

Co-ordination Compounds with the N₂S-Donor Ligand 1,5-Bis(3,5-dimethylpyrazol-1-yl)-3-thiapentane†

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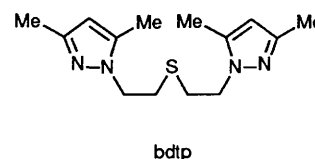
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With the ligand 1,5-bis(3,5-dimethylpyrazol-1-yl)-3-thiapentane (bdtp) the compounds [M(bdtp)(NCS)₂] (M = Co or Zn), [Ni(bdtp)(NCS)₂(H₂O)], Cu(bdtp)(F)(BF₄), M(bdtp)Cl₂ (M = Co or Cu), Zn(bdtp)Cl₂·0.5EtOH, M(bdtp)(NO₃)₂ (M = Co or Cu), Cu(bdtp)X (X = Br or Cl), [Cu(bdtp)]BF₄·H₂O and Ag(bdtp)(NO₃) have been isolated. X-Ray single-crystal structures of [Co(bdtp)(NO₃)₂], Cu(bdtp)Br and Ag(bdtp)(NO₃) were determined. The compound [Co(bdtp)(NO₃)₂] crystallizes in the monoclinic space group *P*2₁/*n*, with *a* = 8.984(2), *b* = 15.342(3), *c* = 14.888(3) Å, β = 107.28(2)°, *Z* = 4 and *R* 0.038 for 2727 observed [*F* > 2σ(*F*)] reflections. The cobalt(II) atom is pseudo-octahedrally co-ordinated by three ligand donors, one mono- and one di-dentate nitrate. The Co–N [2.072(3) and 2.083(3) Å] and Co–S bond lengths [2.584(1) Å] are normal. The compound Cu(μ(bdtp)Br) crystallizes in the monoclinic space group *P*2₁/*n*, with *a* = 9.017(2), *b* = 14.09(2), *c* = 13.660(3) Å, β = 97.80(2)°, *Z* = 4 and *R* 0.040 for 1655 observed reflections. The pseudo-tetrahedral co-ordination environment of the copper(I) atom is made up by two pyrazole nitrogens [2.120(5) and 2.014(5) Å], one thioether [2.461(2) Å] and one bromide [2.432(1) Å]. The ligand acts as a link between two successive copper centres, resulting in a polymeric compound structurally isomorphous to Cu(bdtp)Cl. The compound Ag(bdtp)(NO₃) crystallizes in the monoclinic space group *P*2₁/*n*, with *a* = 18.710(4), *b* = 8.828(2), *c* = 11.162(5) Å, β = 103.13(3)°, *Z* = 4 and *R* 0.038 for 2346 observed reflections. The structure, with bridging ligands, is similar to that of Cu(bdtp)Br. The silver(I) atoms are co-ordinated, in a very distorted-tetrahedral fashion, by two nitrogens [2.483(5) and 2.216(4) Å], one thioether [2.571(2) Å] and a monodentate nitrate anion [2.503(5) Å].

Many different strategies are used to obtain a greater insight into the relation between the structure and activity of the active sites of metalloproteins.¹ One, the synthesis of low-molecular-weight co-ordination compounds as models for the active site, has been of growing interest in the past years. The models do not usually mimic all properties of the active site, but they definitely contribute to the knowledge of topics such as thioether–metal interactions.²

Our contribution to this new field of bioinorganic chemistry is the synthesis of model compounds, inspired by the active site of the type I copper proteins.² This class of proteins shows remarkable spectroscopic and chemical features. The copper atom in the active site is co-ordinated by two imidazole nitrogen donors, one thiolate sulfur donor and one thioether sulfur donor in a distorted-tetrahedral arrangement.³ The ligands developed in our laboratories during the last few years comprise N₂S₂ donors,^{4–8} with two pyrazole heterocycles and two thioethers to mimic the donor set in the proteins. They show interesting behaviour towards many first-row transition metals, *viz.* non-co-ordination of thioethers and a remarkable range of co-ordination geometries.

Our present approach is the development and study of N₂S ligands and the subsequent introduction of the thiolate function as a further step towards modelling the N₂SS[−] donor set, present in the proteins. In this report the results obtained with 1,5-bis(3,5-dimethylpyrazol-1-yl)-3-thiapentane (bdtp) are presented. Besides a unique tetranuclear copper(I) cluster⁹ and a copper(I) tetrafluoroborate compound,¹⁰ no extensive co-ordination chemistry of this ligand has yet been reported. The ligand had been synthesised earlier by Sorrell and



Malachowski.¹⁰ The present synthetic route is derived from an earlier reported N₂S₂-ligand synthesis,⁴ and offers an easier method.

