

## Crystal Structure of Indium(III) Dithizonate \*

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The crystal structure of indium(III) dithizonate,  $[\text{In}(\text{Hdz})_3]$ , has been determined by single-crystal X-ray diffraction methods at 295(1) K, and refined by least squares to a conventional residual of 0.043 for 3 081 'observed' reflections. Crystals are triclinic, space group  $P\bar{1}$ , with  $a = 18.469(6)$ ,  $b = 14.928(7)$ ,  $c = 7.570(4)$  Å,  $\alpha = 80.31(4)$ ,  $\beta = 86.58(4)$ ,  $\gamma = 75.48(4)$ °, and  $Z = 2$ . The asymmetric unit of the structure is the mononuclear  $[\text{In}(\text{Hdz})_3]$  molecule; the indium atom is trigonally bipyramidal, five co-ordinated, one ligand being unidentate and co-ordinated equatorially through the sulphur [ $\text{In}-\text{S}$  2.468(3) Å], while the other two are bidentate ( $\text{N}, \text{S}$ ), spanning axial and equatorial positions. The axial  $\text{In}-\text{N}$  distances are 2.372(6) and 2.334(6) Å, while the associated equatorial  $\text{In}-\text{S}$  distances are 2.477(3) and 2.467(3) Å.

Dithizone (Figure 1) is a well known<sup>1</sup> analytical reagent due to its ability to form intensely coloured, solvent-extractable complexes with a wide variety of metal ions. It is known to undergo both single and double deprotonation but its best characterised complexes are those of the monoanion, commonly simply referred to as 'dithizonate ion',  $\text{Hdz}^-$ .<sup>2</sup> A number of forms are possible for these complexes given that the dithizonate ion may exist in tautomeric forms, both of which might give rise to linkage isomers (Figure 2). Crystallographic studies are an obvious means of resolving such ambiguities and indeed available data<sup>3-8</sup> suggest that form (A) must be strongly preferred, since it is observed in all known cases.<sup>†</sup> However, it is not apparent that these results can be regarded as an adequate characterisation of the co-ordination properties of dithizonate ligand, since they refer to metals in a single oxidation state and with, in most cases, low co-ordination numbers. Thus, there remains a need for more extensive structural characterisation of metal dithizonates and this can be further justified in relation to development of an understanding of the solubility, photochemistry, redox chemistry, and substitutional reactions of these compounds. There is a quite remarkable range even of long-known characteristics which await full elucidation.<sup>10,11</sup>

Accordingly, we have considered initially the possibility of isolating the dithizonate complex of a metal ion in a high oxidation state and potentially with a high co-ordination number. To minimise possible problems arising from redox reactions with the ligand, we have turned our attention to the non-transition metals of Group 3. In this paper, we report the synthesis and structure determination of the indium(III) complex, characterizing in the process the first structurally known unidentate  $\text{Hdz}^-$  ligand.

### Experimental

*Preparation of  $[\text{In}(\text{Hdz})_3]$ .*—A solution of dithizone ( $\text{H}_2\text{dz}$ , 0.765 g) in acetone (40 cm<sup>3</sup>) was added to a thick paste

\* (1,5-Diphenyl-3-mercaptopformazanato-S)bis(1,5-diphenyl-3-mercaptopformazanato- $N^1\text{S}$ )indium(III).

Supplementary data available (No. SUP 23560, 21 pp.): thermal parameters, H-atom geometries, phenyl-ring planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

† Note that dithizone itself exists in the thione form in the solid<sup>9</sup> and recent evidence indicates that there is a single form present in solution (H. M. N. H. Irving, *J. Chem. Soc., Chem. Commun.*, 1981, 735).

