 10 May 2003, pp. 571–577

Taylor & Francis
Taylor & Francis Group

DIRECT SYNTHESIS OF A DIMERIC MIXED-ANIONS BISMUTH(III) COMPLEX: SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF $[BI_2(PHEN)_4(NO_3)_{4.4}I_{0.6}]I_3$ (A NEW DIMERIC COMPOUND)

ALI REZA MAHJOUB* and ALI MORSALI

Department of Chemistry, School of Science, Tarbiat Modarres University
P.O. Box 14155-4838 Tehran, I.R. Iran

(Received 4 June 2002; Revised 8 July 2002; In final form 16 February 2003)

A direct synthetic method of mixing $Bi(NO_3)_3$ and NaI with 1,10-phenanthroline yielded red crystals of $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$. In this complex the cationic part is in fact binuclear and contains two $[Bi(phen)(NO_3)_{1.7}I_{0.3}]$ groups linked *via* a bridging NO_3^- anion. The I_3^- anion was not coordinated to bismuth(III) and the lone pair of valence electrons of the bismuth(III) ions appears to be stereochemically inactive. There are two independent NO_3^- anions, one coordinated to bismuth but another shares a position with I^- anion. The final results of crystallography show that 40% of these positions are occupied by NO_3^- anions and 60% by I^- anions that are coordinated to bismuth atom in bidentate fashion (NO_3^-) and in unidentate fashion (I^-). An interesting point is that the I_3^- anion was produced by direct synthetic method (Branched tube method). There is a π–π stacking interaction between the parallel aromatic rings around the Bi(III) ion.

Keywords: Bismuth(III) complexes; Crystal structure; Mixed-ligands complexes

INTRODUCTION

Thallium(I), lead(II), and bismuth(III) compounds are of interest for coordination sphere distortions which may be a consequence of the presence of a lone pair. The coordination chemistry of bismuth(III) is sparse when compared with that of other metals [1–2]. Extensive recent structural studies of bismuth(III) compounds [3–5] have provided a basis for rather detailed analysis showing that there are no coordination sphere distortions which may be a consequence of the presence of such pairs. From work on mixed-ligand complexes described in earlier papers [6–12], it comes as little surprise to find further examples of these complexes. In recent reports of the crystal structure of the different monomeric, dimeric, and polymeric mixed–ligand complexes of lead(II), $[Pb(phen)_2(NCS)(NO_3)]$ [11], $[Pb(phen)(CH_3CO_2)(NCS)]_2$ [12],

---

*Corresponding author.

ISSN 0095-8972 print: ISSN 1029-0389 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0095897031000110628

$[Pb(phen)(CH_3CO_2)(NO_3)]_n$ [9], $[Pb(phen)(CH_3CO_2)(ClO_4)]_n$ [8], $[Pb(phen)_2(ClO_4)(NO_3)]$, and $[Pb_2(BTZ)_4(NO_3)(H_2O)](ClO_4)_3$ [10] {BTZ = 4,4′–Bithiazole} described the presence of the lone pair and its influence upon the coordination stereochemistry of metal ions and also their structures. This manuscript shows the nature of adducts formed in a mixed-anion bismuth(III) complex.

EXPERIMENTAL

Physical Measurements

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. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

Preparation of $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$

The $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$ complex was prepared by diffusion along a thermal gradient in methanol solution (the branched tube method), [1,10-Phenanthroline (0.2 g, 1 mmol) was placed in one arm of the branched tube and a mixture of bismuth(III) nitrate (0.5 mmol) and NaI (0.5 mmol), in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 60°C while the other was at ambient temperature. After 7 days red crystals, (mp 285°C) had deposited in the cooler arm] (Found: C, 30.00; H, 1.60; N, 9.60. $C_{48}H_{32}Bi_2I_{3.6}N_{12.40}O_{13.20}$ requires C, 30.75; H, 1.71; N, 9.29%).

IR(cm^{-1}) bands: 630(w), 720(s), 810(s), 843(s), 1024(w), 1093(w), 1140(w), 1213(w), 1267(s), 1296(s), 1370(vs) ,1413(vs), 1442(vs), 1505(w), 1530(s), 1610(w), 3050(w).