Experimental

Synthesis of the Ligand.—The materials were all commercially available and were used without purification. The synthesis of tosylated 1-(2'-hydroxyethyl)-3,5-dimethylpyrazole is described elsewhere.⁴ This compound (25 g, 85 mmol), Na₂S·7H₂O (8.25 g, 40 mmol) and NaOH (0.6 g, 15 mmol) were refluxed in water (*ca.* 50 cm³) during 5 h. After cooling to room temperature the crude ligand crystallized as a white powder (6.2 g, 60%). Diethyl ether was used to recrystallize it. ¹H NMR (CDCl₃): δ 2.16 (s, 6 H), 2.24 (s, 6 H), 2.80 (t, 4 H), 4.04 (t, 4 H) and 5.75 (s, 2 H).

Synthesis of the Co-ordination Compounds.—Co-ordination compounds based on divalent nickel, cobalt, copper and zinc were prepared by dissolving the appropriate hydrated metal salt (2 mmol) in warm ethanol or methanol (7–10 cm³) and adding this solution to a warm solution of the ligand in the same solvent. The metal-to-ligand ratio was varied from 1:1 to 1:3. Triethyl orthoformate (*ca.* 2 cm³) was then added as a dehydrating agent. After cooling to room temperature, mainly

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Crystallographic data^a for the structures of [Co(bdtp)(NO₃)₂] **1**, Cu(bdtp)Br **2** and Ag(bdtp)(NO₃) **3**

	1	2	3
Formula	C ₁₄ H ₂₂ CoN ₆ O ₆ S	C ₁₄ H ₂₂ CBrcuN ₄ S	C ₁₄ H ₂₂ AgN ₅ O ₃ S
<i>M</i>	461.36	421.87	448.25
<i>a</i> /Å	8.984(2)	9.017(2)	18.710(4)
<i>b</i> /Å	15.342(3)	14.09(2)	8.828(2)
<i>c</i> /Å	14.888(3)	13.660(3)	11.162(5)
α /°	90	90	90
β /°	107.28(2)	97.80(2)	103.13(3)
γ /°	90	90	90
<i>U</i> /Å ³	1959	1709	1795
<i>Z</i>	4	4	4
<i>F</i> (000)	956	856	
<i>D_c</i> /cm ⁻³	1.55	1.63	1.65
μ (Mo-K α)/cm ⁻¹	10.1	37	12.4
Crystal size/mm	0.33 × 0.33 × 0.5	0.30 × 0.18 × 0.13	<i>b</i>
2 θ range/°	2–28	3–29	2–30
<i>h, k, l</i> range	–11 to 11, 0–19, 0–21	–11 to 12, 0–17, 0–19	–26 to 26, 0–12, 0–15
Measured data	4838	5656	6186
Independent data	4666	5413	6069
Observed data [<i>F</i> > 2 σ (<i>F</i>)]	2727	1655	2346
Transmission (%)	92–103	85–116	86–113
<i>R</i>	0.038	0.040	0.038
<i>R'</i>	0.044	0.039	0.039

^a Details in common: CAD4 diffractometer; scan method ω -2 θ ; $w = 1/\sigma^2(F)$; λ (Mo-K α) = 0.710 73 Å monoclinic, space group *P2₁/n*. ^b Crystal was lost after collection of the diffraction data.

Table 2 Fractional coordinates of the non-hydrogen atoms ($\times 10^5$ for Co and S, $\times 10^4$ for others) of [Co(bdtp)(NO₃)₂] with estimated standard deviations (e.s.d.s) in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Co(1)	3 250(5)	17 169(3)	29 644(3)
N(11)	2 169(3)	898(2)	4 870(2)
N(12)	1 577(3)	795(2)	3 905(2)
C(13)	2 049(4)	–4(2)	3 734(3)
C(14)	2 924(4)	–396(3)	4 560(3)
C(15)	2 981(4)	187(2)	5 273(3)
C(16)	1 636(6)	–380(3)	2 769(3)
C(17)	3 738(4)	115(3)	6 307(3)
C(18)	1 859(4)	1 674(3)	5 356(3)
C(19)	170(4)	1 749(3)	5 325(3)
S(20)	–11 431(11)	20 287(7)	41 819(7)
N(21)	1 217(3)	3 530(2)	3 798(2)
N(22)	1 748(3)	2 787(2)	3 480(2)
C(23)	3 296(4)	2 843(3)	3 791(3)
C(24)	3 737(4)	3 602(3)	4 312(3)
C(25)	2 393(4)	4 028(3)	4 296(3)
C(26)	4 329(4)	2 158(3)	3 583(3)
C(27)	2 169(6)	4 894(3)	4 700(3)
C(28)	–464(4)	3 674(3)	3 561(3)
C(29)	–1 218(4)	3 215(2)	4 223(3)
N(30)	1 305(3)	2 170(3)	1 354(2)
O(31)	1 260(3)	1 508(1)	1 874(2)
O(32)	518(3)	2 816(2)	1 383(2)
O(33)	2 150(4)	2 134(3)	846(2)
N(40)	–2 493(4)	1 294(3)	1 949(3)
O(41)	–2 017(3)	2 077(2)	2 115(2)
O(42)	–1 497(3)	716(2)	2 299(2)
O(43)	–3 823(3)	1 123(2)	1 488(2)

crystalline products were obtained. When the product was a powder or an oil, acetonitrile or acetone was used as solvent. If no solid compound could be obtained using these methods, cooling to –23 °C and/or addition of diethyl ether was tried to invoke precipitation. The compounds with thiocyanate as anion were prepared by adding ammonium thiocyanate to the corresponding ligand and metal nitrate solution. The presence of nitrate in the product was checked using infrared spectroscopy. The reaction with copper(II) bromide in ethanol, and also in ethanol–acetone (1:1), resulted in almost immediate