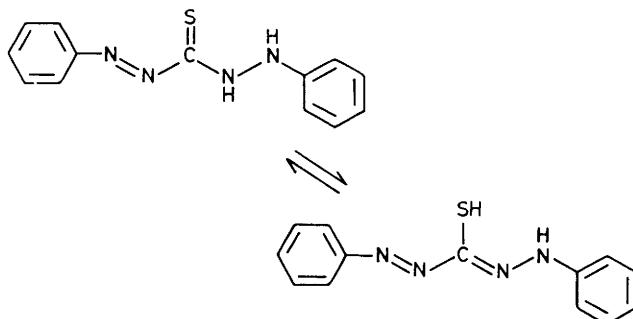
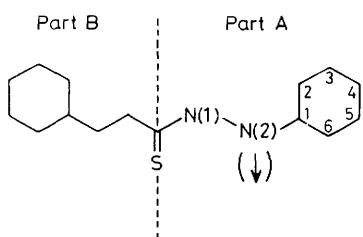


Figure 1. Thione-thiol tautomers of 1,5-diphenyl-3-mercaptopformazan, 'Dithizone',  $\text{H}_2\text{dz}$

prepared from finely ground  $\text{In}(\text{OH})_3$  (0.166 g) and water. The mixture was stirred until the  $\text{In}(\text{OH})_3$  had completely dissolved, a deep red solution resulting. This was filtered and taken to dryness under vacuum (rotary evaporator). The residue was redissolved in acetone and again taken to dryness in order to remove the last traces of water. This final deep red residue was dissolved in dichloromethane (20 cm<sup>3</sup>), filtered, and mixed with hexane until turbidity was just detectable. On standing at room temperature, clusters of thin red plates were slowly deposited. One further recrystallisation was generally necessary to provide crystals suitable for X-ray diffraction, although on prolonged (days) storage in solution some decomposition was evident. The purity of the complex was readily monitored by t.l.c. on silica using  $\text{CH}_2\text{Cl}_2$ -hexane as eluant.

*Crystallography.*—*Crystal data.*  $\text{C}_{39}\text{H}_{33}\text{InN}_2\text{S}_3$ ,  $M = 880.7$ , Triclinic, space group  $P\bar{1}$  ( $C_1^1$ , no. 2),  $a = 18.469(6)$ ,  $b = 14.928(7)$ ,  $c = 7.570(4)$  Å,  $\alpha = 80.31(4)$ ,  $\beta = 86.58(4)$ ,  $\gamma = 75.48(4)$ °,  $U = 1.191(2)$  Å<sup>3</sup>,  $D_m = 1.46(1)$ ,  $Z = 2$ ,  $D_c = 1.47$  g cm<sup>-3</sup>,  $F(000) = 894$ , monochromatic Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 6.9$  cm<sup>-1</sup>, specimen size 0.22 × 0.12 × 0.06 mm, 295(1) K.

*Structure determination.* The linewidths of the reflections obtained from the crystals were unusually wide, and a number of specimens were examined before an acceptable one was found; nevertheless, the precision of the cell determination and of the data remain somewhat below optimum. A unique data set was measured using a Syntex  $P2_1$  four-circle diffractometer in conventional 2θ-θ scan mode; 5 139 in-



dependent reflections were measured within the limit  $2\theta = 55^\circ$ , and 3 081 of these with  $I > 3\sigma(I)$  were considered 'observed' and used in the structure solution and refinement after analytical absorption correction. Least-squares refinement was basically  $9 \times 9$  block diagonal with  $(x,y,z,U)_H$  included in the block of the parent atom. Anisotropic thermal parameters were refined for the non-hydrogen atoms, with the corresponding isotropic form for the hydrogens. At convergence,  $R, R'$  were 0.043, 0.046, reflection weights being  $\sigma^2(F_o) + 0.0005(F_o)^2$ . Neutral-atom scattering factors were employed, those for the non-hydrogen atoms being corrected for anomalous dispersion ( $f', f''$ ).<sup>12</sup> Computation used the X-RAY 76 program system<sup>13</sup> implemented on a Perkin-Elmer 3240 computer.

Ligand numbering is as above, each ligand ( $n = 1-3$ ) being divided into two sections A, B, section A being chelated in ligands 1 and 2. Hydrogen-atom numbering follows that of the parent carbon.