Crystallography

Determination of the Structures

Crystallographic measurements were made at 110 K using a Siemens R3m/V diffractmeter. The intensity data were collected within the range $2.29° \leq \theta \leq 25.06°$ for $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$ and $1.31° \leq \theta \leq 28.00°$ using graphite monochromataed Mo-K_α radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 12651 unique reflections were measured, from which 7894 with $I > 2\sigma(I)$ were used in the refinement. The structure has 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 1.158 are 0.0500, 0.0956, respectively. The final difference density map showed a maximum peak and hole of 3.785, $-2.447\,e\,Å^{-3}$. Corrections for Lorentz and polarization effects as well as the empirical correction for absorption using the Psi-scan programs were applied. All structural calculations were carried out with a PDP – 11/23+ computer using the SDP – PLUS program package [13,14].

TABLE I Crystal data and structure refinement for $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$

Identification code	$Bi_2(phen)_4$
Empirical formula	$C_{48}H_{32}Bi_2I_{3.60}N_{12.40}O_{13.20}$
Formula weight	1868.46
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 9.550(2)$ Å $\alpha = 90°$ $b = 31.181(7)$ Å $\beta = 94.008(6)°$ $c = 17.727(4)$ Å $\gamma = 90°$
Volume	5266(2) $Å^3$
Z	4
Density (calculated)	2.357 Mg/m^3
Absorption coefficient	8.863 min^{-1}
$F(000)$	3477
Crystal size	$0.32 \times 0.20 \times 0.15\,mm^3$
θ range for data collection	1.31 to 28.00°
Index ranges	$-12 \leq h \leq 12, -41 \leq k \leq 41, -23 \leq l \leq 23$
Reflections collected	54580
Independent reflections	12651 [$R(int) = 0.0688$]
Completeness to $\theta = 28.00°$	99.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7572 and 0.5421
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12651/42/730
Goodness-of-fit on F^2	1.158
Final R indices for 7894 refl. with $[I > 2\sigma(I)]$	$R1 = 0.0500$, $wR2 = 0.0956$
R indices (all data)	$R1 = 0.0876$, $wR2 = 0.1026$
Largest diff. peak and hole	3.785 and $-2.447\,eÅ^{-3}$

Crystal data and structure refinement are given in Table I, selected bond lengths and angles are given in Table II. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are available in the supplementary material from AM. ORTEP diagrams and a perspective view of the packing in the unit cells are shown in Figs. 1 and 2.

DISCUSSION

Synthesis

Reaction between 1,10-phenanthroline (phen) and an equimolar mixture of bismuth(III) nitrate and sodium iodide by diffusion along a thermal gradient in methanol solution (the branched tube method), provided crystalline material analyzing as $[Bi_2(phen)_4\text{-}(NO_3)_{4.4}I_{0.6}]I_3$. The IR spectrum of the $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$, complex shows $\nu(NO_3)$ at *ca.* 1370 cm^{-1}.

Crystal Structure of $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$

An attempt to isolate $Bi(phen)_2(NO_3)_2I$ led to the isolation of $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$ in which there are two independent NO_3^- anions, one coordinated to bismuth and

TABLE II Selected bond lengths (Å) and angles (°) for the $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$