Table 3 Selected bond lengths (Å) and angles (°) of [Co(bdtp)(NO₃)₂] with e.s.d.s in parentheses

Co(1)–N(12)	2.072(3)	Co(1)–S(20)	2.584(1)
Co(1)–N(22)	2.083(3)	Co(1)–O(31)	2.062(3)
Co(1)–O(41)	2.180(3)	Co(1)–O(42)	2.249(3)
N(30)–O(31)	1.285(4)	N(30)–O(32)	1.226(5)
N(30)–O(33)	1.222(6)	N(40)–O(41)	1.275(5)
N(40)–O(42)	1.257(4)	N(40)–O(43)	1.216(4)
N(12)–Co(1)–S(20)	86.54(9)	N(12)–Co(1)–N(22)	98.0(1)
N(12)–Co(1)–O(31)	99.2(1)	N(12)–Co(1)–O(41)	143.3(1)
S(20)–Co(1)–N(22)	88.9(1)	S(20)–Co(1)–O(31)	173.32(8)
S(20)–Co(1)–O(41)	75.74(9)	N(22)–Co(1)–O(31)	93.6(1)
N(22)–Co(1)–O(41)	113.3(1)	O(31)–Co(1)–O(41)	97.6(1)
O(42)–Co(1)–N(12)	90.6(1)	O(42)–Co(1)–N(22)	171.0(1)
O(42)–Co(1)–S(20)	88.86(9)	O(42)–Co(1)–O(31)	87.7(1)
Co(1)–S(20)–C(19)	106.8(1)	Co(1)–S(20)–C(29)	103.9(2)
C(19)–S(20)–C(29)	103.0(2)	O(31)–N(30)–O(32)	119.8(4)
O(31)–N(30)–O(33)	118.3(4)	O(32)–N(30)–O(33)	121.9(4)
Co(1)–O(31)–N(30)	116.4(2)	O(41)–N(40)–O(42)	115.3(3)
O(41)–N(40)–O(43)	122.0(3)	O(42)–N(40)–O(43)	122.7(4)
Co(1)–O(41)–N(40)	94.8(2)		

decolourization of the solution. On cooling, colourless air-stable crystals separated.

The copper(I) compounds were prepared,¹¹ under a di-nitrogen atmosphere, using the corresponding copper(I) salts {in the case of copper(I) tetrafluoroborate [Cu(MeCN)₄]BF₄}, and carefully degassed and dried solvents. The solvents used were methanol for the tetrafluoroborate compound (in contrast to acetonitrile–propan-2-ol, reported earlier¹⁰) and acetonitrile for the chloride and bromide.

Experiments with silver(I) nitrate were undertaken by adding bdtp (2 mmol) solved in hot (40–50 °C) tetrahydrofuran (thf) (20 cm³) to silver(I) nitrate (2 mmol) in hot methanol (20 cm³). After cooling and reducing the volume of the solvent by 50%, white crystals precipitated. In the case of silver(I) tetrafluoroborate (light sensitive) the solvents acetonitrile and methanol were used. The glassware was wrapped with aluminium foil to prevent light-induced decomposition.

Characterization Procedures.—Metal contents were determined by ethylenediaminetetraacetate (edta) titration, after

Table 4 Fractional coordinates ($\times 10^5$ for Cu and Br, $\times 10^4$ for others) of the non-hydrogen atoms of Cu(bdtp)Br with e.s.d.s in parentheses

Atom	x	y	z
Cu(1)	32 591(11)	19 404(7)	22 156(7)
Br(1)	14 922(11)	15 872(7)	33 619(7)
S(1)	3 998(2)	3 561(1)	2 783(1)
N(11)	2 872(7)	3 293(4)	503(4)
N(12)	2 219(6)	2 505(4)	853(4)
C(13)	786(8)	2 563(6)	444(5)
C(14)	528(9)	3 378(6)	-141(6)
C(15)	1 884(9)	3 825(6)	-92(5)
C(16)	-277(8)	1 783(6)	615(5)
C(17)	2 301(9)	4 742(6)	-546(6)
C(18)	4 465(7)	3 443(5)	803(5)
C(19)	4 797(8)	4 051(5)	1 744(5)
N(21)	4 556(6)	117(4)	1 559(4)
N(22)	4 862(6)	990(4)	2 007(4)
C(23)	6 347(8)	1 089(5)	2 028(5)
C(24)	6 960(8)	314(5)	1 602(5)
C(25)	5 810(8)	-306(5)	1 309(4)
C(26)	7 109(8)	1 967(5)	2 477(6)
C(27)	5 776(8)	-1 250(5)	799(5)
C(28)	3 032(7)	-274(5)	1 475(5)
C(29)	2 859(7)	-876(5)	2 375(5)

