Synthesis, Characterization, and Crystal Structures of Bismuth Complexes with 2,6-Diacetylpyridine Bis(2-thenoylhydrazone) (H_2dapt): [Bi(Hdapt)Cl_2]·dmso·H_2O and [Bi(dapt)Cl]·dmso, containing a Quinquedentate Ligand†

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Some new bismuth complexes with 2,6-diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) have been prepared by treating the hydrazone with bismuth chloride. The chelating behaviour of the ligand has been investigated by means of i.r. spectroscopy and also by *X*-ray analysis which showed in [Bi(Hdapt)Cl_2] a seven-co-ordinated pentagonal-bipyramidal geometry, and in [Bi(dapt)Cl] a six-co-ordinated pentagonal pyramidal environment, in which the hydrazone occupies the basal plane.

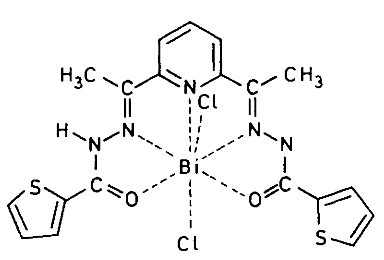
During a systematic investigation on bismuth complexes with uni- or bi-dentate N,S-containing ligands[1] we were interested in the synthesis and structural characterization of complexes containing hard-donor hydrazonic polydentate ligands. The structural properties of bismuth complexes with uni- or bi-dentate ligands have been studied, but there are very few investigations on compounds with terdentate ligands[2,3] and, as far as we know, there are no structural works concerning polydentate ones. In previous works these ligands showed a common tendency to occupy the basal plane of a pentagonal bipyramid forming four chelate rings, the geometry of the co-ordination polyhedron being determined mainly by the chelating power of the ligand rather than the properties of the metal ions. In the present complexes [Bi(Hdapt)Cl_2] (**1**) and [Bi(dapt)Cl] (**2**) [H_2dapt = 2,6-diacetylpyridine bis(2-thenoylhydrazone)] we find pentagonal bipyramidal and pyramidal co-ordination, the first being usually found for these hydrazonic complexes, the latter being unexpected based on the behaviour previously observed for the ligand.

Experimental

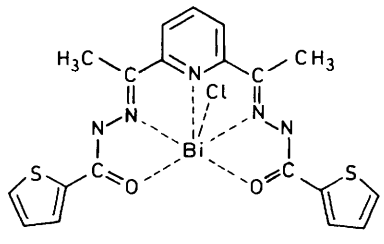
Bismuth(III) chloride, 2,6-diacetylpyridine, and thiophene-2-carbohydrazide were commercially available and used without further purification.

Preparations.—2,6-Diacetylpyridine bis(2-thenoylhydrazone) (H_2dapt) was obtained as previously described.[4]

[Bi(Hdapt)Cl_2]·dmso·H_2O (**1**). Bismuth(III) chloride (0.6 g, 2 mmol) dissolved in anhydrous acetone (2 cm^3) was added to an acetone suspension of H_2dapt (0.8 g in 5 cm^3). The reaction mixture was stirred at room temperature for about 30 min and then pyridine (*ca.* 3 cm^3) was added. The colour changed from yellow to orange. After filtration, the orange solution was taken to dryness under reduced pressure and the resulting solid dissolved in dimethyl sulphoxide (dmso) and recrystallized over a few days as red prismatic crystals (yield ≈ 80%).



(**1**)



(**2**)

[Bi(dapt)Cl]·dmso (**2**). An excess of sodium formate (1 g) was added to a pyridine solution (10 mmol) of [Bi(Hdapt)Cl_2]·dmso·H_2O (0.2 g in 50 cm^3). The solution was stirred for *ca.* 30 min and then filtered and slowly evaporated until orange prismatic crystals were isolated (yield ≈ 80%).

Exchange reactions. The synthesis of all complexes was performed according to the following general procedure. Complex (**1**) was dissolved in dmso at room temperature and a solution of the sodium salt (NaX, X = Br, I, NCS, or N_3) (1:2 molar ratio) in the same solvent was then added. After some days, by slow evaporation of the solvent, yellow-orange microcrystalline products separated out. Experimental chemical analyses (Table 1) are in agreement with the formulae [Bi(Hdapt)X_2]·dmso·H_2O (X = Br, I, or NCS) and [Bi(dapt)(N_3)]·dmso.