Bi(1):			
Bi(1)–N(1)	2.458(7)	N(1)–Bi(1)–N(2)	68.4(2)
Bi(1)–N(2)	2.473(7)	N(1)–Bi(1)–N(4)	73.5(2)
Bi(1)–N(4)	2.483(7)	N(2)–Bi(1)–N(4)	87.4(2)
Bi(1)–N(3)	2.494(7)	N(1)–Bi(1)–N(3)	85.7(2)
Bi(1)–O(8′)	2.589(7)	N(1)–Bi(1)–N(3)	85.7(2)
Bi(1)–O(4)	2.629(6)	N(2)–Bi(1)–N(3)	148.1(2)
Bi(1)–O(5)	2.630(6)	N(4)–Bi(1)–N(3)	66.9(2)
Bi(1)–O(7′)	2.684(7)	N(1)–Bi(1)–O(8′)	72.2(2)
Bi(1)–O(1)	2.706(6)	N(2)–Bi(1)–O(8′)	115.2(2)
Bi(1)–O(2)	2.895(6)	N(2)–Bi(1)–O(2)	165.7(7)
Bi(1)–I(5)	3.090(3)	N(4)–Bi(1)–O(8′)	126.9(2)
Bi(2)–Br(1)	2.925(3)	N(3)–Bi(1)–O(8′)	71.2(2)
Bi(1)–O(1)	2.46(2)	N(1)–Bi(1)–O(4)	143.6(2)
Bi(1)–O(2)	2.67(2)	N(2)–Bi(1)–O(4)	117.6(2)
O(8′)–Bi(1)–O	94.2(2)	N(4)–Bi(1)–O(4)	71.1(2)
O(4)–Bi(1)–O(1)	74.78(18)	N(3)–Bi(1)–O(4)	72.6(2)
O(5)–Bi(1)–O(1)	67.76(18)	O(8′)–Bi(1)–O(4)	124.7(2)
O(7′)–Bi(1)–O(1)	70.88(19)	N(1)–Bi(1)–O(5)	124.1(2)
N(1)–Bi(1)–O(2)	143.7(2)	N(2)–Bi(1)–O(5)	69.1(2)
N(2)–Bi(1)–O(2)	131.1(2)	N(4)–Bi(1)–O(5)	69.9(2),
N(3)–Bi(1)–O(5)	115.4(2)	N(3)–Bi(1)–O(5)	115.4(2)
N(3)–Bi(1)–O(2)	80.8(2)	N(3)–Bi(1)–O(5)	115.4(2)
O(8′)–Bi(1)–O(2)	71.58(19)	O(8′)–Bi(1)–O(5)	166.6(2)
O(4)–Bi(1)–O(2)	62.23(17)	O(4)–Bi(1)–O(5)	48.54(18)
O(5)–Bi(1)–O(2)	91.99(18)	N(1)–Bi(1)–O(7′)	72.3(2)
O(7′)–Bi(1)–O(2)	85.87(19)	N(2)–Bi(1)–O(7′)	70.2(2)
O(1)–Bi(1)–O(2)	45.70(17)	N(4)–Bi(1)–O(7′)	144.1(2)
N(1)–Bi(1)–I(5)	70.74(17)	N(3)–Bi(1)–O(7′)	120.4(2)
N(2)–Bi(1)–I(5)	94.54(17)	O(8′)–Bi(1)–O(7′)	144.1(2)
N(4)–Bi(1)–I(5)	140.56(17)	O(5)–Bi(1)–O(7′)	79.0(6)
N(3)–Bi(1)–I(5)	94.12(17)	O(4)–Bi(1)–O(7′)	122.9(2)
O(8′)–Bi(1)–I(5)	23.00(16)	N(1)–Bi(1)–O(1)	140.4(2)
O(4)–Bi(1)–I(5)	138.29(15)	N(2)–Bi(1)–O(1)	85.7(2)
O(5)–Bi(1)–I(5)	146.54(14)	N(4)–Bi(1)–O(1)	136.8(2)
O(7′)–Bi(1)–I(5)	26.54(15)	N(3)–Bi(1)–O(1)	125.9(2)
O(1)–Bi(1)– I(5)	82.52(14)	O(8′)–Bi(1)–I(5)	23.00(16)
Bi(1)–O(1)–Bi(2)	161.33(2)		
Bi(2):			
Bi(2)–N(5)	2.440(7)	N(6)–Bi(2)–O(10)	72.7(2)
Bi(2)–N(6)	2.458(7)	N(8)–Bi(2)–O(10)	136.0(2)
Bi(2)–N(8)	2.511(7)	O(15′)–Bi(2)–O(10)	68.3(2)
Bi(2)–O(15′)	2.561(7)	O(11)–Bi(2)–O(10)	48.35(18)
Bi(2)–O(11)	2.588(5)	N(7)–Bi(2)–O(10)	146.2(2)
Bi(2)–N(7)	2.619(8)	N(5)–Bi(2)–O(14′)	152.4(2)
Bi(2)–O(10)	2.668(6)	N(6)–Bi(2)–O(14′)	124.1(2)
Bi(2)–O(14′)	2.6743(7)	N(8)–Bi(2)–O(14′)	78.8(2)
Bi(2)–O(1)	2.749(6)	O(15′)–Bi(2)–O(14′)	50.5(2)
Bi(2)–O(3)	2.803(6)	O(11)–Bi(2)–O(14′)	130.1(2)
I(1)–I(2)	2.8952(12)	N(7)–Bi(2)–O(14′)	71.1(2)
I(2)–I(3)	2.9344(12)	O(10)–Bi(2)–O(14′)	86.5(2)
N(5)–Bi(2)–O(3)	68.4(2)	N(5)–Bi(2)–O(1)	114.5(2)
N(6)–Bi(2)–O(3)	120.4(2)	N(6)–Bi(2)–O(1)	139.1(2)
N(8)–Bi(2)–O(3)	125.3(2)	N(8)–Bi(2)–O(1)	139.0(2)
O(15′)–Bi(2)–O(2)	158.2(2)	O(15′)–Bi(2)–O(1)	112.1(2)
O(11)–Bi(2)–O(3)	63.98(18)	O(11)–Bi(2)–O(1)	72.68(18)
N(7)–Bi(2)–O(3)	69.54(19)	N(7)–Bi(2)–O(1)	77.0(2)
O(10)–Bi(2)–O(3)	98.56(18)	O(10)–Bi(2)–O(1)	72.62(18)
O(14′)–Bi(2)–N(3)	113.6(2)	O(14′)–Bi(2)–O(1)	74.32(19)
O(1)–Bi(2)–O(3)	46.20(17)	N(5)–Bi(2)–O(15′)	133.0(2)
N(5)–Bi(2)–N(6)	67.7(2)	N(6)–Bi(2)–O(15′)	73.6(2)
N(5)–Bi(2)–N(8)	78.6(2)	N(8)–Bi(2)–O(15′)	70.4(2)
N(6)–Bi(2)–N(8)	81.8(2)		