Table 5 Selected bond lengths (Å) and angles ($^\circ$) of Cu(bdtp)Br with e.s.d.s in parentheses

Cu(1)-Br(1)	2.432(1)	Cu(1)-N(12)	2.120(5)
Cu(1)-S(1)	2.461(2)	Cu(1)-N(22)	2.014(5)
Br(1)-Cu(1)-S(1)	99.07(6)	N(12)-Cu(1)-N(22)	111.3(2)
Br(1)-Cu(1)-N(12)	113.0(2)	Cu(1)-S(1)-C(19)	102.8(2)
Br(1)-Cu(1)-N(22)	120.2(2)	Cu(1)-S(1)-C(29)	99.0(2)
S(1)-Cu(1)-N(12)	90.1(2)	C(19)-S(1)-C(29)	101.4(3)
S(1)-Cu(1)-N(22)	119.0(2)		

Table 6 Fractional coordinates ($\times 10^5$ for Ag and S, $\times 10^4$ for others) of the non-hydrogen atoms of Ag(bdtp)(NO₃) with e.s.d.s in parentheses

Atom	x	y	z
Ag(1)	16 984(3)	36 276(6)	82 596(5)
S(1)	23 273(5)	10 621(23)	81 314(18)
N(11)	4 067(2)	723(5)	9 038(4)
N(12)	4 101(2)	156(5)	7 926(4)
C(13)	4 614(3)	953(7)	7 556(5)
C(14)	4 912(3)	2 039(7)	8 440(6)
C(15)	4 558(3)	1 867(6)	9 366(5)
C(16)	4 806(4)	590(8)	6 362(6)
C(17)	4 651(3)	2 712(7)	10 557(6)
C(18)	3 587(3)	53(7)	9 757(5)
C(19)	2 891(3)	939(7)	9 690(5)
N(21)	1 122(2)	877(6)	9 826(4)
N(22)	1 339(2)	2 347(6)	10 014(4)
C(23)	1 526(3)	2 487(8)	11 239(6)
C(24)	1 422(3)	1 131(8)	11 802(6)
C(25)	1 175(3)	118(8)	10 896(7)
C(26)	1 805(4)	3 962(8)	11 816(6)
C(27)	978(4)	-1 522(7)	10 951(7)
C(28)	955(3)	290(7)	8 575(5)
C(29)	1 615(3)	-314(7)	8 158(5)
N(31)	2 900(4)	5 891(8)	9 835(5)
O(32)	2 861(3)	4 521(6)	9 665(5)
O(33)	3 533(4)	6 368(7)	9 959(7)
O(34)	2 407(5)	6 680(8)	9 874(7)

destruction of the compound by heating with concentrated nitric acid.¹² Elemental analysis (C,H,N) was performed by the Microanalytical Laboratory of University College (Dublin). Infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a data station. Samples were prepared as KBr pellets or as Nujol mulls. The VIS/NIR spectra

Table 7 Selected bond lengths (Å) and angles ($^\circ$) of Ag(bdtp)(NO₃) with e.s.d.s in parentheses

Ag(1)-S(1)	2.571(2)	S(1)-C(19)	1.821(5)
Ag(1)-N(22)	2.483(5)	S(1)-C(29)	1.809(6)
Ag(1)-O(32)	2.503(5)	N(31)-O(32)	1.224(8)
Ag(1)···S(1')	3.412(2)	N(31)-O(33)	1.24(1)
Ag(1)-N(12)	2.216(4)	N(31)-O(34)	1.61(1)
S(1)-Ag(1)-N(22)	81.5(1)	C(19)-S(1)-C(29)	102.3(3)
S(1)-Ag(1)-O(32)	88.2(1)	S(1')-Ag(1)-S(1)	103.35(2)
S(1)-Ag(1)-N(12)	139.3(1)	S(1')-Ag(1)-N(12)	72.7(1)
N(22)-Ag(1)-O(32)	90.1(2)	S(1')-Ag(1)-N(22)	156.1(1)
N(22)-Ag(1)-N(12)	118.8(2)	S(1')-Ag(1)-O(32)	67.0(1)
O(32)-Ag(1)-N(12)	123.7(2)	Ag(1)-S(1')-Ag(1')	151.50(6)
Ag(1)-S(1)-C(19)	99.9(2)	Ag(1)-S(1')-C(19)	98.2(2)
Ag(1)-S(1)-C(29)	104.0(2)	Ag(1)-S(1')-C(29)	93.2(2)

Primed atoms related to unprimed ones by the symmetry operation $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

were recorded on a Perkin-Elmer 330 spectrophotometer in the diffuse reflectance mode with MgO as reference. X-Ray powder patterns were collected on a Guinier-De Wolff type camera, using Cu-K α radiation. Proton NMR spectra were recorded on a JEOL JNM-FX 200 spectrometer (200 MHz, Fourier transform), X-band EPR spectra of powdered samples on a Varian E3 spectrophotometer at liquid-nitrogen temperature. Magnetic susceptibility measurements of Cu(bdtp)(F)(BF₄) (290–5.5 K) were performed on a Manics DSM8 magnetometer, equipped with a data station.

