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Preliminary Communication

Main group metal halide complexes with sterically hindered thioureas

XV. The crystal and molecular structures of two unique monomeric bismuth(III) thiocyanate complexes with 1,3-dimethyl-2(3*H*)-imidazolethione

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Abstract

Two new bismuth(III) thiocyanate complexes with a sterically hindered thiourea, 1,3-dimethyl-2(3*H*)-imidazolethione (dmit), have been prepared and characterized via X-ray crystallography and IR spectroscopy. One complex, $[Bi(S)NCS(dmit)_3]\cdot 2H_2O$ (I), could not be obtained in analytically pure form, but an individual crystal reveals a slightly distorted octahedral structure with one of the water molecules occupying the position *trans* to the sulfido group. The other complex, $[Bi(SCN)(NCS)_2(dmit)_3]$ (II), was also a distorted octahedral with the dmit ligands in a meridional configuration. Two of the thiocyanates are N-bonded and the other is S-bonded. IR spectra show characteristic thiocyanate CN stretches correlating to the bonding mode for both complexes, and neither complex shows strong evidence of a stereoactive lone pair.

Keywords: Crystal structures; Bismuth complexes; Thiocyanate complexes; Thiourea complexes

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1. Introduction

Anhydrous bismuth(III) thiocyanate has long eluded researchers in being isolated as a stable substance. There have been many complexes of this compound generated with a variety of Lewis bases [1–5], but to date there have been only a few crystallographic studies reported in the literature that have the tris(thiocyanato)bismuth(III) moiety as part of the structure [3–5]. While attempting to generate complexes of Bi(III) thiocyanate and the sterically hindered thiourea, 1,3-dimethyl-2(3*H*)-imidazolethione (dmit), we synthesized two novel complexes employing methods already reported in the literature.

2. Results and discussion

A method reported by Baranyi et al. [2] failed to yield an analytically pure complex of bismuth(III) thiocyanate and dmit, but after several recrystallization attempts from hot CH_3CN, small well-formed reddish-orange crystals could be manually extracted from a microcrystalline powder mixture. An X-ray structure [1]

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[1] Crystallographic data for $C_{16}H_{28}N_7O_2S_5Bi$ (**I**). Cell parameters: space group $P2_1/n$, $a=15.046(3)$ Å, $b=11.905(3)$ Å, $c=15.590(5)$ Å, $\beta=94.91(2)°$, $Z=4$, $V=2782(1)$ Å^3, $D_c=1.717$ g/cm^3, $T=24$ °C, $\mu=6.78$ mm^{-1} (Mo K_α, $\lambda=0.71073$ Å), $R=0.058$, $R_w=0.061$. Intensity data were collected out to $2\theta=55°$ on a Syntex $P2_1$ diffractometer using the omega scan mode. A total of 6386 unique reflections were measured, and 2924 with $F_o>2.5\sigma(F_o)$ were used along with 275 parameters in the final least-squares cycle. A psi-zero correction was made for absorption. Solution and refinement of the structure were performed using standard methods and programs as previously described [18].

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revealed this compound to be a remarkable 1:3 thiobismuthyl isothiocyanate complex with dmit. The complex, tris[1,3-dimethyl-2(3*H*)-imidazolethione]sulfido-(thiocyanato-N)bismuth(III), $[Bi(S)NCS(dmit)_3]\cdot 2H_2O$ (I), is shown in Fig. 1. The molecular structure of I is essentially octahedral with the sulfido group occupying the position *trans* to the coordinated water molecule, and the ligands plus the N-bonded thiocyanate occupying the remaining sites. Another water molecule outside the coordination sphere is hydrogen bonded to the coordinated water molecule at a distance of 2.30(3) Å (O2–O1). The non-bonded coordination sphere contacts in I range from 3.56 Å (S4–N7) to 4.42 Å (S2–S3) and the angles from 81.9 to 101.3°. The structure is also unique in the sense that it shows a monomeric thiocyanate complex, probably due to the steric bulk of the ligands. The thiocyanato group is a well-known bidentate bridging ligand for both main group and transition metals [3–7]. Table 1 reports the bond distances and angles within the coordination sphere. While oxohalides and thiohalides of bismuth(III) are common, this is first evidence of the pseudohalide analog, and further investigation will attempt to isolate larger, stoichiometrically pure bulk samples.

