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Differential binding of a facultative tridentate ligand 4-(benzimidazol-2-yl)-3-thiabutanoic acid to Cu^{II} and Ni^{II}

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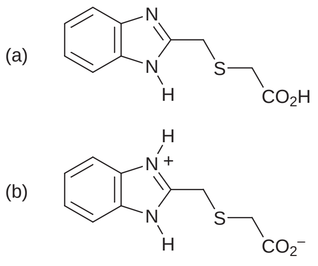
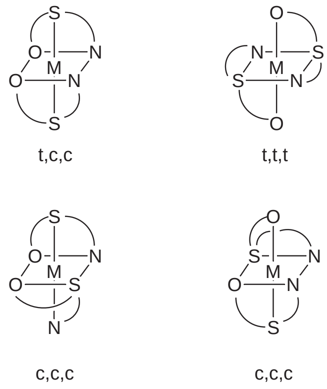
The crystal structure of a new tridentate ligand 4-(benzimidazol-2-yl)-3-thiabutanoic acid (HL), which provides a benzimidazole, a thioether and a carboxyl donor group that can be regarded as mimics of His, Met and Asp/Glu side chains in proteins, has been determined, together with those of its octahedral [CuL$_2$] (brilliant blue) and [NiL$_2$] (bright turquoise) complexes and the ligand field spectra of the chelates, for which the ligands provide an S$_2$N$_2$O$_2$ donor set, in each case, but different positional isomers for the copper (t,c,c) and the nickel (c,c,c) chelates.

The customary geometry of Cu^{II} in biological systems with His donors is distorted tetrahedral.[1,2] Where a Met donor is present the Cu···S distance is apparently quite variable[3] and may be the key to the rate at which electron transfer occurs in Type I blue copper proteins. For the known nickel sites in biological systems, four-co-ordinate square planar and six-co-ordinate octahedral geometries are known[4–7] and the availability of hard and soft donors is highly relevant. Geometrical information concerning biomimetic and related nickel complexes has been reviewed.[8] Tridentate 4-(benzimidazol-2-yl)-3-thiabutanoic acid (HL) (Scheme 1), produced as a synthon for asymmetric bis(benzimidazoles),[9] features as an interesting biomimetic ligand in its own right. It contains benzimidazole, thioether and carboxyl donors (N, S and O donors) which can be regarded as mimics of the amino acid side chains of His, Met and Glu or Asp, which are involved, for example, in the co-ordination of Cu in electron transport proteins[1] and of nickel in various enzymes.[8] Thus the co-ordination of the new ligand to metal ions of biological interest may assist the search for new structural models of metalloenzymes. 4-(5-Methylimidazol-4-yl)-3-thiabutanoic acid (abbreviated Hitba), reported by Bouwman and Reedijk,[10] also has donor N, S and O in a superficially rather similar relation to those of our new ligand; however the side chain is anchored to the 4 position of imidazole, not the 2 position as in the benzimidazole. The respective nitrogen donors are of different basicity (relevant pK of benzimidazole 5.5 and histidine 6.0) and have different steric requirements in the two ligands, since the side chain is on the polar side of the imidazole ring of the new ligand on the hydrophobic side for Hitba. The preparation and structure of the bis-chelates formed by HL with Ni^{II} and Cu^{II} are described in this paper. The data of Darensbourg and co-workers[11,12] provide a useful comparison for the nickel(II) structure; their recent attempts to obtain five-co-ordinate Ni^{II} produced instead six-co-ordinate Ni^{II} with S$_2$N$_2$OX and S$_2$N$_2$O$_2$ donor sets[11,12] or square planar Ni^{II} with an S$_2$N$_2$ donor set. Bouwman and Reedijk[10] found octahedral co-ordination of Co^{II} and Cu^{II} with the S$_2$N$_2$O$_2$ donor set. Allowing for Jahn–Teller distortion of the copper(II) complex, they inferred a similar structure for the nickel(II) chelate. The positional isomers are different from those reported here. A suitable descriptor of the geometry is shown in Scheme 2 for the chelates prepared in this work and the [Cu(itba)$_2$] chelate; this follows ref. 8, in describing the *cis*/*trans* relation of the two sulfur, the two nitrogen and the two oxygen (or oxygen/halogen) atoms, in that sequence, thus the [Cu(itba)$_2$] chelate is t,t,t. The formation of complexes in solution was studied by UV/VIS spectra, and these are compared with literature data where possible.