X-Ray Single-crystal Structure Determinations.—Suitable single crystals were isolated from the reaction mixtures. Crystal data for the compounds [Co(bdtp)(NO₃)₂], Cu(bdtp)Br and Ag(bdtp)(NO₃) are collected in Table 1. Scattering factors and anomalous dispersion corrections were taken from ref. 13. The procedure used for the crystal structure determinations was the same for the three crystals.

The positions of the heavy atoms were found using the Patterson function. The coordinates of the remaining non-hydrogen atoms were determined using Fourier difference maps. The coordinates of the hydrogen atoms were calculated at 0.95 Å from the parent atom, and coupled to the parent atom during the refinement. The model was refined using a locally developed least-squares program, using anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. An absorption correction was applied using the program DIFABS.¹⁴ Fractional coordinates of the non-hydrogen atoms and selected bond lengths and bond angles are collected in Tables 2–7.

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

Results

Characterization data for the co-ordination compounds obtained with bdtp are collected in Table 8. The elemental analyses are in good agreement with the formulations. All compounds have a metal-to-ligand ratio of 1:1. Experiments designed to obtain 1:2 compounds using an excess of ligand resulted solely in the formation of 1:1 compounds.

The compounds [Co(bdtp)(NCS)₂] and [Zn(bdtp)(NCS)₂] have similar infrared spectra and X-ray powder patterns, indicating very similar structures and co-ordinating geometries. The ligand-field spectrum of [Co(bdtp)(NCS)₂] clearly shows the presence of a five-co-ordinated cobalt(II) species.¹⁵ The C–N stretch in the infrared spectra of these two compounds (2060 and 2080, and 2080 and 2090 cm⁻¹, respectively) is in accord with the thiocyanate anions co-ordinating through their nitro-

Table 8 Characterization data (calculated values in parentheses) for co-ordination compounds with bdtP

Compound	Colour	M.p./°C	% M	Electronic bands (10^3 cm^{-1})
[Co(bdtP)(NCS) ₂] ^a	Purple	233	12.9 (13.0)	18.4, 16.7, 12.4, 5.9
[Zn(bdtP)(NCS) ₂]	White	152	14.1 (14.2)	
[Ni(bdtP)(NCS) ₂ (H ₂ O)]	Green	207	12.4 (12.5)	25.7, 16.2, 9.5
Cu(bdtP)(F)(BF ₄) ^b	Green	210 (decomp.)	14.1 (14.2)	26.2, 14.2
Co(bdtP)Cl ₂	Blue	235	14.1 (14.4)	23.0 (sh), 17.2, 15.4
Zn(bdtP)Cl ₂ ·0.5EtOH ^c	White	196	14.6 (14.9)	
Cu(bdtP)Cl ₂	Green	215	14.7 (15.4)	16.6, 18.7
[Co(bdtP)(NO ₃) ₂]	Purple	188	12.6 (12.8)	20.5 (sh), 18.4, 16.0 (sh), 8.0
Cu(bdtP)(NO ₃) ₂	Green	175	13.5 (13.6)	24.9, 13.8, 9.9
Cu(bdtP)Br ^d	White	156	15.0 (15.1)	
Cu(bdtP)Cl	White	135	16.9 (16.8)	
[Cu(bdtP)]BF ₄ ·H ₂ O ^e	White	> 260	14.7 (14.3)	
Ag(bdtP)(NO ₃)	White	153	24.2 (24.6)	

^a Infrared and X-ray powder pattern isomorphous with [Zn(bdtP)(NCS)₂]. ^b C, 37.2 (37.55); H, 5.00 (4.95); F, 19.7 (21.2); N, 12.40 (12.50%). ^c C, 40.80 (41.15); H, 5.50 (5.75); N, 12.65 (12.80); O, 2.00 (1.85%). ^d Infrared and X-ray powder pattern isomorphous with Cu(bdtP)Cl. ^e C, 38.20 (37.65); H, 5.20 (5.40); N, 12.65 (12.55%).

gen atoms.¹⁶ Thus, they most likely contain a $\text{MN}_2\text{SN}'_2$ chromophore. The corresponding nickel compound must be formulated with an additional water molecule, [Ni(bdtP)(NCS)₂(H₂O)]. From infrared spectroscopy it is deduced that this molecule is co-ordinated (sharp OH stretch at 3450 cm^{-1}), and that the thiocyanate anions co-ordinate through their nitrogen atoms¹⁶ (C–N stretch 2100 cm^{-1}). The ligand-field spectrum is in good agreement with a six-co-ordinated nickel(II) high-spin species,¹⁵ indicating a $\text{NiN}_2\text{SON}'_2$ chromophore.