Measurements.—Elemental C, H, N, and S analyses were carried out on Perkin-Elmer model 240 automatic equipment. Infrared spectra (4 000—200 cm^{-1}) for KBr pellets were recorded on a Perkin-Elmer model 283B spectrophotometer.

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† Dichloro[2,6-diacetylpyridine bis(2-thenoylhydrazonato)(1 −)-*NN'N''OO'*]bismuth–dimethyl sulphoxide–water(1/1/1) and chloro-[2,6-diacetylpyridine bis(2-thenoylhydrazonato)(2 −)-*NN'N''OO'*]bismuth–dimethyl sulphoxide(1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical data*

Compound	Analysis/% C	H	N	S
H_2dapt	38.9	2.9	16.5	10.3
	(39.0)	(3.0)	(16.5)	(10.5)
[Bi(Hdapt)Cl_2]·dmso·H_2O	31.8	3.1	8.7	12.2
	(31.9)	(3.2)	(8.9)	(12.2)
[Bi(Hdapt)Br_2]·dmso·H_2O	29.0	2.5	8.1	11.2
	(28.7)	(2.8)	(7.9)	(10.9)
[Bi(Hdapt)I_2]·dmso·H_2O	25.6	2.4	9.8	7.1
	(25.9)	(2.6)	(9.9)	(7.2)
[Bi(Hdapt)$(SCN)_2$]·dmso·H_2O	33.9	2.8	12.0	19.6
	(33.1)	(3.0)	(11.8)	(19.2)
[Bi(dapt)Cl]·dmso	34.2	3.0	9.3	13.9
	(34.4)	(3.3)	(10.0)	(13.8)
[Bi(dapt)(N_3)]·dmso	32.2	1.6	19.6	12.3
	(32.0)	(2.3)	(19.2)	(12.9)

* Calculated values in parentheses.

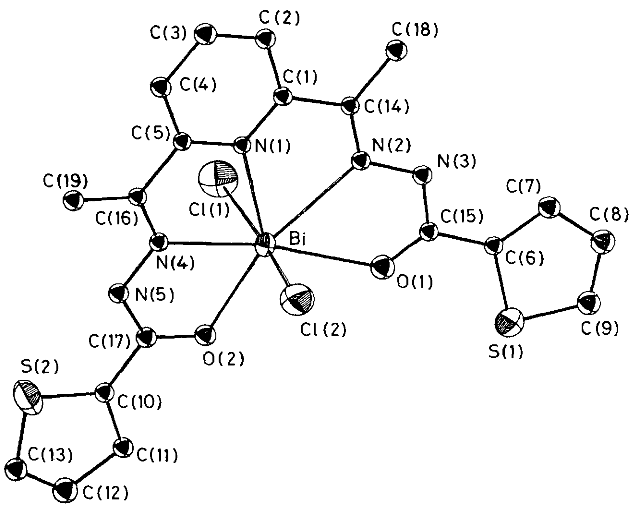

Figure 1. ORTEP drawing of complex (**1**)

Table 2. Experimental data for the crystallographic analyses*

	(**1**)	(**2**)
Formula	$C_{21}H_{24}BiCl_2N_5O_4S_3$	$C_{21}H_{21}BiClN_5O_3S_3$
M	786.52	731.67
Space group	$P\bar{1}$	$P2_1/n$
a/Å	10.479(3)	8.304(4)
b/Å	15.193(3)	20.583(8)
c/Å	10.369(3)	15.316(8)
α/°	100.50(2)	90
β/°	116.83(2)	104.33(5)
γ/°	73.23(3)	90
U/Å^3	1 407.8(7)	2 536(2)
Z	2	4
D_c/g cm^{-3}	1.85	1.92
D_m/g cm^{-3}	1.91	1.90
Reflections for lattice parameters: number	15	14
Reflections for lattice parameters: θ range	18—22	15—19
F(000)	764	1 416
Crystal size/mm	0.23 × 0.36 × 0.68	0.16 × 0.33 × 0.39
μ/cm^{-1}	66.82	73.05
Scan speed/° min^{-1}	4.8	3.6
Scan width/°	1.40	1.80
θ range/°	3—24	3—23
h range	±10	−9 to 8
k range	±17	0—22
l range	0—11	0—16
Standard reflection	−2 4 2	0 10 0
Scan mode	ω—2θ	ω—2θ
No. of reflections measured	4 433	3 776
No of reflections used in the refinement [$I > 3\sigma(I)$]	3 410	2 029
No. of refined parameters	157	162
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0604	0.0606
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0635	0.0578
k,g in $w = k[\sigma^2(F_o) + gF_o^2]^{-1})$	1, 2.6 × 10^{-3}	1.0, 1.27 × 10^{-3}
Max., min. height in final ΔF map, ρ/e Å^{-3}	0.98, −1.14	0.42, −0.41