Scheme 1



Scheme 2 Positional isomers for S$_2$N$_2$O$_2$ donor sets from the new ligand and from Hitba. Clockwise from top left, t,c,c for copper chelate **I**, t,t,t for the [Cu(itba)$_2$] chelate,[10] c,c,c for the first molecule of the nickel chelate **E**, c,c,c for the second molecule **F**. The descriptor refers to mutual relation (*cis* or *trans*) of the two sulfur, the two nitrogen and the two oxygen atoms in sequence for these N,S,O tridentate donors, and follows the nomenclature from ref. 8

Experimental

Reagents and solvents used were of commercially available reagent grade quality. Elemental analysis was performed on a Carlo Erba 1106 elemental analyser; fast atom bombardment and electron impact mass spectra were obtained on a KRATOS MS80 RF, UV/VIS solution spectra in methanol solution with a Perkin-Elmer 550S instrument from 300 to 800 nm and fingerprint IR spectra (from KBr discs) on a Nicolet 20 PC-IR spectrometer.

Preparations

4-(Benzimidazol-2-yl)-3-thiabutanoic acid (HL). This compound was prepared as previously described.[9] Crystals suitable

Table 1 Crystallographic data

	$HL\cdot H_2O$	$[CuL_2]\cdot 2H_2O$	$[NiL_2]\cdot 3CH_3OH$
Formula	$C_{10}H_{12}N_2O_3S$	$C_{20}H_{22}CuN_4O_6S_2$	$C_{23}H_{30}N_4NiO_7S_2$
M	240.3	542.1	597.3
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$I2/a$ (non-standard $C2/c$)	$P2_1/n$	$P2_1/n$
a/Å	14.716(2)	13.6273(9)	19.2174(8)
b/Å	8.9259(13)	9.0560(6)	13.7698(6)
c/Å	16.860(3)	18.5755(12)	21.2575(9)
β/°	102.929(4)	105.149(2)	106.469(2)
U/Å^3	2158.5(6)	2212.7(3)	5394.4(4)
Z	8	4	8
μ/mm^{-1}	0.29	1.22	0.92
Reflections measured	4483	13 398	32 938
Unique reflections	1789	5150	12 423
R_{int}	0.0384	0.0209	0.0396
$R\ [F^2 > 2\sigma(F^2)]$	0.0371	0.0272	0.0642
$wR\ (F^2$, all data)	0.0944	0.0653	0.1328

for X-ray diffraction were obtained by slow evaporation of an aqueous solution.

[CuL$_2$]. The compound $CuBr_2$ (0.12 g, 0.54 mmol) in distilled deionised water (10 cm^3) was added to a hot stirred solution of HL (0.23 g, 1.04 mmol) in distilled deionised water (25 cm^3). The resulting pale blue solution was refluxed for 2 h, after which time the complex precipitated as a pale blue solid, and was collected by miniature filtration apparatus, washed with cold water, and recrystallised from a saturated aqueous solution to give brilliant blue single crystals suitable for X-ray diffraction. Yield 0.18 g, 36 mmol, 67%. Analytical data were obtained for a dried, powdered sample (Found: C, 43.9; H, 4.1; N, 10.2. $C_{20}H_{18}CuN_4O_4S_2\cdot 2.5H_2O$ requires C, 43.6; H, 4.2; N, 10.2%).

[NiL$_2$]. In a similar procedure to that described above for [CuL$_2$], a turquoise precipitate was isolated from the addition of HL (0.20 g, 0.90 mmol) and $NiBr_2$ (0.10 g, 0.46 mmol). Turquoise single crystals suitable for X-ray diffraction were grown from a saturated methanolic solution; they lost solvent slowly on exposure to air. Yield 0.14 g, 0.28 mmol, 61%. Data for a sample powdered and dried *in vacuo* [Found: C, 45.0; H, 4.4; N, 9.8%; FAB m/z 501 (M + H$^+$). $C_{20}H_{18}N_4NiO_4S_2\cdot CH_3OH\cdot 1.5H_2O$ requires C, 45.0; H, 4.5; N, 10.0%]. Crystals of a corresponding zinc complex could not be obtained pure.