The successful route to the tris-thiocyanato complex was achieved by using a method similar to the one reported by Bertazzi et al. [3]. The complex, *mer*-tris(1,3-dimethyl-2(3*H*)-imidazolethione)di(thiocyanato-N)(thiocyanato-S)bismuth(III) (II) was synthesized in about 40% yield using large molar excesses of NH_4SCN and dmit combined with $Bi(NO_3)_3\cdot 5H_2O$ in methanol. The reaction mixture was allowed to evaporate to dryness at room temperature (about 22 °C) over a period of several days. The residue was then brought up in water, and deep ruby-red, analytically pure crystals of II were filtered off and allowed to dry in a desiccator over anhydrous $CaSO_4$ (Drierite, m.p. 129–131 °C). A single-crystal X-ray structure[2] of II shows a unique monomeric structure with the thiourea ligands bonded in a meridional fashion (Fig. 2) similar

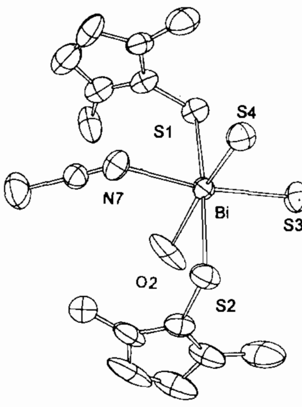

Fig. 1. ORTEP drawing of I with thermal ellipsoids drawn at the 50% probability level. Only the coordination sphere atoms are labeled.

Table 1
Coordination sphere distances (Å) and angles (°) for I with e.s.d.s in parentheses. Atomic designators are found in Fig. 1. Designators separated with '···' notation represent non-bonded distances

Bi–S1	2.807(5)	S1···S3	3.69(1)
Bi–S2	2.891(5)	S1···S4	4.16(1)
Bi–S3	2.819(6)	S1···N7	3.60(2)
Bi–S4	2.649(6)	S2···S3	4.42(1)
Bi–N7	2.456(18)	S2···S4	3.64(1)
Bi–O2	2.832(21)	S2···N7	3.82(2)
		S3···S4	4.00(1)
S1–Bi–S3	81.9(2)	S4···N7	3.56(2)
S1–Bi–S4	99.2(2)	S1···O2	4.02(3)
S1–Bi–N7	85.9(4)	S2···O2	3.99(2)
S1–Bi–O2	90.9(4)	S3···O2	3.91(2)
S2–Bi–S3	101.3(2)	N7···O2	3.81(3)
S2–Bi–N7	91.0(4)		
S2–Bi–S4	81.4(2)		
S2–Bi–O2	88.5(4)		
S3–Bi–S4	94.0(2)		
S3–Bi–O2	87.5(5)		
S4–Bi–N7	88.4(4)		
N7–Bi–O2	92.0(7)		
S1–Bi–S2	176.8(2)		
N7–Bi–O2	170.0(3)		
S3–Bi–N7	167.7(4)		

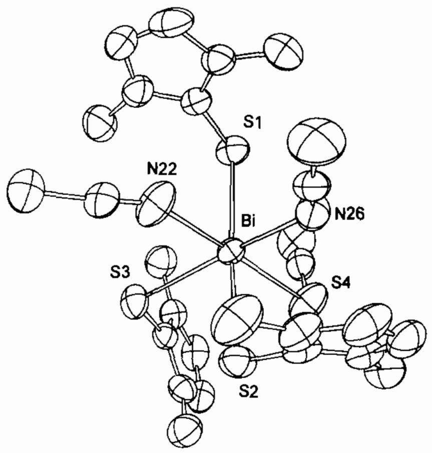

Fig. 2. ORTEP drawing of II with thermal ellipsoids drawn at the 50% probability level. Only the coordination sphere atoms are labeled.

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[2] Crystallographic data for $C_{18}H_{24}N_9S_6Bi$ (II). Cell parameters: space group $P1$, $a=11.150(3)$ Å, $b=8.557(2)$ Å, $c=16.456(4)$ Å, $\alpha=82.85(2)°$, $\beta=72.70(2)°$, $\gamma=73.32(2)°$, $Z=2$, $V=1435(1)$ Å^3, $D_c=1.777$ g/cm^3, $T=24$ °C, $\mu=6.57$ mm^{-1} (Mo K_α, $\lambda=0.71073$ Å), $R=0.049$, $R_w=0.045$. Intensity data were collected out to $2\theta=60°$ on a Syntex $P2_1$ diffractometer using the omega scan mode. A total of 8330 unique reflections were measured, and 4885 with $F_o>2.5\sigma(F_o)$ were used along with 307 parameters in the final least-squares cycle. A psi-zero correction was made for absorption. Solution and refinement of the structure were performed using standard methods and programs as previously described [18]. Elemental analysis gave satisfactory results.