* Details common to both complexes: temperature 293 K; diffractometer Philips PW 1100; maximum intensity variation 3.5, radiation Mo$-K_\alpha$ λ = 0.7093 Å.

Data Collection, Solution and Refinement of the Structures.—Crystal data, obtained from diffractometry, and details associated with the data collection are given in Table 2. After the usual Lorentz and polarization reduction of the data an empirical absorption correction was applied.[5] The structures were solved by the heavy-atom method and refined by full-matrix least-squares cycles with anisotropic thermal parameters for Bi, S, and Cl atoms and isotropic for the others; hydrogen atoms were not located. 42 Reflections for complex (**1**) and 51 for (**2**) were excluded from the final refinements as probably affected by extinction or counting errors. The final atom co-ordinates are reported in Tables 3 and 4 for (**1**) and (**2**) respectively, the dmso atoms are indicated as S(D), O (D) and C (D), for both compounds, the atomic scattering factors used, corrected for anomalous dispersion, were taken from ref. 6. All the calculations were performed on a GOULD 32/77 computer using the SHELX 76,[7] ORTEP,[8] and PARST[9] programs.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Infrared Spectra.—The main vibrational bands of H_2dapt and the bismuth(III) complexes are listed in Table 5 together with the relative assignments.

A similar spectroscopic pattern is observed for the complexes of general formula [Bi(Hdapt)X_2] (X = Cl, Br, I, or SCN): the amide I [ν(CO)] and amide II [δ(NH) + ν(CN)] bands undergo negative ($\Delta\nu$ 30 cm^{-1}) and positive ($\Delta\nu$ *ca.* 10 cm^{-1}) shifts respectively. Such shifts of ν(CO) and ν(CN) bands toward lower frequencies on complexation indicate that both carbonyl oxygens and azomethine nitrogens co-ordinate to the metal.[10-12] A negative shift is also observed for the ν(CN) band in the azomethine group upon co-ordination.

It is worthy of note that two intense absorptions are present in the spectrum of [Bi(Hdapt)$(SCN)_2$] which are indicative of thiocyanate and isothiocyanate groups.[12]

The disappearance of the ν(NH) bands as a consequence of the deprotonation of the ligand is clear in the spectrum of [Bi(dapt)Cl] and [Bi(dapt)(N_3)]. For both these compounds the amide I band undergoes a high negative shift and a decrease in intensity.

Description of the Structures.—A perspective view of the [Bi(Hdapt)Cl_2] molecule with the numbering scheme is