X-Ray crystallography

Crystal data are in Table 1, together with other information on the structure determinations. For all three structures: T = 160 K, λ(Mo-Kα) = 0.710 73 Å. Hydrogen atoms were located in difference syntheses and included in the refinement with idealised positions and riding model constraints. Programs were as in refs. 13 and 14. Selected geometry for the three structures is given in Tables 2–4.

CCDC reference number 186/981.

See http://www.rsc.org/suppdata/dt/1998/1973/ for crystallographic files in .cif format.

Results and Discussion

Crystal structure of the acid HL·H$_2$O

The compound (Fig. 1) is present in the crystal in zwitterionic form with essentially symmetric ionised carboxylate groups and with both nitrogens of the benzimidazole bearing protons, as shown in Scheme 1(b). The intermolecular interactions provided by hydrogen bonding involve both oxygens of the carboxylate, both N–H groups of the benzimidazole, and both hydrogens of the molecule of water of crystallisation. Each carboxylate O atom receives one hydrogen bond from an N–H group and one from a water molecule. The water molecules function as hydrogen bond donors but not acceptors. The hydrogen bonding, for which geometrical information is given in Table 5, generates a two-dimensional network of molecules.

Table 2 Selected bond lengths (Å) and angles (°) for HL·H$_2$O

O(1)–C(1)	1.259(3)	O(2)–C(1)	1.252(2)
C(1)–C(2)	1.522(3)	C(2)–S	1.800(2)
S–C(3)	1.808(2)	C(3)–C(4)	1.478(3)
C(4)–N(1)	1.329(3)	C(4)–N(2)	1.331(3)
N(1)–C(5)	1.393(3)	N(2)–C(6)	1.389(3)
C(5)–C(6)	1.397(3)		
O(2)–C(1)–O(1)	123.73(19)	O(2)–C(1)–C(2)	119.35(19)
O(1)–C(1)–C(2)	116.88(17)	C(1)–C(2)–S	117.08(14)
C(2)–S–C(3)	99.90(10)	C(4)–C(3)–S	114.02(14)
N(1)–C(4)–N(2)	110.10(17)	N(1)–C(4)–C(3)	125.91(18)
N(2)–C(4)–C(3)	123.92(18)	C(4)–N(1)–C(5)	108.52(16)
C(4)–N(2)–C(6)	108.62(16)		

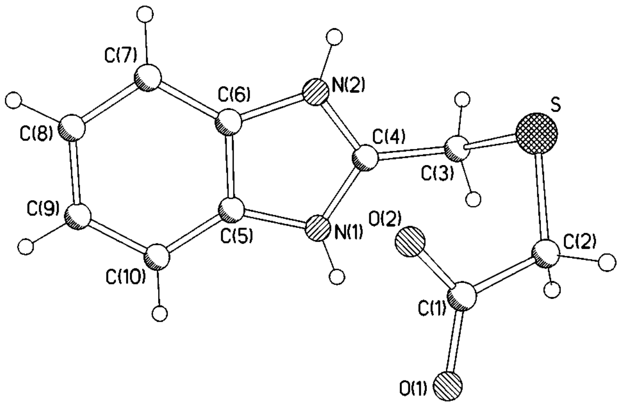


Fig. 1 Structure of HL, including hydrogen atoms and atom labelling

Metal complexes

From the complexation of HL with Cu^{II} and Ni^{II} in methanol, neutral, solvated ML_2 complexes, the latter of unusual colour, precipitated. Crystal structure determination reveals approximately octahedral co-ordination through an $S_2N_2O_2$ donor set in each case, but different isomeric polyhedra (Scheme 2).

Crystal structure of [CuL$_2$]·2H$_2$O. The two oxygen and two nitrogen donors form a square planar co-ordination around the central copper, with a slight tetrahedral distortion, the O(1)–Cu–N(3) and O(3)–Cu–N(1) bond angles being reduced to 169.22(6) and 167.84(6)° respectively. Each oxygen is *trans* to nitrogen and *cis* to the other oxygen. The two sulfurs are approximately axial [S(2)–Cu–S(1) 161.98(2)°] and at distances of 2.7439(5) and 2.7460(5) Å from the central copper (Fig. 2).