*Abnormal features.* In view of the various possible locations for the non-aromatic hydrogen atoms throughout the system, some care was taken to locate and refine hydrogen parameters wherever possible. All hydrogen atoms except that associated with N(2B) of ligand 1 were successfully located and refined in  $(x,y,z,U)$ ; the remaining hydrogen associated with ligand 1 is presumed associated with N(B2) because of the similarity of the geometry of that atom to that of N(2B2) and also on

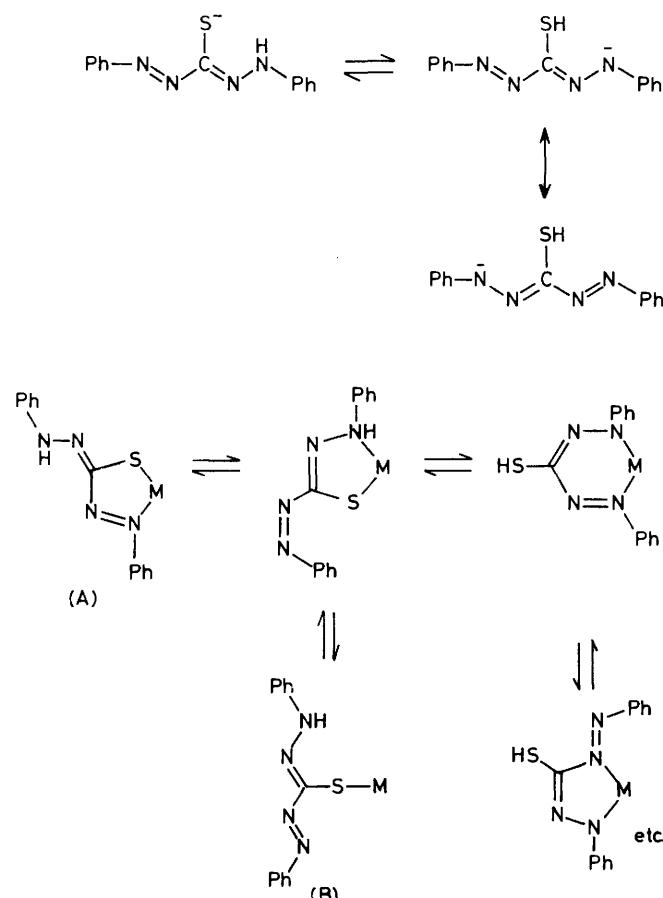


Figure 2. Isomeric forms of dithizonate ion and its metal complexes

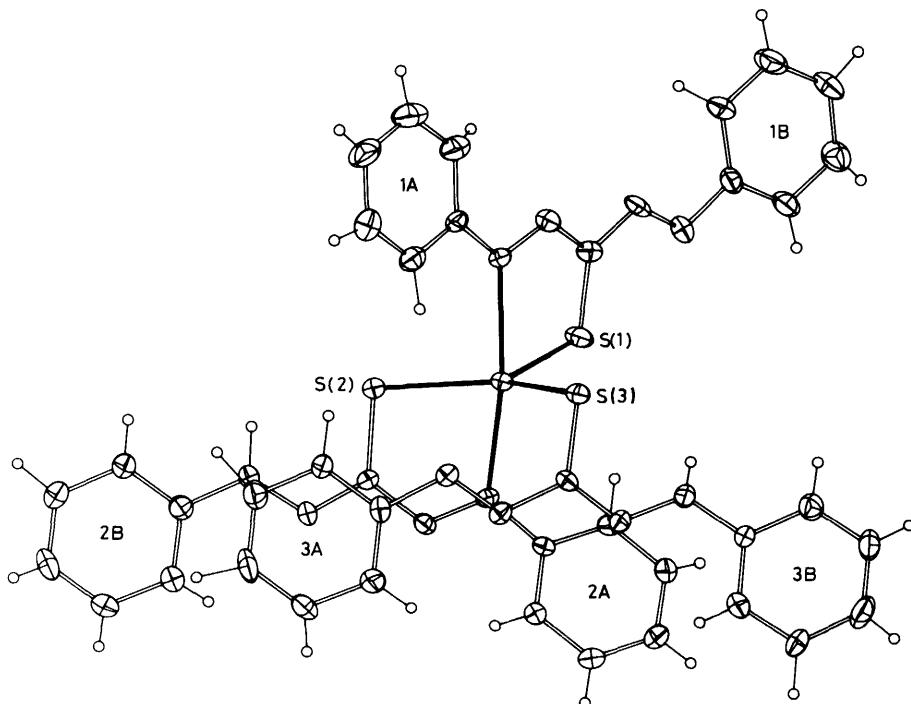


Figure 3. A single molecule of indium dithizonate, showing non-hydrogen atoms with 20% probability thermal ellipsoids and ligand numbering

## Non-hydrogen atom co-ordinates \*

Ligand 1			Ligand 2			Ligand 3		
<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
0.177 96(3)	0.189 17(4)	0.129 26(9)	0.214 5(1)	0.018 4(1)	0.230 4(2)	0.159 9(1)	0.332 3(1)	0
0.131 5(1)	0.239 3(2)	-0.180 9(2)	0.314 8(4)	0.007 0(5)	0.228 4(10)	0.249 0(4)	0.330 4(5)	0
0.036 0(4)	0.269 5(6)	-0.124 1(11)						

## section A

0.005 1(3)	0.242 6(4)	0.037 9(9)	0.347 8(3)	0.074 2(4)	0.149 5(8)	0.294 6(3)	0.252 3(4)	0
0.048 2(3)	0.198 2(4)	0.169 4(8)	0.169 4(8)	0.307 0(3)	0.153 7(4)	0.267 6(3)	0.180 5(4)	0