Table 3. Atomic co-ordinates (× 10^4) for [Bi(Hdapt)Cl$_2$]·dmso·H$_2$O (**1**), with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Bi	2 586(1)	2 498(0)	2 660(1)	C(5)	6 324(14)	1 791(10)	4 006(14)
S(1)	−1 355(5)	111(3)	1 345(5)	C(6)	−1 238(15)	1 218(10)	1 467(15)
S(2)	1 050(4)	6 209(3)	1 432(4)	C(7)	−2 639(15)	1 887(10)	1 067(15)
S(D)	7 307(7)	4 713(4)	1 406(6)	C(8)	−3 733(19)	1 341(13)	724(19)
Cl(1)	2 375(4)	2 082(3)	−23(4)	C(9)	−3 208(17)	460(12)	826(17)
Cl(2)	3 073(5)	2 635(3)	5 443(5)	C(10)	2 861(14)	5 600(10)	2 314(14)
O(1)	245(11)	2 277(7)	1 951(10)	C(11)	3 851(17)	6 165(11)	2 690(17)
O(2)	2 098(13)	4 320(8)	2 430(12)	C(12)	3 097(19)	7 067(13)	2 213(18)
O(3)	9 085(17)	−1 941(11)	3 668(17)	C(13)	1 614(18)	7 190(12)	1 542(18)
N(1)	5 099(11)	1 500(7)	3 507(11)	C(14)	3 795(14)	289(10)	2 938(14)
N(2)	2 614(12)	941(8)	2 633(12)	C(15)	173(16)	1 433(11)	1 893(15)
N(3)	1 311(12)	708(8)	2 203(12)	C(16)	6 148(14)	2 801(10)	3 894(14)
N(4)	4 812(12)	3 268(8)	3 309(12)	C(17)	3 105(15)	4 658(10)	2 596(14)
N(5)	4 546(12)	4 182(8)	3 072(12)	C(18)	3 765(15)	−710(10)	2 725(15)
C(1)	5 192(14)	593(10)	3 480(14)	C(19)	7 522(16)	3 159(11)	4 472(16)
C(2)	6 540(15)	−67(11)	3 961(15)	O(D)	6 301(15)	4 556(10)	1 959(15)
C(3)	7 851(17)	284(11)	4 561(16)	C(1D)	6 734(24)	5 939(16)	1 099(24)
C(4)	7 717(15)	1 222(10)	4 611(15)	C(2D)	9 014(32)	4 762(21)	2 955(32)

Table 4. Fractional atomic co-ordinates (× 10^4) for [Bi(dapt)Cl]·dmso, (**2**), with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Bi	321(1)	965(0)	1 322(1)	C(7)	−71(26)	824(10)	4 742(15)
Cl	2 908(9)	1 609(4)	1 758(5)	C(8)	−733(35)	885(15)	5 548(21)
S(1)	−2 174(10)	1 779(4)	4 458(5)	C(9)	−1 916(38)	1 389(15)	5 469(22)
S(2)	4 010(8)	−860(3)	−502(5)	C(10)	3 436(27)	−654(11)	488(16)
O(1)	401(19)	922(8)	2 947(11)	C(11)	4 058(24)	−1 110(9)	1 189(14)
O(2)	2 256(19)	80(8)	1 304(11)	C(12)	4 953(26)	−1 616(10)	846(15)
N(1)	−562(20)	1 846(8)	214(12)	C(13)	5 013(30)	−1 571(12)	−10(18)
N(2)	−926(21)	1 914(8)	1 899(12)	C(14)	−1 573(32)	2 386(13)	1 408(19)
N(3)	−1 166(24)	1 873(9)	2 761(14)	C(15)	−435(24)	1 365(10)	3 199(14)
N(4)	1 077(20)	791(7)	−132(12)	C(16)	506(29)	1 173(11)	−802(17)
N(5)	1 849(21)	234(8)	−246(12)	C(17)	2 440(25)	−75(10)	543(14)
C(1)	−1 274(24)	2 358(10)	462(14)	C(18)	−2 606(32)	2 903(14)	1 672(19)
C(2)	−1 805(26)	2 872(11)	−145(15)	C(19)	590(33)	1 034(14)	−1 750(19)
C(3)	−1 537(34)	2 842(14)	−1 031(20)	S(D)	−4 236(18)	−154(7)	3 758(9)
C(4)	−911(31)	2 266(12)	−1 286(18)	C(1D)	−3 758(42)	140(16)	2 732(24)
C(5)	−347(25)	1 781(10)	−635(15)	C(2D)	−6 025(45)	319(17)	3 714(25)
C(6)	−764(27)	1 276(11)	4 109(16)	O(D)	−4 617(54)	−767(24)	3 658(31)

Table 5. Selected vibrational bands (cm^{-1})