Table 3 Selected bond lengths (Å) and angles (°) for $[CuL_2]\cdot 2H_2O$

Cu–N(1)	1.9899(14)	Cu–N(3)	1.9693(14)
Cu–O(1)	1.9539(12)	Cu–O(3)	2.0028(12)
Cu–S(1)	2.7460(5)	Cu–S(2)	2.7439(5)
C(10)–O(1)	1.274(2)	C(10)–O(2)	1.238(2)
C(20)–O(3)	1.284(2)	C(20)–O(4)	1.234(2)
O(1)–Cu–N(3)	169.22(6)	N(1)–Cu–O(3)	167.84(6)
S(2)–Cu–S(1)	161.978(16)	O(1)–Cu–N(1)	90.85(6)
N(3)–Cu–N(1)	92.29(6)	O(1)–Cu–O(3)	90.06(5)
N(3)–Cu–O(3)	89.04(6)	O(1)–Cu–S(2)	89.11(4)
N(3)–Cu–S(2)	80.21(4)	N(1)–Cu–S(2)	114.59(4)
O(3)–Cu–S(2)	77.55(4)	O(1)–Cu–S(1)	79.86(4)
N(3)–Cu–S(1)	110.85(4)	N(1)–Cu–S(1)	80.05(4)
O(3)–Cu–S(1)	88.18(4)		

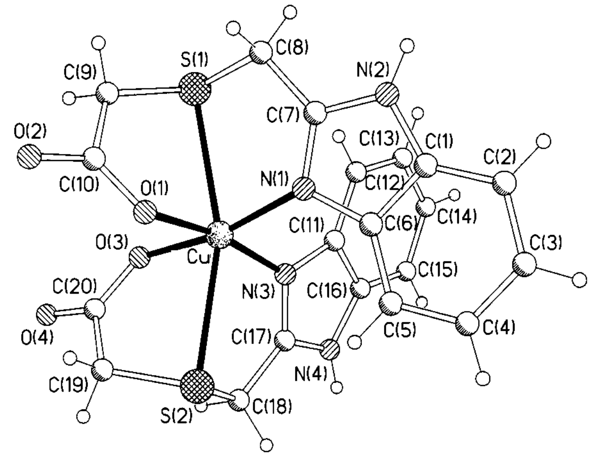


Fig. 2 Structure of the $[CuL_2]$ complex

Table 4 Selected bond lengths (Å) and angles (°) for $[NiL_2]\cdot 3CH_3OH$

Ni(1)–N(1)	2.045(3)	Ni(1)–N(3)	2.047(3)
Ni(1)–O(1)	2.076(3)	Ni(1)–O(3)	2.027(3)
Ni(1)–S(1)	2.4750(10)	Ni(1)–S(2)	2.4807(11)
C(10)–O(1)	1.272(5)	C(10)–O(2)	1.233(5)
C(20)–O(3)	1.253(4)	C(20)–O(4)	1.254(5)
Ni(2)–N(5)	2.036(3)	Ni(2)–N(7)	2.044(3)
Ni(2)–O(5)	2.081(3)	Ni(2)–O(7)	2.023(3)
Ni(2)–S(3)	2.4659(11)	Ni(2)–S(4)	2.4569(10)
C(30)–O(5)	1.272(4)	C(30)–O(6)	1.238(5)
C(40)–O(7)	1.258(4)	C(40)–O(8)	1.246(4)
N(3)–Ni(1)–O(1)	167.29(12)	O(3)–Ni(1)–S(1)	168.52(9)
N(1)–Ni(1)–S(2)	173.50(10)	O(3)–Ni(1)–N(1)	92.28(11)
O(3)–Ni(1)–N(3)	94.29(12)	N(1)–Ni(1)–N(3)	102.15(13)
O(3)–Ni(1)–O(1)	89.04(11)	N(1)–Ni(1)–O(1)	89.96(12)
N(1)–Ni(1)–S(1)	82.20(9)	N(3)–Ni(1)–S(1)	96.71(9)
O(1)–Ni(1)–S(1)	80.93(8)	O(3)–Ni(1)–S(2)	83.13(8)
N(3)–Ni(1)–S(2)	82.86(9)	O(1)–Ni(1)–S(2)	85.37(8)
S(1)–Ni(1)–S(2)	101.48(4)	N(7)–Ni(2)–O(5)	168.27(12)
O(7)–Ni(2)–S(4)	169.98(8)	N(5)–Ni(2)–S(3)	175.36(9)
O(7)–Ni(2)–N(5)	92.78(11)	O(7)–Ni(2)–N(7)	93.70(11)
N(5)–Ni(2)–N(7)	100.07(12)	O(7)–Ni(2)–O(5)	90.57(11)
N(5)–Ni(2)–O(5)	90.61(12)	N(5)–Ni(2)–S(4)	82.75(9)
N(7)–Ni(2)–S(4)	95.90(9)	O(5)–Ni(2)–S(4)	80.54(7)
O(7)–Ni(2)–S(3)	83.76(8)	N(7)–Ni(2)–S(3)	83.28(9)
O(5)–Ni(2)–S(3)	86.35(8)	S(4)–Ni(2)–S(3)	100.17(4)