0.012 0(4)	0.168 2(5)	0.328 5(11)	0.347 3(4)	0.221 9(5)	0.008 4(10)	0.314 7(4)	0.103 6(5)	0
-0.064 0(6)	0.169 9(8)	0.336 1(19)	0.315 0(5)	0.292 9(6)	-0.124 7(13)	0.280 4(5)	0.035 7(6)	0
-0.095 2(7)	0.135 8(10)	0.491 2(19)	0.351 9(6)	0.360 9(8)	-0.197 7(17)	0.321 2(5)	-0.040 7(6)	0
-0.054 1(6)	0.100 4(8)	0.643 9(17)	0.420 3(6)	0.338 5(7)	-0.134 5(16)	0.396 4(7)	-0.050 7(7)	0
0.020 0(6)	0.180 4(7)	0.626 4(16)	0.452 6(5)	0.288 0(7)	-0.004 6(15)	0.429 9(6)	0.015 8(7)	0
0.053 2(5)	0.134 0(6)	0.483 0(12)	0.416 6(5)	0.220 6(7)	0.067 1(16)	0.390 4(5)	0.094 2(7)	0

## section B

-0.016 6(3)	0.317 8(4)	-0.239 2(9)	0.359 4(3)	-0.067 4(4)	0.307 9(9)	0.279 2(3)	0.401 9(4)	0
0.005 6(4)	0.348 7(4)	-0.402 9(9)	0.331 3(4)	-0.135 0(4)	0.396 8(10)	0.240 6(5)	0.479 2(5)	0
-0.050 2(4)	0.396 8(5)	-0.527 6(11)	0.376 1(4)	-0.217 5(6)	0.491 4(11)	0.269 1(4)	0.559 6(5)	0
-0.031 1(6)	0.445 8(7)	-0.680 0(13)	0.454 1(5)	-0.235 4(7)	0.478 0(15)	0.224 8(6)	0.641 3(6)	0
-0.085 6(6)	0.494 4(8)	-0.806 4(16)	0.495 3(6)	-0.317 6(7)	0.570 3(15)	0.250 7(7)	0.720 8(7)	0
-0.159 1(5)	0.491 8(7)	-0.774 7(15)	0.461 4(7)	-0.380 2(8)	0.672 1(18)	0.320 2(8)	0.720 6(8)	0
-0.177 8(6)	0.439 3(8)	-0.620 1(15)	0.385 2(6)	-0.363 0(7)	0.683 6(16)	0.364 8(6)	0.639 6(6)	0
-0.124 5(5)	0.390 9(7)	-0.493 0(14)	0.342 3(6)	-0.280 7(6)	0.592 2(13)	0.339 4(5)	0.559 7(7)	0