H$_2$dapt	[Bi(Hdapt)Cl$_2$]	[Bi(Hdapt)Br$_2$]	[Bi(Hdapt)I$_2$]	[Bi(Hdapt)-(SCN)$_2$]	[Bi(dapt)Cl]	[Bi(dapt)(N$_3$)]	Assignment
3 160m	3 160w			3 160w			ν(NH)
3 050m	3 050vw	3 050vw	3 050vw	3 080vw	3 050w	3 060vw	ν(CH)$_{\text{aryl}}$
2 920vw	2 900vw	2 900vw	2 900vw	2 920w	2 900vw	2 900w	ν(CH)$_{\text{alkyl}}$
1 640vs	1 620s	1 630m	1 630m	1 620s			ν(CO)
1 565m 1 520w	1 520 (sh)	1 610ms	1 610ms	1 600 (sh)	1 590w	1 590w	Ring
1 510m	1 510s	1 520vs	1 520vs	1 520vs	1 515ms	1 515ms	δ(NH), ν(CN)
1 415ms	1 415m	1 395s	1 395s	1 390vs	1 390m	1 390m	δ(CH)
1 385ms	1 385m	1 370vs	1 370vs	1 370vs	1 360vs	1 360vs	δ(CH)

depicted in Figure 1: the bismuth atom is seven-co-ordinated with the ligand occupying five equatorial positions and two chlorines at the apical sites of a distorted pentagonal bipyramid. The girdle of atoms around the metal is moderately puckered, but the five donor atoms are almost coplanar; bismuth is out of this plane by only −0.0132(8) Å. From the bond lengths of Bi–O 2.70(1), 2.33(1) Å and Bi–N 2.67(1), 2.47(1), and 2.35(1) Å (Table 6) it is seen that the ligand is asymmetrically bonded and this co-ordination type has also been found in some nickel complexes.[13–15] The two Bi–O bond distances, although very different, fall in the expected range, and the longest Bi–N bond distance [2.67(1) Å] agrees with the values 2.56(1)—2.61(1) Å found in [Bi(S$_2$CNEt$_2$)I$_2$L][2] (L = 2,2′-bipyridine or 2,2′:6′,2″-terpyridine) or in [BiCl$_5$(py)]$^{2-}$ (py = pyridine) [2.615(8) Å],[16] [Bi(S$_2$CNEt$_2$)X$_2$(py)$_3$] [2.668(7)—2.794(8) Å],[17] and in bismuth dithizonate[18] [dithizone = PhNNC(S)NHNCPh] [2.678(9)—2.746(10) Å]; the two remaining values are shorter than the above literature values.

On the whole the behaviour of the ligand indicates an increase in the chelation power from O(2) to O(1) with the

Table 6. Bond distances (Å) and angles (°) in complex (**1**)

(*a*) Co-ordination polyhedron

Bi–Cl(1)	2.660(5)	Bi–N(1)	2.47(1)	O(1)–Bi–N(2)	67.8(4)	O(1)–Bi–N(4)	162.9(4)
Bi–Cl(2)	2.673(5)	Bi–N(2)	2.35(1)	N(2)–Bi–N(1)	67.5(4)	N(2)–Bi–N(4)	129.3(4)
Bi–O(1)	2.33(1)	Bi–N(4)	2.67(1)	N(1)–Bi–N(4)	62.0(4)	N(2)–Bi–O(2)	171.0(4)
Bi–O(2)	2.70(1)			N(4)–Bi–O(2)	59.2(4)	N(1)–Bi–O(1)	135.2(4)
				N(1)–Bi–O(2)	121.2(4)	O(1)–Bi–O(2)	103.7(4)

Cl(1)–Bi–O(1)	91.3(3)	Cl(2)–Bi–O(1)	90.6(3)	Bi–O(1)–C(15)	116(1)	Bi–N(1)–C(5)	125(1)
Cl(1)–Bi–N(2)	85.0(3)	Cl(2)–Bi–N(2)	87.2(3)	Bi–N(2)–N(3)	119(1)	Bi–N(4)–N(5)	121(1)
Cl(1)–Bi–N(1)	87.6(3)	Cl(2)–Bi–N(1)	84.5(3)	Bi–N(2)–C(14)	123(1)	Bi–N(4)–C(16)	120(1)
Cl(1)–Bi–N(4)	89.7(3)	Cl(2)–Bi–N(4)	91.2(3)	Bi–N(1)–C(1)	116(1)	Bi–O(2)–C(17)	121(1)
Cl(1)–Bi–O(2)	92.8(3)	Cl(2)–Bi–O(2)	95.7(3)				
Cl(1)–Bi–Cl(2)	170.6(2)						