Table 5 Hydrogen bonding in the crystal structures

Donor atom D	Acceptor atom A	D···A/Å	D–H···A/°
$HL\cdot H_2O$			
N(1)	O(1)	2.680	163
N(2)	O(2)	2.689	165
O(3) (solvent)	O(1)	2.938	162
	O(2)	2.865	156
$[CuL_2]\cdot 2H_2O$			
N(2)	O(10) (solvent)	2.815	169
N(4)	O(3) (co-ordinated)	2.723	168
O(10) (solvent)	O(1) (co-ordinated)	2.907	160
	O(2) (unco-ordinated)	2.753	173
O(11) (solvent)	O(4) (unco-ordinated)	2.903	163
		3.055	160
$[NiL_2]\cdot 3CH_3OH$			
N(2)	O(8) (unco-ordinated)	2.777	145
N(4)	O(1) (co-ordinated)	2.749	174
N(6)	O(4) (unco-ordinated)	2.740	151
N(8)	O(5) (co-ordinated)	2.759	172
O(50) (solvent)	O(8) (unco-ordinated)	2.770	172
O(51) (solvent)	O(4) (unco-ordinated)	2.679	140
O(52) (solvent)	O(54) (solvent)	2.684	163
O(53) (solvent)	O(2) (unco-ordinated)	2.775	172
O(54) (solvent)	O(6) (unco-ordinated)	2.714	166
O(55) (solvent)	O(53) (solvent)	2.815	167

The donor set can be described as t,c,c and is shown in Scheme 2. A search of the Cambridge Structural Database[15] yielded 103 observations of Cu–S (thioether) distances in octahedral environments; statistical analysis of this set of structures gives a mean of 2.488 (sample σ 0.186 Å, minimum 2.294 and maximum 3.014 Å). Only 13% of the structures have distances >2.74 Å. The Cu–S is slightly longer than for the recently examined[16] cucumber basic protein (*ca.* 2.63 Å) but much shorter than the interaction in a typical azurin,[17] where it is 3.13 Å. The Cu–S distances in our complex can thus be regarded as long in the context of small molecules, but within the known range for small electron transfer proteins, and an example of axial distortion due to the Jahn–Teller effect. The $[Cu(itba)_2]$ complex[10] (**J** in Table 6) has bond lengths very close to those found here. However, Bouwman and Reedijk[10] found that donor atoms were in mutually *trans* positions (see t,t,t in Scheme 2). This itba chelate is unsolvated, and has hydrogen bonding between carboxyl and imidazole nitrogen. Thus the detailed co-ordination geometries are in fact quite different, possibly because of the different steric requirements round the nitrogens in the two different ligands, the different hydrophobicities, and the slightly lower basicity of the benzimidazole nitrogen; the crystal packing is also different, partly because of the difference in solvation.

The structure is a dihydrate, the water molecules providing a link between metal complexes by a three-dimensional hydrogen bonding network involving the water molecules (as donors and, in one case, as acceptor), the co-ordinated and unco-ordinated oxygen of each carboxyl (as acceptors), and the benzimidazole N–H groups (as donors). Geometrical details of the hydrogen bonds are given in Table 5.

Crystal structure of $[NiL_2]\cdot 3CH_3OH$. The crystal structure of the brilliant turquoise nickel complex contains two crystallographically independent molecules of the nickel chelate. Molecule 1 (Fig. 3) has the two sulfurs *cis* [at 101.48(4)°], the nitrogens *cis* [102.15(13)°] and the oxygens *cis* [89.04(11)°]. One sulfur is *trans* to oxygen, and the other to nitrogen. The second molecule is the same positional isomer, with slightly different angles, having *cis* sulfurs [at 100.17(4)°], *cis* nitrogens [100.07(12)°], *cis* oxygens [90.57(11)°], and essentially the same bond lengths.