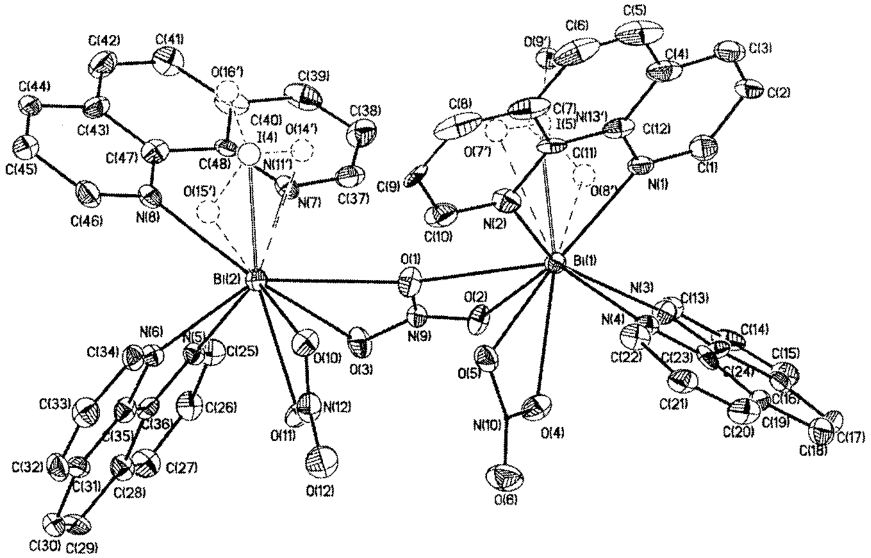

FIGURE 1 *ORTEP* diagram of $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$.