(*b*) Ligand molecule

S(2)–C(10)	1.74(1)	S(1)–C(6)	1.70(2)	N(4)–C(16)	1.28(2)	N(2)–C(14)	1.29(2)
S(2)–C(13)	1.72(2)	S(1)–C(9)	1.71(2)	C(16)–C(19)	1.51(2)	C(14)–C(18)	1.50(2)
C(13)–C(12)	1.36(2)	C(9)–C(8)	1.30(2)	C(16)–C(5)	1.51(2)	C(14)–C(1)	1.49(2)
C(12)–C(11)	1.42(2)	C(8)–C(7)	1.48(3)	C(17)–N(5)	1.37(2)	C(15)–N(3)	1.33(2)
C(11)–C(10)	1.41(3)	C(7)–C(6)	1.45(2)	C(5)–N(1)	1.33(2)	C(1)–N(1)	1.35(2)
C(10)–C(17)	1.44(2)	C(6)–C(15)	1.46(2)	C(5)–C(4)	1.38(2)	C(1)–C(2)	1.41(2)
C(17)–O(2)	1.23(2)	C(15)–O(1)	1.30(2)	C(4)–C(3)	1.39(2)	C(2)–C(3)	1.45(2)
N(5)–N(4)	1.38(2)	N(3)–N(2)	1.36(2)				

C(10)–S(2)–C(13)	91(1)	C(6)–S(1)–C(9)	91(1)	C(17)–N(5)–N(4)	115(1)	C(15)–N(3)–N(2)	113(1)
S(2)–C(13)–C(12)	113(1)	S(1)–C(9)–C(8)	114(2)	N(5)–N(4)–C(16)	119(1)	N(3)–N(2)–C(14)	118(1)
C(13)–C(12)–C(11)	114(2)	C(9)–C(8)–C(7)	115(2)	N(2)–C(14)–C(18)	122(1)	N(4)–C(16)–C(19)	127(1)
C(12)–C(11)–C(10)	111(2)	C(8)–C(7)–C(6)	105(1)	N(4)–C(16)–C(5)	115(1)	N(2)–C(14)–C(1)	116(1)
C(11)–C(10)–S(2)	111(1)	C(7)–C(6)–S(1)	114(1)	C(19)–C(16)–C(5)	118(1)	C(18)–C(14)–C(1)	122(1)
C(17)–C(10)–S(2)	118(1)	C(15)–C(6)–S(1)	121(1)	C(16)–C(5)–N(1)	117(1)	C(14)–C(1)–N(1)	118(1)
C(17)–C(10)–C(11)	131(2)	C(15)–C(6)–C(7)	125(2)	C(16)–C(5)–C(4)	120(1)	C(14)–C(1)–C(2)	119(1)
C(10)–C(17)–O(2)	122(2)	C(6)–C(15)–O(1)	120(1)	C(1)–C(2)–C(3)	116(1)	C(2)–C(3)–C(4)	119(2)
N(5)–C(17)–O(2)	124(1)	N(3)–C(15)–O(1)	125(2)	C(3)–C(4)–C(5)	119(1)	C(4)–C(5)–N(1)	123(1)
C(10)–C(17)–N(5)	114(1)	C(6)–C(15)–N(3)	115(1)	C(5)–N(1)–C(1)	119(1)	N(1)–C(1)–C(2)	123(1)

Table 7. Bond distances (Å) and angles (°) in complex (**2**)

(*a*) Co-ordination polyhedron

Bi–Cl	2.472(7)	Bi–N(1)	2.47(2)	Bi–O(2)	2.43(2)	Bi–N(4)	2.48(2)
Bi–O(1)	2.47(2)	Bi–N(2)	2.47(2)				