The molecules are linked by a complex two-dimensional hydrogen bonding network involving the six crystallographically independent molecules of methanol of crystallisation, the unco-ordinated and half the co-ordinated carboxylate oxygen atoms, and the benzimidazole N–H groups. Geometrical details are given in Table 5.

Table 6 makes a comparison of the geometries for the nickel complexes (**E** and **F**) found in this work with those for several

Table 6 Comparison of metal co-ordination distances for complexes of Ni and Cu

	S_2N_2	S_2N_2	S_2N_2OX	S_2N_2OX	S_2N_2OX	S_2N_2OX	S_2N_2OX	S_2N_2OX	S_2N_2OX	S_2N_2OX
M	Ni[a]	Ni[a]	Ni[a]	Ni[a]	Ni	Ni	Ni[b]	Ni[c]	Cu	Cu[d]
Compound	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**
X	—	—	Cl	Br	O	O	O	O	O	O
M–N	1.974	1.98	2.101	2.088	2.045	2.044	2.108	2.094	1.969	1.986
M–N	1.970	1.97	2.110	2.060	2.047	2.036	2.100		1.990	
M–S	2.207	2.174	2.400	2.390	2.475	2.466	2.402	2.435	2.746	2.715
M–S	2.213	2.143	2.444	2.380	2.481	2.457	2.438		2.744	
M–O			2.293	2.270	2.027	2.023	2.062	2.067	1.954	1.988
M–X			2.465	2.510	2.076	2.081	2.096		2.003	
Descriptor			c,c,t	c,c,t	c,c,c	c,c,c	c,c,t	c,c,t	t,c,c	t,t,t

[a] Ref. 11: **A** = [*N*,*N*′-bis(5-hydroxy-3-thiapentyl)-1,5-diazacyclooctane-*N*,*N*′,*S*,*S*′]nickel(II) iodide, **B** = [(5-hydroxy-2,2,8,8-tetramethyl-3,7-dithianonanediyl)-1,5-diazacyclooctane-*N*,*N*′,*S*,*S*′]nickel(II) bromide, **C** = [*N*,*N*′-bis(5-hydroxy-3-thiapentyl)-1,5-diazacyclooctane-*O*,*N*,*N*′,*S*,*S*′]-chloronickel(II) iodide, **D** = [(5-hydroxy-3,7-dithianonanediyl)-1,5-diazacyclooctane-*O*,*N*,*N*′,*S*,*S*′]bromonickel(II) bromide. This work: **E**, **F** and **I**. [b] Ref. 12: **G** = [*N*-(3-thiabutyl)-*N*′-(3-thiapentanoate)-1,5-diazacyclooctane]nickel(II) iodide (polymer). [c] Ref. 18: **H** = Δ-[1,5-diazacyclooctane-1,5-diylbis(3-thiapentanoato)]nickel(II). [d] Ref. 10: **J** = [Cu(itba)$_2$].

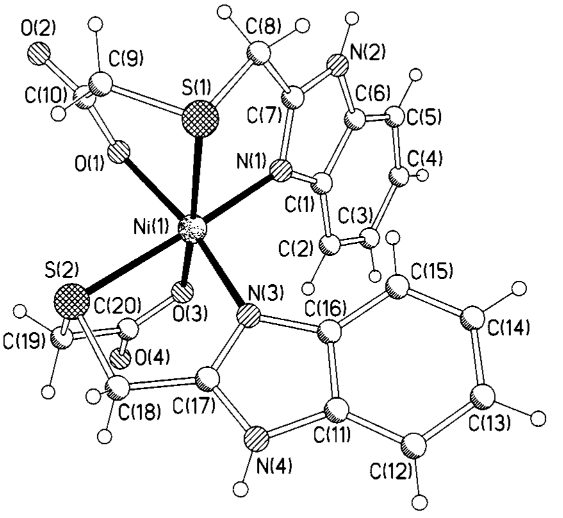


Fig. 3 One of the crystallographically independent molecules of the [NiL$_2$] complex