Elemental analysis of the compound of bdtP with copper(II) tetrafluoroborate shows that decomposition of the tetrafluoroborate anion has taken place, resulting in the formulation Cu(bdtP)(F)(BF₄). The infrared spectrum does not show vibrations at 750 and 350 cm^{-1} , thus strongly suggesting that the tetrafluoroborate anion is not co-ordinated.¹⁷ EPR spectroscopy, at room and liquid-nitrogen temperature, shows an axial-type spectrum ($g_{\parallel} = 2.29$ and $g_{\perp} = 2.06$) with no half-field signal. Magnetic susceptibility measurements are in good agreement with a normal copper(II) co-ordination compound showing no interaction between the copper atoms. Thus it is not likely that a dinuclear copper unit, with bridging fluorides, is present.

The compound Co(bdtP)Cl₂ shows a ligand-field spectrum corresponding to a cobalt(II) species co-ordinated by four donors in a tetrahedral fashion.¹⁵ This chromophore is most likely CoN_2Cl_2 as encountered earlier.^{4,6} The corresponding zinc compound contains half a molecule of ethanol in the crystal lattice, as confirmed by ¹H NMR spectroscopy and elemental analysis, but the co-ordination geometry cannot be deduced using infrared and ligand-field spectroscopy. The infrared spectrum of Cu(bdtP)Cl₂ shows a band at 310 cm^{-1} assigned to the Cu–Cl vibration.

With nitrate two co-ordination compounds were obtained, *viz.* [Co(bdtP)(NO₃)₂] and Cu(bdtP)(NO₃)₂. The X-ray structure of [Co(bdtP)(NO₃)₂] (see below) shows that the nitrate anions co-ordinate in different ways, *i.e.* one is monodentate and the other didentate. The infrared spectrum of the copper(II) compound when compared shows a different pattern to the cobalt(II) compound, in the 1700 – 1800 cm^{-1} region. Although the interpretation of nitrate combination bands is not unambiguous,^{16,18,19} the pattern suggests monodentate nitrate anions.

The reaction of copper(II) bromide with bdtP resulted in the isolation of a copper(I) co-ordination compound, with the formula [Cu₄(bdtP)₂Br₄]. This compound and its X-ray single-crystal structure has been described elsewhere.⁹ Experiments starting from copper(I) bromide resulted not only in the reproduction of this tetranuclear compound but also in the synthesis of a compound with a different metal-to-bromide

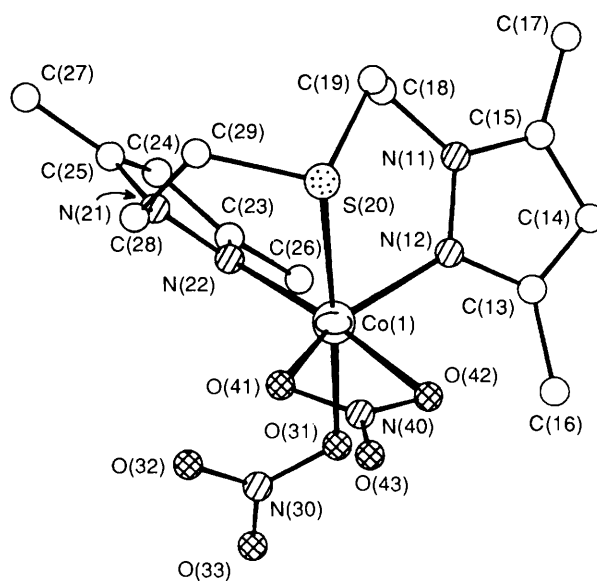


Fig. 1 A PLUTO²⁰ projection of [Co(bdtP)(NO₃)₂]. Hydrogen atoms omitted for clarity

ratio. An X-ray single-crystal structure of this latter compound, Cu(bdtP)Br, is described below. The compounds Cu(bdtP)Cl and Cu(bdtP)Br have identical infrared spectra and X-ray powder patterns, thus both compounds must be structurally isomorphous.

Using [Cu(MeCN)₄]BF₄ as starting material the compound [Cu(bdtP)]BF₄·H₂O, according to elemental analysis and infrared spectroscopy, was obtained. The infrared spectrum shows the symmetric and asymmetric H–O stretch of a non-co-ordinate water molecule (3550 and 3640 cm^{-1}), most likely occupying a cavity in the crystal lattice. No vibrations were observed near 750 or 350 cm^{-1} , which indicates that the tetrafluoroborate anion is neither involved in a strong hydrogen bridge, nor in co-ordination to the copper(I).¹⁷

The experiments with silver(I) resulted in the isolation of the compound Ag(bdtP)(NO₃), for which the X-ray single-crystal structure is described below.