Hydrogen co-ordinates are (*x*, *y*, *z*): ligand 2 [attached to N(2B)] 0.279(5), -0.128(6), 0.412(11), *r*(N-H) = 0.95(8) Å; ligand 3 [attached to N(2B)] 0.204(5), 0.480(7) Å.

\* 0.73(10) Å.

**Table 2.** Metal-atom environment. The first column in the matrix is the metal-ligand distance (Å), the other entries being the angles (°) subtended at the metal by the atoms in question

Atom	<i>r</i> (M-L)	N(1A2)	S(2)	N(2A2)	S(3)
S(1)	2.477(3)	77.5(2)	115.57(9)	100.9(2)	106.99(8)
N(1A2)	2.372(6)		93.7(1)	169.6(2)	89.2(2)
S(2)	2.467(3)			77.6(2)	136.96(10)
N(2A2)	2.334(6)				101.0(2)
S(3)	2.468(3)				

the grounds of chemical reasonableness. In view of the considerable distance of N(1B2) from any potentially hydrogen-bonding neighbour, however, the non-location of this hydrogen atom remains something of a quandary.

### Discussion

Indium dithizonate is readily prepared by a simple and rather obvious procedure and recrystallisation to form crystals of a size suitable for *X*-ray diffraction experiments presents little difficulty. These properties contrast with those of many dithizonates, including the well known copper(II) and nickel(II) compounds, for example, which precipitate readily in an impure, microcrystalline form but can then only be dissolved with great difficulty to form a solution from which redeposition does not occur. The complex [In(Hdz)] dissolves readily in a variety of organic solvents and although decomposition in solution does occur, it is only obvious after a period of days under conditions where no special precautions to exclude oxygen or water are taken.

The unit-cell contents comprise discrete molecular units, the asymmetric unit consisting of the indium atom in association with three dithizonate ligands. Given the unlikelihood of the indium oxidation state being other than +3, and the similarity of disposition and geometries of ligands 1 and 2, it seems reasonable, in spite of the non-location and refinement of one hydrogen atom, to postulate its association with N(1B2), so that all ligands are of stoichiometry  $C_{13}H_{11}N_4S^-$  and ligands 1 and 2 are equivalent.

In spite of the large size of the indium atom, we find its co-ordination array to be sparse, being five-co-ordinate trigonal bipyramidal. Two of the ligands are bidentate, co-ordinating in their common chelating mode, while the third is unidentate by way of the sulphur (Figure 3). The co-ordination environment has pseudo- $C_2$  symmetry, with the bidentate ligands spanning axial and equatorial sites, whereas the equivalence within the indium-nitrogen and indium-sulphur sets of bond lengths is surprisingly uneven. (The deviation of the indium atom from the plane of the three sulphur atoms is 0.10 Å.) The presence of these discrepancies, together with the five-co-ordinate nature of the indium environment, suggest that steric crowding about the metal due to the presence of the phenyl substituents on the ligands may be considerable. In keeping with the low co-ordination number, the bond lengths around the central metal atom are short.