relevant complexes found in the literature (**C**, **D**, **G**, **H**). The Ni–S length appears elongated by 0.17–0.3 Å in the octahedral (S_2N_2OX) relative to the square planar (S_2N_2) environment as shown in Table 6 (**A**, **B**). The Ni–N distances are slightly longer in the octahedral form. In the molecules reported here the distances from nickel to oxygen and to nitrogen are marginally shorter, while the nickel–sulfur distances are longer than with the diazaoctane ligand.[11,12] Nickel to sulfur distances in thiomacrocycle complexes[19] range from 2.3694 to 2.442 Å. A search of the Cambridge Structure Database[15] for bonds from Ni to S (thioether) indicated a bimodal distribution with the shorter distance median *ca.* 2.2 Å presumably corresponding to four-co-ordination and a longer one, median about 2.4 Å, corresponding to six-co-ordination. Restricting the search to six-co-ordinate Ni, there were 197 observations; statistical analysis of this set of data gave a mean Ni–S of 2.426 Å (sample σ 0.06, minimum 2.313, maximum 2.943 Å). The structures of the chelates **C**, **D**, **G** and **H** in Table 6, determined by Darensbourg and co-workers,[11,12,18] involve a diazacyclooctane ligand, having the two nitrogens forced to lie *cis* and pendant donor chains completing the donor sequence OSNNSO. These all have the descriptor c,c,t with oxygen *trans*. A tridentate ligand with the ONS sequence used by Choudhury *et al.*[20] gave bis-chelates of nickel(II) with axial nitrogens, descriptor c,t,c. Bouwman and Reedijk[10] prepared a nickel(II) complex of Hitba (NSO sequence) which seemed isostructural with its copper(II) and cobalt(II) analogues but X-ray data were only quoted for a powder sample. This would require mutually *trans* ligands (descriptor t,t,t), which again is quite different to what is observed here.

Comparing the copper(II) and nickel(II) structures, it can be seen that the positional isomer found for the former is different from those found for the latter (Scheme 2). The Cu–S bond length considerably exceeds the Ni–S one (Table 6) while the Cu–N and Cu–O distances are shorter than the nickel ones. The axial elongation found in **I** accords with the expectation of Jahn–Teller distortion. Neither complex is perfectly octahedral nor are the L–M–L angles perfectly rectangular so the description of *fac* or *mer* does not strictly apply. However *fac* is more accurate for Ni (where *trans* angles are almost linear). For Cu^{II} the preference for tight square planar co-ordination is satisfied by the two nitrogen and two oxygen donors which define a plane, while weaker axial interaction with the thioether sulfurs completes the Jahn–Teller axially distorted octahedron. The positional isomer found for the copper(II) complex **I** is different to that found for the [Cu(itba)$_2$] (Scheme 2 and **J** in Table 6) with a very similar donor set, and very similar bond lengths (Table 6).

UV/VIS spectra. Octahedral nickel(II) complexes have three spin-allowed ligand field transitions. In the spectra of the turquoise nickel complex in methanolic solution two of these arise at 605 and 383 nm with ε values of 20.9 and 30.9 dm^3 mol^{-1} cm^{-1} respectively; the UV region is complicated by the absorptions of the ligand and charge transfer bands. These wavelengths are similar to those for a green macrocycle complex of Ni^{II},[19] [Ni$_2$([12]aneS$_4$)$_2$Cl$_2$][BF$_4$]$_2$ absorbing at 608 (ε 31) and 384 nm (ε 93 dm^3 mol^{-1} cm^{-1}). All the chelates with c,c,t geometries in Table 6 had similar UV absorptions in solution. The Darensbourg data for absorbance of the S_2N_2OCl complex (**C** in Table 6) which is blue-green are 598 (ε 87) and 382 nm (ε 119 dm^3 mol^{-1} cm^{-1}) in CH$_3$CN.[11,12] For comparison, the polymer **G** absorbed at 592 (ε 100) and 376 nm, while **H** (described as aquamarine blue) absorbed at 600 (ε 49) and 364 (ε 31 dm^3 mol^{-1} cm^{-1}). The [Ni(itba)$_2$] complex was reported to be lilac, and thus unlikely to be the same isomer. The relevant ligand field absorptions[10] were at 694, 546 and 350 nm. The brilliant blue copper(II) complex obtained in this work absorbs at 645 nm with an ε value of 50.3 dm^3 mol^{-1} cm^{-1}. The [Cu(itba)$_2$] complex has a sharp absorption band at 617 and a broad one at 787 nm in this region. These visible spectral data are consistent with the different positional isomers discovered in the crystal structure analyses.

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