Bismuth(III) Thiocyanate Adducts with Tridentate Nitrogen Donors

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As part of our continuing interest in the complex formation between multidentate ligands and the Group V elements antimony and bismuth [1, 2], we have prepared a series of bismuth(III) 1:1 complexes with tridentate neutral nitrogen donors which formally contain the $Bi(CNS)_3$* unit. The required ligands 2,2′:6′,2″-terpyridine (terpy), 2,4,6-tris(2′-pyridyl)-1,3,5-triazine (tpta) and pyridine-2-aldehyde-2′-pyridylhydrazone (paphyH) were commercial products whereas 2,6-bis(2′-quinolyl)pyridine (dqp) was prepared according to the literature [3, 4].

The adducts $Bi(CNS)_3$terpy (**I**), $Bi(CNS)_3$tpta (**II**) and $Bi(CNS)_3$paphyH (**III**) were quantitatively obtained upon adding 2 mmol of the appropriate ligand dissolved in 4.5 M NH_4CNS methanolic solution to 2.2 mmol of bismuth nitrate dissolved in the same thiocyanate methanolic solution. In the case of $Bi(CNS)_3$dqp (**IV**), a complete reaction occurred when a stirred suspension of the ligand (0.3 mmol) was treated with the bismuth solution and the stirring continued for 2 h. The complexes were filtered, washed with methanol and dried under vacuum. The new adducts are yellow microcrystalline solids which are stable in air, insoluble in common polar and nonpolar organic solvents and do not show a sharp melting or decomposition point.

Elemental analysis were carried out in the Istituto di Chimica Farmaceutica, University of Cagliari. *Anal.* Found (calc.) for $C_{18}H_{11}N_6S_3Bi$ (**I**): C, 34.72-(35.06); H, 1.69(1.80); N, 13.69(13.63). Found (calc.) for $C_{21}H_{12}N_9S_3Bi$ (**II**): C, 36.08(36.26); H, 1.68(1.74); N, 18.17(18.12). Found (calc.) for $C_{14}H_{10}N_7S_3Bi$ (**III**): C, 28.98(28.92); H, 1.64(1.73); N, 16.77(16.86). Found (calc.) for $C_{26}H_{15}N_6S_3Bi$ (**IV**): C, 43.27(43.58); H, 1.97(2.11); N, 11.63-(11.73)%.

Infrared spectra (4000–180 cm^{-1}) were recorded as Nujol mulls between CsI plates; no reaction between samples and the CsI plates was observed. Relevant bands are reported in Table 1.

TABLE 1. Relevant IR Absorptions (cm^{-1}) for $Bi(CNS)_3L$

L				Assignments
terpy	tpta	dqp	paphyH	
			3180vw(br)	ν(NH)
2120w	2120w	2096ms	2112m	ν(CN)
2086ms	2086s	2080s	2086s	
2062s	2063s		2068s	
1987s	1970s			
1591m	1598vw	1588ms	1618m	heterocyclic ring stretching vibrations
1572mw	1571w	1564mw	1606ms	
	1546s	1510ms	1546m^a	
	1516m	1480s	1482m	
476w	490vw^b	453w	462w	δ(NCS)
463vw	465w	438w^b	438w	
428w^b				

^{a}Mainly ν(CN) aldiminic. ^{b}Uncertain assignment.

Results and Discussion

Bismuth(III) thiocyanate adducts with 1,10-phenanthroline (phen) [5, 6] and 2,2′-bipyridyne (bipy) [6] have been previously isolated, and present findings extend the chemistry of this class of compounds. The ligands considered in this work are known to behave normally as terdentate (see for example refs. 1–4 and refs. therein). Their coordination in **I**, **II** and **III** is inferred from the infrared shifts to higher wavenumber of the highest lying heterocyclic ring stretching with respect to those in the free ligand (terpy: 1282, 1561; tpta: 1583, 1569, 1522; paphyH: 1595, 1570, 1540 (ν(CN) aldiminic), 1470). In the case of **IV**, the band at 1595 cm^{-1} in the free ligand is found slightly shifted to lower frequency and the one at 1501 cm^{-1} noticeably split into two components, analogously to reported spectral data for a number of transition metal dqp complexes [4].

Information on the thiocyanate bonding mode must rely essentially on ν(CN) absorptions since bands of the ligands prevent any safe ν(CS) assignment and also introduce some uncertainty in the δ(NCS) range. We observe that a main distinction should be made between complexes **I** and **II**, on one side, and complexes **III** and **IV**, on the basis of the presence in the former group of the absorption occurring noticeably below 2000 cm^{-1}. Such low ν(CN) frequencies are not usually encountered in spectra of thiocyanate derivatives and indicate a considerable decrease in the electron density at the C–N bond. An extension of accepted empirical criteria for deciding on the thiocyanate bonding mode [7] would

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*In formulae, the thiocyanate group is written CNS to indicate ionic, as well as unspecified or unknown mode of bonding.

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interpret such low frequency modes as being caused by particularly strong metal–NCS interactions or by thiocyanate groups bridging solely through the nitrogen atom (1,1-μ-N). The latter hypothesis was first proposed in the case of some organotin(IV) thiocyanate derivatives [8]. The remaining ν(CN) components in **I** and **II** appear rather sharp and well formed and their frequency points mainly to S-bonding; however, the absorption at about 2060 cm^{-1} could arise from N-bonding, while high energy bands do not exclude 1,3-μ bridging groups [7]. The ν(CN) absorptions observed with **III** and **IV** appear similar to the high frequency ones of the former adducts and, analogously, they are in accord with the presence of S-bonded as well as 1,3-μ bridging groups. For these compounds, terminal N-bonded thiocyanates are excluded also on the basis of assigned δ(NCS) bands.

Worthy of note are the ν(CN) patterns reported forBi(NCS)$_3$(phen) (2100m(sh), 2080s and 1970s cm^{-1}) and Bi(NCS)$_3$(bipy) (2120s, 2085s and 2070s cm^{-1}, the low energy band being missing in this latter [6] which appear to correlate with present findings.

Thus, in this class of bismuth thiocyanate adducts, in spite of the same simple stoichiometry and the similarity in the chelating ligand, the variable nature of the bismuth–thiocyanate interaction is apparent. The observation that differently bonded thiocyanate groups can be present in the same compound renders conceivable quite a number of structural arrangements and it seems that an exhaustive comprehension of this structural aspect could derive mainly from X-ray studies. The extremely low solubility shown by compounds prepared in this work would exclude molecular or simple cation–anion formulations as proposed for Group V trihalides terpy adducts [2, 9]. IR data in all cases do not exclude bridging thiocyanate groups (although of different nature) and, in this respect, the formation of polynuclear bismuth–thiocyanato anionic species should be considered.

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