Although the data are not of sufficiently good quality to enable location of one of the key hydrogen atoms, nevertheless, since most previous dithizonate structure determinations are largely old and/or were carried out in the presence of very heavy atoms, the present determination provides one of the more precise definitions of geometry, both in the common chelating mode, and particularly about a large metal atom, and also the only example so far of a unidentate dithizonate ligand. A comparison of the present ligand parameters is

**Table 3.** Ligand non-hydrogen geometries. The two values for each entry are for sections A and B respectively

Distances/Å			
	Ligand 1	Ligand 2	Ligand 3
S-C	1.754(8)	1.763(8)	1.761(8)
C-N(1)	1.363(10), 1.328(9)	1.374(10), 1.310(8)	1.410(9), 1.305(11)
N(1)-N(2)	1.293(8), 1.326(9)	1.290(8), 1.317(10)	1.274(10), 1.324(9)
N(2)-C(1)	1.403(10), 1.410(10)	1.419(10), 1.407(9)	1.437(9), 1.409(12)
C(1)-C(2)	1.39(1), 1.34(1)	1.37(1), 1.40(1)	1.38(1), 1.38(1)
C(1)-C(6)	1.38(1), 1.40(1)	1.37(1), 1.36(1)	1.39(1), 1.38(1)
C(2)-C(3)	1.36(2), 1.40(1)	1.38(2), 1.37(1)	1.38(1), 1.37(2)
C(3)-C(4)	1.37(2), 1.37(2)	1.37(2), 1.36(2)	1.37(1), 1.36(2)
C(4)-C(5)	1.37(2), 1.37(2)	1.35(1), 1.37(2)	1.35(2), 1.38(1)
C(5)-C(6)	1.36(1), 1.39(1)	1.36(2), 1.38(1)	1.39(1), 1.37(2)
Angles/°			
	Ligand 1	Ligand 2	Ligand 3
In-S-C	96.8(3)	96.9(3)	105.2(3)
In-N(2)-N(1)	117.3(5)	119.5(5)	—
In-N(2)-C(1)	126.4(5)	123.7(4)	—
S-C-N(1)	125.5(5), 123.6(6)	125.5(5), 123.4(6)	123.5(6), 123.4(5)
N(1)-C-N(1)	110.7(6)	111.1(6)	112.5(7)
C-N(1)-N(2)	119.5(6), 117.3(6)	117.6(6), 116.9(6)	114.8(6), 117.2(7)
N(1)-N(2)-C(1)	116.0(6), 117.4(6)	114.6(6), 122.5(7)	112.9(6), 120.6(8)
N(2)-C(1)-C(2)	122.2(8), 119.2(8)	117.7(7), 120.4(8)	115.7(7), 119.1(8)
N(2)-C(1)-C(6)	119.1(7), 119.9(7)	123.9(9), 118.9(8)	123.9(7), 122.1(7)
C(2)-C(1)-C(6)	118.6(9), 120.9(8)	118.4(8), 120.7(8)	120.4(7), 118.9(9)
C(1)-C(2)-C(3)	119.7(11), 120.3(10)	120.4(9), 118.1(9)	119.8(9), 119.7(10)
C(2)-C(3)-C(4)	121.7(12), 120.2(10)	119.7(10), 121.1(10)	119.9(9), 121.2(9)
C(3)-C(4)-C(5)	118.3(11), 119.0(9)	119.9(11), 120.7(10)	120.0(8), 119.7(12)
C(4)-C(5)-C(6)	121.6(11), 121.5(10)	120.5(10), 119.4(10)	121.6(10), 119.5(11)
C(5)-C(6)-C(1)	120.1(9), 118.0(9)	121.0(9), 119.9(9)	118.2(9), 121.1(8)

made with those of the parent dithizone (see footnote † on p. 1109) in Table 4.