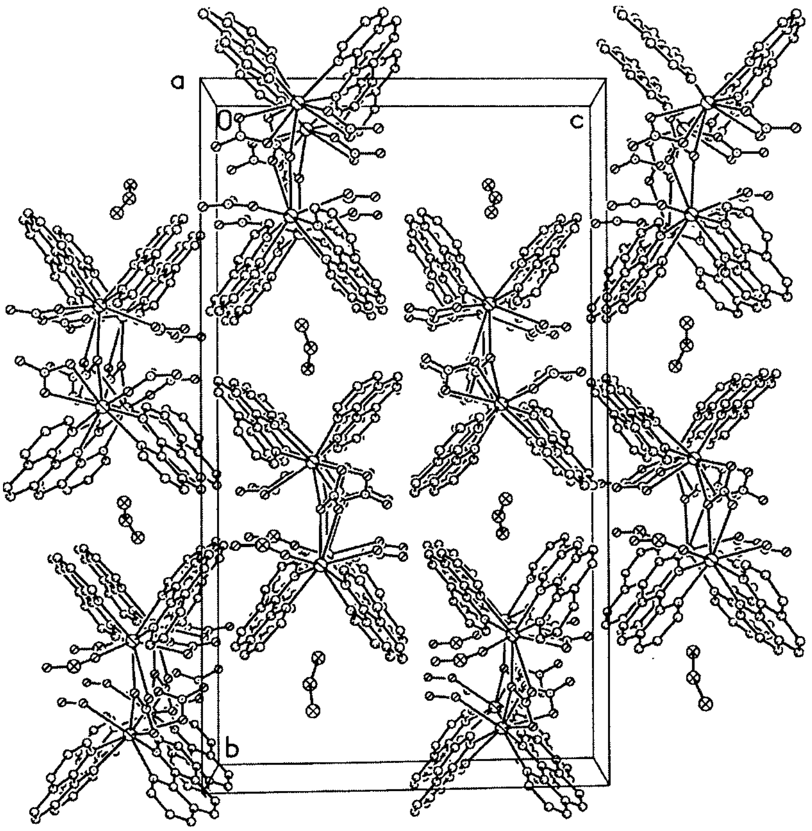

FIGURE 2 The Unit cell of $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$.

another sharing a position with I^-. The final results of crystallography show 40% of these positions occupied by NO_3^- anions and 60% by I^- anions that are coordinated to bismuth in bidentate fashion (NO_3^-) and in unidentate fashion (I^-). The title structure (Fig. 1) is interesting for the presence of an unequally bridging NO_3^- ion; another interesting point is that the I_3^- anion arose from the direct synthetic method (Branched tube method). The structure consists of a binuclear $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$ complex, with two bismuth(III) ions linked by the asymmetrically coordinated NO_3^- to two different Bi^{3+} ions, so that the bridging unit is the compact Bi–O–N–O–Bi and the Bi–O(NO_3) distances are 2.706 Å [Bi(1)–O(1)], 2.895 Å [Bi(1)–O(2)], 2.749 Å [Bi(2)–O(1)], and 2.803 Å [Bi(2)–O(3)]. The bridging oxygen of nitrate ion increases the coordination number of both bismuth(III) ions. The environment of both bismuth atoms is similar, with a coordination number of ten (NO_3^- coordinated) or nine (I^- coordinated).

The arrangement of the two 1,10-phenanthroline ligands and NO_3^- anions suggests the coordination geometry around the bismuth(III) ions is regular and there is no gap in the geometry around the bismuth(III) ions from the lone pair of electrons on the bismuth(III). In a recent report[5] of syntheses and structural characterization of a dimeric mixed-anions lead(II) complex, $[Pb_2(BTZ)_4(NO_3)(H_2O)](ClO_4)_3$ {BTZ = 4,4′-Bithiazole} described the presence of lone pair and its influence upon the coordination stereochemistry of mixed-anion lead(II). The similarity of $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$ with $[Pb_2(BTZ)_4(NO_3)(H_2O)](ClO_4)_3$ with an unequally bridging NO_3^- ion in the two dimeric complexes is contrasted by the different π–π stacking [1,13] interaction (charge-transfer arrays) between the parallel aromatic rings belonging to adjacent chains in $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$, as shown in Fig. 2. The planar species with mean molecular planes close to parallel and separated by a distance of ~3.5 Å are close to that of the planes in graphite. The lone pair in $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$ is inactive.