Crystal Structures.—[Co(bdtP)(NO₃)₂]. The structure of this compound consists of monomeric [Co(bdtP)(NO₃)₂] units (see Fig. 1), packed according to normal van der Waals forces. The cobalt(II) atom is co-ordinated by the three ligand donors, *viz.* two pyrazole nitrogens and one thioether sulfur, and two nitrate anions. One nitrate anion is monodentate [Cu–O $2.062(3) \text{ \AA}$] and the other is didentate [Cu–O $2.180(3)$ and $2.249(3) \text{ \AA}$]. The

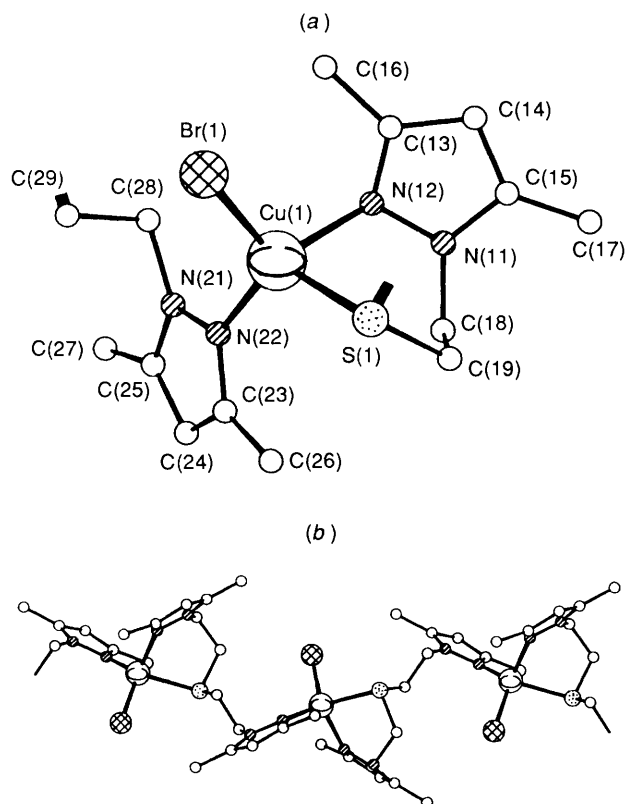


Fig. 2 PLUTO²⁰ drawings of Cu(bdtp)Br: (a) the asymmetric unit showing the co-ordination geometry and the labelling scheme used; (b) several asymmetric units, showing the polymeric nature of the compound. Hydrogen atoms omitted for clarity

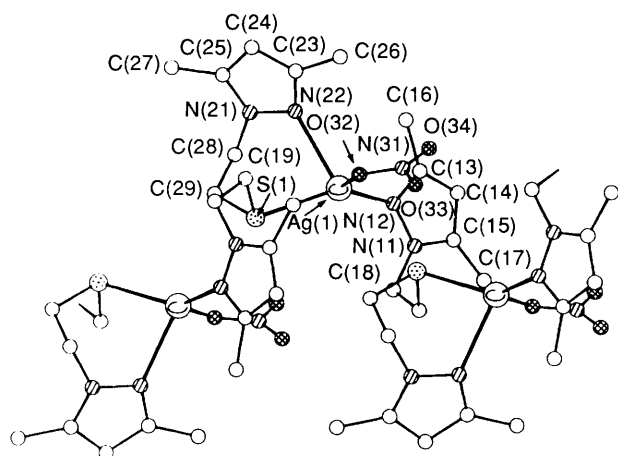


Fig. 3 A PLUTO²⁰ drawing of several asymmetric units of Ag(bdtp)(NO₃) showing both the labelling scheme and the polymeric nature of the compound. Hydrogen atoms omitted for clarity

Co–N bond lengths [2.072(3) and 2.083(3) Å] and the Co–S bond length [2.584(1) Å] can be regarded as normal.²¹ The co-ordination geometry is distorted octahedral, as can be deduced from the bond angles collected in Table 3. The angles at cobalt(II) formed by the ligand bites are 86.54(9) and 88.9(1)°, which is close to the ideal octahedral geometry. This is most likely due to the large bite of the ligand, *i.e.* capable of forming six-membered chelate rings.

Cu(bdtp)Br. The structure of Cu(bdtp)Br is illustrated in Fig. 2 which shows the labelling scheme and co-ordination geometry (a) and the polymeric nature of the compound (b). The co-ordination environment of the copper(I) atom is made up by two pyrazole nitrogens [2.120(5) and 2.014(5) Å], one thioether

[2.461(2) Å] and one bromide [2.432(1) Å] (see Table 5). The bond lengths can be regarded as normal for this type of compound. The two nitrogen donors do not originate from the same ligand. The polymeric nature of Cu(bdtp)Br is thus generated by the ligand, which acts as a link between two successive copper centres along the chain. Inspection of the crystal packing of the chains did not reveal other than normal van der Waals contacts. The co-ordination geometry is distorted tetrahedral, as can be deduced from the bond angles in Table 5. The nitrogen–thioether bite of the ligand, forming a six-membered chelate ring, is 90.1(2)°, which is similar to the corresponding bite in [Co(bdtp)(NO₃)₂]. Although the nitrogen–thioether bite forms a six-membered chelate ring, the actual bond angle at the copper(I) atom (*ca.* 90°) may still be too small to allow for tetrahedral co-ordination of bdtp with all three donors to one copper(I) atom.