**Table 4.** Comparative dithizone geometries. Parameters are tabulated for: (i) the non-protonated section (A) of the unidentate ligand 3; (ii) the co-ordinated sections (A) of the bidentate ligands 1 and 2; (iii) the parent ligand H<sub>2</sub>dz (ref. 9; both sections protonated, average value given); (iv) the protonated sections (B) of the bidentate ligands 1 and 2; and (v) the protonated section (B) of the unidentate ligand 3

Distances/Å	(i)	(ii)	(iii)	(iv)	(v)
C–S	1.761(8)	1.754(8), 1.763(8)	1.71		
C–N	1.410(9)	1.363(10), 1.374(10)	1.345	1.328(9), 1.310(8)	1.305(11)
N–N(H)	1.274(10)	1.293(8), 1.290(8)	1.295	1.326(9), 1.317(10)	1.324(9)
N(H)–C(aryl)	1.437(9)	1.403(10), 1.419(10)	1.385	1.410(10), 1.407(9)	1.409(12)
Angles/°	(i)	(ii)	(iii)	(iv)	(v)
N–C–S	123.5(6)	125.5(5), 125.5(5)	125	123.6(6), 123.4(6)	123.4(6)
N–C–N	112.5(7)	110.7(6), 111.1(6)	110		
C–N–N(H)	114.8(6)	119.5(6), 117.6(6)	115	117.3(6), 116.9(6)	117.2(7)
N–N(H)–C(aryl)	112.9(6)	116.0(6), 114.6(6)	122	117.4(6), 122.5(7)	120.6(8)

**Table 5.** Ligand least-squares planes defined by the N<sub>2</sub>CSN<sub>2</sub> fragment of each ligand and given in the form  $pX + qY + rZ = s$ , where the orthogonal right-hand frame (X, Y, Z) has X parallel to  $\alpha$  and Z in the  $\alpha\beta$  plane.  $\sigma$  (defining atoms) and atom deviations,  $\delta$ , are in Å;  $\theta(A)$  and  $\theta(B)$  are the dihedral angles (°) of phenyl-ring planes A and B to the N<sub>2</sub>CSN<sub>2</sub> plane

	Ligand		
	1	2	3
10 <sup>4</sup> <i>p</i>	3 382	0 458	-3 009
10 <sup>4</sup> <i>q</i>	8 437	3 888	3 233
10 <sup>4</sup> <i>r</i>	4 169	9 202	8 972
<i>s</i>	3.652	1.945	2.793
$\sigma$	0.027	0.037	0.009
$\delta N(A, B1)$	-0.04, -0.01	-0.03, -0.02	0.01, 0.01
$\delta N(A, B2)$	0.03, 0.03	0.05, 0.05	-0.01, -0.01
$\delta C$	0.01	-0.03	-0.01
$\delta S$	-0.03	-0.01	0.01
$\delta In$	0.584	0.588	-1.795
$\delta C(A, B1)$	-0.09, -0.05	0.14, 0.10	0.06, 0.02
$\theta(A, B)$	18.7, 18.6	21.5, 8.4	17.8, 4.5

We observe initially that the carbon–sulphur distance appears to increase on co-ordination towards the single-bond value; the angle subtended at the sulphur is 96.8° in the situation where it is incorporated in a chelate ring, enlarging to 105.2(3)° in the unidentate case. The indium atom lies out of the chelate ring plane by 0.58 Å, the envelope conformation presumably arising from the size of the indium atom, but with respect to the unidentate ligand, in which the N<sub>2</sub>CSN<sub>2</sub> fragment is still planar, the indium atom lies well out of the plane. The carbon–sulphur distance is not substantially affected by these changes, neither are the phenyl-ring attitudes which are substantially coplanar with the rest of the ligand throughout (Table 5). The C–N distances change quite markedly ranging from a near single-bond value in non-protonated ligand 3, section A to a highly conjugated value in the protonated forms, the value for the metal–nitrogen co-ordinated form lying midway between. Concomitant changes are observed in

the order of the N–N bond. The angular trends are less clear-cut presumably because of the superposition of ring strain. In the unidentate ligand the two extreme forms represented by the two halves of the ligand of structure (B) (Figure 2) are well described by the observed bonding parameters.

In the present context of the structural characterization of a crystalline dithizone complex with the (unusual) stoichiometry [M(Hdz)<sub>3</sub>], we wish to draw attention to a further example of the genre, also with a main group metal, namely bismuth, in which the metal environment is six-co-ordinate, pseudo-octahedral.<sup>14</sup>

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