O(1)–Bi–N(2)	65.1(6)	O(1)–Bi–N(1)	130.3(6)	Cl–Bi–O(1)	86.7(4)	Bi–O(1)–C(15)	114(1)
N(2)–Bi–N(1)	65.6(6)	O(1)–Bi–N(4)	161.1(5)	Cl–Bi–N(2)	83.8(4)	Bi–N(2)–N(3)	118(1)
N(1)–Bi–N(4)	65.6(6)	N(2)–Bi–O(2)	158.6(6)	Cl–Bi–N(1)	83.2(4)	Bi–N(2)–C(14)	123(2)
N(4)–Bi–O(2)	64.4(5)	N(1)–Bi–O(2)	128.8(6)	Cl–Bi–N(4)	85.6(4)	Bi–N(1)–C(1)	118(1)
O(1)–Bi–O(2)	97.6(5)	N(2)–Bi–N(4)	130.9(5)	Cl–Bi–O(2)	82.6(4)	Bi–N(1)–C(5)	120(1)
N(1)–Bi–O(1)	130.3(3)			Bi–N(4)–N(5)	118(1)	Bi–N(4)–C(16)	120(1)
				Bi–O(2)–C(17)	116(1)		

(*b*) Ligand molecule

S(1)–C(6)	1.74(2)	S(2)–C(10)	1.75(3)	N(3)–N(2)	1.38(3)	N(5)–N(4)	1.34(2)
S(1)–C(9)	1.71(3)	S(2)–C(13)	1.76(2)	N(2)–C(14)	1.26(3)	N(4)–C(16)	1.29(3)
C(9)–C(8)	1.41(4)	C(13)–C(12)	1.33(4)	C(14)–C(18)	1.49(4)	C(16)–C(19)	1.50(4)
C(8)–C(7)	1.47(4)	C(12)–C(11)	1.45(3)	C(14)–C(1)	1.53(4)	C(16)–C(5)	1.49(3)
C(7)–C(6)	1.36(3)	C(11)–C(10)	1.42(3)	C(1)–N(1)	1.31(3)	C(5)–N(1)	1.36(3)
C(6)–C(15)	1.50(3)	C(10)–C(17)	1.46(3)	C(1)–C(2)	1.40(3)	C(5)–C(4)	1.40(3)
C(15)–O(1)	1.26(3)	C(17)–O(2)	1.25(3)	C(2)–C(3)	1.43(4)	C(4)–C(3)	1.39(4)
C(15)–N(3)	1.31(3)	C(17)–N(5)	1.34(3)				

C(6)–S(1)–C(9)	93(1)	C(10)–S(2)–C(13)	92(1)	C(15)–N(3)–N(2)	112(2)	C(17)–N(5)–N(4)	111(2)
S(1)–C(9)–C(8)	110(2)	S(2)–C(13)–C(12)	111(2)	N(3)–N(2)–C(14)	118(2)	N(5)–N(4)–C(16)	121(2)
C(9)–C(8)–C(7)	113(2)	C(13)–C(12)–C(11)	117(2)	N(2)–C(14)–C(18)	125(2)	N(4)–C(16)–C(19)	124(2)
C(8)–C(7)–C(6)	111(2)	C(12)–C(11)–C(10)	109(2)	N(2)–C(14)–C(1)	113(2)	N(4)–C(16)–C(5)	118(2)
C(7)–C(6)–S(1)	113(2)	C(11)–C(10)–S(2)	112(2)	C(18)–C(14)–C(1)	122(2)	C(19)–C(16)–C(5)	118(2)
C(15)–C(6)–C(7)	127(2)	C(17)–C(10)–S(2)	122(2)	C(14)–C(1)–N(1)	120(2)	C(16)–C(5)–N(1)	115(2)
C(15)–C(6)–S(1)	120(2)	C(17)–C(10)–C(11)	127(2)	C(14)–C(1)–C(2)	120(2)	C(16)–C(5)–C(4)	124(2)
C(6)–C(15)–O(1)	116(2)	C(10)–C(17)–O(2)	117(2)	C(1)–C(2)–C(3)	120(2)	C(2)–C(3)–C(4)	117(2)
N(3)–C(15)–O(1)	130(2)	N(5)–C(17)–O(2)	128(2)	C(3)–C(4)–C(5)	119(2)	C(4)–C(5)–N(1)	120(2)
C(6)–C(15)–N(3)	114(2)	C(10)–C(17)–N(5)	115(2)	C(5)–N(1)–C(1)	122(2)		