to that observed by Battaglia et al. [8] for $BiBr_3(etu)_3$ (etu = ethylenethiourea). The thiocyanates are bonded with two different orientations, two N-bonded and one S-bonded. The N-bonded thiocyanates are *cis* to each other and *trans* to the S-bonded thiocyanate. The bond angles, distances and non-bonded distances (Table 2) indicate a structure of nearly octahedral site symmetry. Non-bonded distances in the coordination sphere of bismuth range from 3.36 Å (N22–N26) to 4.22 Å (S1–S3), and the internal L–Bi–L (L = ligand) angles range from 82.3 to 97.2° (Table 2).

There is no strong evidence for a stereoactive lone pair in the coordination sphere of either **I** or **II**. Lone pair stereoactivity in AX_6E complexes (A = central atom, X = ligand, E = lone pair) is quite obvious in cases where the coordination geometry leaves no alternative explanation – cases such as the C_{5v} site-symmetric pentagonal pyramidal structure observed for $Sb(oxalate)_3{}^{3-}$ [9] and for $Sb(diphenyldithiophosphinate)_3$ [10]. Even the oft-cited C_{3v} trigonally distorted octahedron has been interpreted as unequivocal evidence of lone pair stereoactivity by Lawton et al. [11] in examples like $Bi(dtp)_3$ (dtp = S,S′-diisopropylphosphorodithioate) or more recently by Crispini et al. [12] for $[Bi(SeCN)_6]^{3-}$. In the case of 'narrow-bite' ligands like thiocarbamates or dtp, Wynne [13] has proposed that observed distortions could be the result of the steric limitations of the ligand rather than genuine lone pair stereoactivity. The internal coordination sphere bond angles and non-bonded contacts for both **I** and **II** show no systematic distortion patterns like those mentioned above. What is observed, however, are relative bond lengthening (cf. **I**, Bi–S2) and angle opening (cf. **I**, S2–Bi–S3; **II**, S1–Bi–S3) with concomitant non-bonded contact expansions (cf. **I**, S2–S3; **II**, S1–S3). Similar perturbations in other analogous AX_6E Bi(III) halogen complexes have been interpreted as evidence of at least 'partial' lone pair stereoactivity [14]. By using In(III) analogs of Bi(III) complexes, Cea-Olivares et al. [15], in conjunction with some of our earlier work [16], have shown that minor deviations from octahedral site symmetry can also be the result of ligand–ligand repulsions, particularly in the case of sterically bulky ligands like tetraphenylimidodithiodiphosphinates. While this explanation may also apply to **I** and **II** given the bulky nature of dmit, in the absence of any supportive studies such as the structures of In(III) analogs of **I** and **II**, it would be highly speculative to attribute the observed minor distortions exclusively to either lone pair stereoactivity or steric restrictions of the ligands.

Table 2
Coordination sphere distances (Å) and angles (°) for **II** with e.s.d.s in parentheses. Atomic designators are found in Fig. 2. Designators separated with '···' notation represent non-bonded distances

Bi–S1	2.828(3)	S1···S3	4.22(1)
Bi–S2	2.807(3)	S1···S4	4.00(1)
Bi–S3	2.789(3)	S1···N22	3.71(2)
Bi–S4	2.870(4)	S1···N26	3.80(2)
Bi–N22	2.397(11)	S2···S3	3.79(1)
Bi–N26	2.416(11)	S2···S4	3.96(1)
		S2···N22	3.79(2)
S1–Bi–S3	97.2(1)	S2···N26	3.54(2)
S1–Bi–S4	88.7(1)	S3···S4	4.15(1)
S1–Bi–N22	90.1(3)	S3···N22	3.45(2)
S1–Bi–N26	92.4(3)	S4···N26	3.90(2)
S2–Bi–S3	85.7(1)	N22···N26	3.36(2)
S2–Bi–S4	89.1(1)		
S2–Bi–N22	92.3(3)		
S2–Bi–N26	85.1(3)		
S3–Bi–S4	94.5(1)		
S3–Bi–N22	82.3(3)		
S4–Bi–N26	94.9(3)		
N22–Bi–N26	88.6(4)		
S1–Bi–S2	176.4(1)		
S3–Bi–N26	166.7(3)		
S4–Bi–N22	176.4(3)		

The bond distances and angles associated with the thiocyanate groups in **I** and **II** compare quite favorably to those reported for the 2,2′-bipyridyl complex [3], and the dmit bond distance and angles are comparable to those noted in other complexes with this ligand [17].