An interesting point is that the I_3^- anions were prepared by direct synthetic method. The triiodides anion can be made by reactions which result in halide-ion transfer between molecular species. Stability is often enhanced by use of a large counter-cation, e.g. Rb^+, Cs^+, NR_4^+, PCI_4^+, etc. Typical examples of linear (or nearly linear) triatomic polyiodides are in Table III [1]. The highest deviations from the linearity of I_3^- is in the $[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]I_3$, probably due to crystal-packing forces and residual interactions between the various ions in the solid state or π–π stacking may help to increase angular deviation.

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 183433.

TABLE 3 Bond lengths (Å) and bond angles (°) for I_3^- with the different cations

Polyiodide	*Cations*	*Structure*	*Bond lengths* (Å)	*bond angles* (°)
I_3^-	$AsPh_4^+$	$[I–I–I]^-$	2.90, 2.90	176
I_3^-	$[PhCONH_2]_2H^+$	$[I–I–I]^-$	2.91, 2.95	177
I_3^-	NEt_4^+	$[I–I–I]^-$	2.91, 2.96	180
I_3^-	Cs^+	$[I–I–I]^-$	2.83, 3.03	180
I_3^-	$[Bi_2(phen)_4(NO_3)_{4.4}I_{0.6}]^+$	$[I–I–I]^-$	2.89, 2.93	169

Acknowledgments

Support of this investigation by Tarbiat Modarres University is gratefully acknowledeged. We thank Institute of Organoelement Compounds of the Russian Academy of Science for determining the crystal structure by X-ray crystallography.

References

[1] N.N. Grenwood and A. Earnshaw, Chemistry of the Elements (Pergamon Press, Oxford, 1984), pp. 235–236.
[2] G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Vols. 1–7 (Pergamon, London, 1987).
[3] L.J. Barbour, S.J. Belfield, P.C. Junk and M.K. Smith, *Aust. J. Chem.* **51**, 337 (1998).
[4] G.M. Bowmaker, F.M.M. Hannaway, P.C. Junk, A.M. Lee and A.H. White, *Aust. J. Chem.* **51**, 325 (1998).
[5] R.D. Hancok, I. Cukrowski, J. Baloyi and J. Mashishi, *J. Chem. Soc. Dalton Trans* 2895 (1993).
[6] L.M. Engelhardt, J.M. Harrowfield, D.L. Kepert, H. Miyamae, J.M. Patrick, B.W. Skelton, A.A. Soudi and H. White, *Aust. J. Chem.* **49**, 1111 (1996).
[7] L.M. Engelhardt, J.M. Harrowfield, D.L. Kepert, H. Miyamae, J.M. Patrick, B.W. Skelton, A.A. Soudi and H. White, *Aust. J. Chem.* **49**, 1111 (1996).
[8] A.K. Hall, J.M. Engelhard, A. Morsali, A.A. Soudi and A. Yanovsky, *Cryst. Eng. Comm.* 013 (2000).
[9] A. Morsali, M. Payheghader and M.S. Salehi, *Zeitschrift für anorganische und allgemeine Chemien* **628**, 12 (2002).
[10] A.R. Mahjoub and A. Morsali, *Chimistry Letters* 1234 (2001).
[11] A.R. Mahjoub and A. Morsali, *Z. Kristallogr. NCS* **216**, 601 (2001).
[12] A.R. Mahjoub and A. Morsali, *Polyhedron* **21**, 1223 (2002).
[13] G. Ferguson, C. Glidewell and E.S. Lavender, *Acta Crystallogr. Sect. B* **B55**, 591 (1999).
[14] G.M. Sheldrick, SHLXTL-97 V5.10, (Bruker AXS Inc., Madison, WI 53719, USA, 1997).