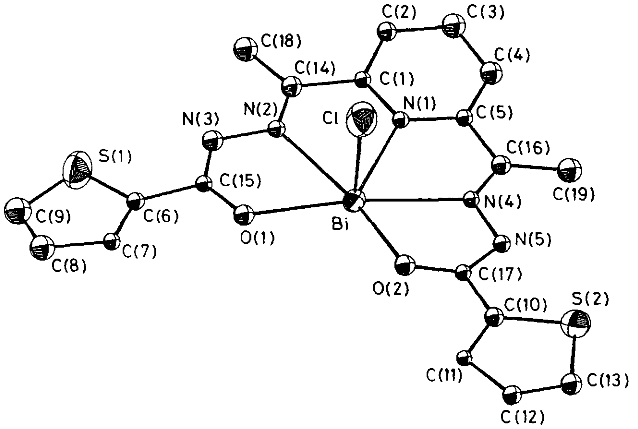

Figure 2. ORTEP drawing of complex (**2**)

maximum in the O(1)–N(2) ring. The two Bi–Cl bond distances are very similar and in the range commonly found,[16,19] the Cl(1)–Bi–Cl(2) angle [170.6(2)°] shows an appreciable displacement from linearity.

Bond distances and angles in the ligand are normal and similar to those found in these systems, the differences being insignificant in view of the relevant estimated standard deviations (e.s.d.s). The trend of these values in the string of atoms from O(1) to N(2), the strongest bonds these atoms form with bismuth, and the presence in the final ΔE map of a peak which can be considered to be due to the hydrogen bonded to the N(5) atom, support the hypothesis that the charge of the monodeprotonated ligand is mainly localized in the O(1)–N(2) region. Monodeprotonation is rather uncommon for these ligands which usually behave as neutral or doubly deprotonated and this fact could also explain the strong asymmetry in the metal chelation.

A perspective view of the [Bi(dapt)Cl] complex with the numbering scheme is shown in Figure 2. The co-ordination around bismuth is pentagonal pyramidal: the apex is occupied by a chlorine and the base by the nitrogen and oxygen atoms from the ligand which is doubly deprotonated and symmetrically chelated.

Pentagonal bipyramidal or pyramidal co-ordination polyhedra are not completely unexpected for bismuth in complexes with polydentate ligands but pyramidal had not previously been found for hydrazone-containing compounds. The bismuth–oxygen distances, 2.43(2) and 2.47(2) Å (Table 7), are intermediate in comparison to the values of 2.70(1) and 2.33(1) Å found in (**1**); the bismuth–nitrogen bonds 2.47(2), 2.47(2), and 2.48(2) Å are practically equal to the Bi–N(pyridine) bond length [2.47(1) Å] in (**1**) so that for these short bonds similar considerations can be applied. The behaviour of the ligand seems to be mainly influenced by the possibility of mono or double deprotonation to form highly stable five-membered chelated rings. The Bi–Cl apical distance [2.472(7) Å] is shorter than the values found in (**1**) and also in bismuth chloro complexes[20] and compares well with the 2.468(4)—2.518(7) Å present in $BiCl_3$ itself.[21] Also in this complex the pentagonal girdle of atoms is not exactly planar, while the five donor atoms are almost planar and bismuth lies 0.237(2) Å below this plane; accordingly the Cl–Bi–X (X = donor atom) angles range from 82.6(4) to 86.7(4)°. Bond distances and angles in the two arms of the ligand are not significantly different and show good agreement with the literature values,[22–24] the high values of their e.s.d.s preventing any comparison.

The packing in complex (**1**) is determined by van der Waals contacts and by the hydrogen bond between N(5) and dmso oxygen [N(5)–H1N 0.98 Å, N(5) $\cdots$ O 2.79(3) Å, H1N $\cdots$ O 1.83 Å, N(5)–H1N $\cdots$ O 169.9°], and in (**2**) by van der Waals contacts and by two long interactions between bismuth and S(2^{I}) [3.511(7) Å] and N(5^{I}) [3.25(2) Å (I $\bar{x}, \bar{y}, \bar{z}$)] in the direction opposite to the Bi–Cl bond forming weakly bonded dimers.

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