The mid-range FT-IR spectrum[3] of **II** shows two peaks in the characteristic ν(CN) region for thiocyanates. A strong broad peak at 2006 cm^{-1} corresponds to the terminal N-bonded group similar to that observed for $[Bi(bipy)_2(CNS)_3]_2$ noted by Bertazzi et al. [3] (cf. 2015 cm^{-1}), while the terminally S-bonded group is assigned to a medium peak at 2095 cm^{-1}, within the range observed for other S-bonded complexes and characteristically higher than the N-bonded vibrations [7]. The peaks related to the carbon–sulfur modes appear to be obscured by dmit bands.

The relationship, if any, between **I** and **II** is still uncertain. It is possible that recrystallization attempts in hot solvents led to partial decomposition of **II** to give mixtures of **I** and **II**. Attempts to isolate analytically pure samples of **I** from reflux reactions involving **II** in various solvents have led to undefinable mixtures. The only evidence that supports this hypothesis comes from a few such attempts which did yield an orange solid exhibiting a strong IR peak at 2041 cm^{-1} with a shoulder around 2000 cm^{-1}. This falls into the characteristic N-bonded region [7], but the samples are still not analytically pure. Alternate synthetic routes are being explored.

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[3] IR data were collected as a powder from evaporation out of a CH_2Cl_2 slurry on a background-subtracted polyethylene film (3M 'IR card') using a Perkin-Elmer Model 1600 FT-IR instrument. Only the peaks of primary interest are reported. All values are in cm^{-1} (±4).

3. Supplementary material

Atomic coordinates, anisotropic thermal parameters and a full list of bond lengths and angles for both compounds are available from the Cambridge Crystallographic Data Center.

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References

[1] A. Rosenheim and W. Vogelsang, *Z. Anorg. Chem., 48* (1906) 205.

[2] A.D. Baranyi, J. Cook and M. Onyszchuk, *Inorg. Nucl. Chem. Lett., 13* (1977) 385.

[3] N. Bertazzi, G. Alonzo, L.P. Battaglia, A. Bonamartini Corradi and G. Pelosi, *J. Chem. Soc., Dalton Trans.*, (1990) 2403.

[4] W. Bensch, F.A. Reifler and H.R. Oswald, *Z. Kristallogr., 200* (1992) 157.

[5] W. Bensch, F.A. Reifler, A. Reller and H.R. Oswald, *Z. Kristallogr., 189* (1989) 169.

[6] E.S. Raper and W. Clegg, *Inorg. Chim. Acta, 180* (1991) 239.

[7] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 4th edn., 1986, p. 283.

[8] L.P. Battaglia, A. Bonamartini Corradi and G. Pelosi, *J. Crystallogr. Spectrosc. Res., 22* (1992) 225.

[9] M.D. Poore and D.R. Russell, *J. Chem. Soc., Chem. Commun.*, (1971) 18.

[10] M.J. Begley, D.B. Sowerby and I. Haiduc, *J. Chem. Soc., Chem. Commun.*, (1980) 64.

[11] S.L. Lawton, C.J. Fuhrmeister, R.G. Haas, C.S. Jarman, Jr. and F.G. Lohmeyer, *Inorg. Chem., 13* (1974) 135.

[12] A. Crispini, R.J. Errington, G.A. Fisher, F.J. Funke, N.C. Norman, A.G. Orpen, S.E. Stratford and O. Sturve, *J. Chem. Soc., Dalton Trans.*, (1994) 1327.

[13] K.J. Wynne, *J. Chem. Ed., 50* (1973) 328.

[14] W. Clegg, M.R.J. Elsegood, V. Graham, N.C. Norman, N.L. Pickett and K. Tavakkoli, *J. Chem. Soc., Dalton Trans.*, (1994) 1741.

[15] R. Cea-Olivares, R.A. Toscano, G. Carreon and J. Valdes-Martinez, *Monatsch. Chem., 123* (1992) 391.

[16] D.J. Williams, C.O. Quicksall and K.M. Barkigia, *Inorg. Chem., 21* (1982) 2097.

[17] D.J. Williams, P.H. Poor, G. Ramirez and B.L. Heyl, *Inorg. Chim. Acta, 147* (1988) 221.

[18] D.J. Williams, G. Ramirez and D. VanDerveer, *J. Crystallogr. Spectrosc. Res., 16* (1986) 309.