Ag(bdtp)(NO₃). The structure of Ag(bdtp)(NO₃) is similar to that of Cu(bdtp)Br, and also consists of a polymeric chain (Fig. 3). The polymeric nature of this compound is generated by the same mechanism as found for Cu(bdtp)Br: the two nitrogen donors to Ag(I) do not originate from the same ligand; the ligand acts as a link between two successive silver centres. The silver(I) atoms are co-ordinated by two nitrogens [2.483(5) and 2.216(4) Å], one thioether [2.571(2) Å] and a monodentate nitrate anion [2.503(5) Å] (see Table 7). The bond lengths can be regarded as normal for silver(I) compounds.²¹ The symmetry-related thioether S(1') is located 3.412(2) Å from the silver(I) atom, but this distance cannot be regarded as co-ordinating or semi-co-ordinating. The co-ordination geometry of the silver(I) atom is very distorted tetrahedral (see Table 7). The ligand bite formed by the nitrogen–thioether donor functions of the ligand is only 81.5(1)°. This angle is smaller than was found for [Co(bdtp)(NO₃)₂] and Cu(bdtp)Br, and this is clearly due to the greater size of the silver(I) compared to cobalt(II) and copper(I). Investigation of intermolecular distances does not reveal other than normal van der Waals contacts between the polymeric chains.

Discussion

The results described above show that the ligand bdtp is capable of forming co-ordination compounds with first-row transition-metal salts and silver(I) nitrate. The copper(I) compounds are air-stable. The ligand forms many different types of chromophores. The thioether donor function most likely co-ordinates to the metal in all compounds, except for Co(bdtp)Cl₂.

In all cases, except for the tetranuclear copper(I) complex [Cu₄(bdtp)₂Br₄], the metal-to-ligand ratio is 1:1. This suggests that co-ordination of two bdtp molecules to one metal induces too much steric hindrance, possibly originating from the methyl groups at the pyrazole ring. When the ligand bdtp reacts with copper(II) tetrafluoroborate decomposition of the tetrafluoroborate anion takes place. This process generates additional fluorides capable of acting as a donor. Since [Cu(bdtp)₂]²⁺ is not readily formed and one bdtp molecule only offers three donors, this mechanism may have taken place in order to attain the necessary number of donors.

The structure of [Co(bdtp)(NO₃)₂] shows that the ligand forms a tridentate chelate. The bites formed by the ligand donors are close to perfect octahedral geometry. The structure of Cu(bdtp)Br shows that the ligand does not form a tridentate chelate, and that the bite is also close to 90°. This suggests that the maximum angle at a copper(I) atom is approximately 90°, and that in the case of tridentate chelation of bdtp the distortion from tetrahedral geometry may be too large to yield a stable conformation. The conformation of the ligand in Cu(bdtp)Br and Ag(bdtp)(NO₃) is very similar, indicating that it must be energetically favourable for adaption to tetrahedral co-ordination. Sorrell and Malachowski¹⁰ reported the crystal structure of a copper(I) tetrafluoroborate compound with the ligand bis[2-(3,5-dimethylpyrazol-1-yl)ethyl] ether, the oxygen

analogue of bdtf. The structure shows a copper(I) atom coordinated in a T-shaped fashion.¹⁰ The bites in this compound are somewhat greater than 90° [94.05(17) and 95.91(18)°], but this most likely originates from the smaller size of the ether oxygen, compared to thioether sulfur. The same T-shaped coordination geometry is also found in the corresponding compound with 2,2'-bis[(*N*-propylbenzimidazol-2-yl)]diethyl sulfide reported by Dagdigian *et al.*²² These two ligands form a six-membered chelate ring similar to that of bdtf. The coordination compounds described in this report, together with the two related crystal structures,^{10,22} strongly suggest that this type of ligand, *viz.* N₂S(O) combined with six-membered chelate rings, is unable to form tridentate chelates towards tetrahedral copper(I) atoms.

Sorrell and Malachowski¹⁰ reported the synthesis of Cu(bdtf)BF₄ using acetonitrile and propan-2-ol as solvents. Our method, using methanol as solvent, results in the presence of an additional water molecule. Infrared spectroscopy indicates that this molecule is neither co-ordinated nor hydrogen bonded, and, therefore, must most likely be situated in a cavity in the crystal lattice. Taking into account the above-mentioned coordination behaviour of bdtf and related ligands, it is not unlikely that a T-shaped co-ordination geometry is also present in this compound.

Acknowledgements

We thank Mr. S. Gorter for the collection of the diffraction data and Mrs. P. J. van Koningsbruggen and Mrs. M. I. de Heer for the magnetic susceptibility measurements.

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Received 26th July 1991; Paper 1/03833H