Unusual Chelating Properties of the Ligand 1,8-Bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo). Crystal Structures of $Ni(bddo)(NCS)_2$, $Zn(bddo)(NCS)_2$ and $Cd_2(bddo)(NCS)_4$†

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The synthesis and characterization of the ligand 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) and its co-ordination compounds with zinc, cobalt, nickel, and cadmium thiocyanate are described. The general formula is $M(bddo)(NCS)_2$ with M = Ni, Co, or Zn. With cadmium, $Cd_2(bddo)(NCS)_4$ was found. *X*-Ray structure determinations were performed on crystals of the compounds $Zn(bddo)(NCS)_2$, $Ni(bddo)(NCS)_2$, and $Cd_2(bddo)(NCS)_4$. The cobalt compound was found to be isomorphous to the zinc compound. The compound $Zn(bddo)(NCS)_2$ crystallizes from ethanol in the orthorhombic space group *Pbcn* with unit-cell dimensions a = 9.521(1), b = 14.835(5), c = 16.840(4) Å, for Z = 4. The structure was refined to R = 0.058 and R' = 0.069 for 1 072 unique reflections with $I > 2\sigma(I)$. The compound consists of chains of zinc atoms linked by ligand molecules. The zinc ion is tetrahedrally co-ordinated by two pyrazole nitrogen atoms and two thiocyanate nitrogen atoms. The sulphur atoms of the ligand bddo do not co-ordinate. The compound $Ni(bddo)(NCS)_2$ crystallizes from ethanol in the tetragonal space group $P4_12_12$ with a = 9.370(3), c = 26.524(7) Å, for Z = 4. The structure was refined to R = 0.041 and R' = 0.034 for 1 441 unique reflections with $I > 3\sigma(I)$. The compound consists of monomeric units of octahedral nickel(II) ions with a *trans,cis,cis*-$NiN_2N'_2S_2$ chromophore. The compound $Cd_2(bddo)(NCS)_4$ crystallizes from ethanol in the triclinic space group $P\bar{1}$ with a = 8.695(3), b = 9.083(5), c = 10.008(3) Å, α = 91.10(3), β = 99.34(3), γ = 108.23(2)°, for Z = 1. The structure was refined to R = 0.029 and R' = 0.033 for 2 794 unique reflections with $I > 3\sigma(I)$. The cadmium ions are octahedrally co-ordinated with a $CdNSN'_2S'_2$ chromophore. Each cadmium ion is linked to two other cadmium ions by double thiocyanate bridges and to a third cadmium ion by one ligand molecule in such a manner that a two-dimensional structure results.

Chelating ligands with a possibility to generate an MN_2S_2 chromphore have been of increasing interest in recent years[1,2] for a variety of reasons. On one hand synthetic analogues for the active site of blue copper proteins (and metallo substituted derivatives) have stimulated the design, synthesis, and study of azole–thioether chelating ligands. On the other hand an interest had developed towards chelating ligands containing a weak donor (sulphur) and a strong donor (nitrogen).

Early results have indicated that thioether sulphur atoms can be forced to chelate to metal ions,[3,4] whereas such donor atoms as such do hardly bind to metal ions. An important parameter seems to be the chelate ring size and therefore we have set up a programme towards a set of ligands containing the N_2S_2 donor set, with pyrazoles and imidazoles as the N donor and thioether as the S donor.

The first example of such a new ligand is 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (abbreviated as bddo). Molecular models of this ligand suggest that a tetrahedral MN_2S_2 chromophore can be formed. To obtain more insight into the co-ordination geometries the ligand could adopt, we have studied co-ordination compounds of bddo with transition-metal salts. In this paper we report the results obtained using zinc(II), cobalt(II), nickel(II), and cadmium(II) thiocyanate. Because of the unusual spectral properties of these compounds an *X*-ray study of $Zn(bddo)(NCS)_2$, $Ni(bddo)(NCS)_2$, and $Cd_2(bddo)(NCS)_4$ was undertaken. A future study will deal with metal salts of other anions.

Results and Discussion

General and Spectroscopy.—The compounds obtained with cobalt(II), nickel(II) and zinc(II) thiocyanate are formulated as $M(bddo)(NCS)_2$ with M = Co, Ni, or Zn, while cadmium thiocyanate forms the compound $Cd_2(bddo)(NCS)_4$. Analytical results for the four co-ordination compounds were satisfactory (Table 1). Colours, melting points, structural and i.r. classifications, and electronic absorption maxima are also collected in Table 1. The i.r. spectra of the compounds with M = Co and Zn are almost identical, as are their *X*-ray powder diffraction patterns, indicating a very similar structure for the two compounds. The electronic spectra of $Ni(bddo)(NCS)_2$ and $Co(bddo)(NCS)_2$ show, respectively, typical octahedral and tetrahedral features.[5] The i.r. spectra of the co-ordination compounds clearly show the presence of the thiocyanate anion and the ligand bddo. The C–N stretching frequency of the thiocyanate anion occurs below 2 100 cm^{-1} in case of M = Ni, Co, or Zn (respectively 2 090, 2 060, and 2 060 cm^{-1}) and above 2 100 cm^{-1} for M = Cd (2 120 cm^{-1}). This indicates that for the compounds with Ni, Co, and Zn the thiocyanate anion is co-ordinating through its nitrogen atom, and that for the cadmium compound a bridging mode through N, S is suggested.[6]

Description of the Structures.—$Zn(bddo)(NCS)_2$. The struc-

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

Table 1. Colours, *X*-ray and i.r. structural classifications, and electronic absorption maxima of the co-ordination compounds of bddo

Compound	Colour	M.p./°C	Analysis[a]/%		I.r.[b]	*X*-Ray[c]	Ligand field bands (10^3 cm^{-1})
			M	S			
$Co(bddo)(NCS)_2$[d]	Blue	199	11.5 (11.4)	24.8 (25.0)	A	I	17.4 (sh), 16.0, 8.0
$Ni(bddo)(NCS)_2$	Green	242 (decomp.)	11.6 (11.4)	24.6 (25.0)	B	II	25.3, 15.5, 9.4
$Zn(bddo)(NCS)_2$	White	205	12.7 (12.6)	24.3 (24.7)	A	I	
$Cd_2(bddo)(NCS)_4$	White	230 (decomp.)	28.3 (28.3)	23.9 (24.2)	C	III	

[a] Calculated values in parentheses; M and S analysis according to ref. 16. [b] Isomorphism based on i.r. spectra. [c] Structural isomorphism based on powder diffraction patterns. [d] C, 43.10 (43.20); H, 5.20 (5.35); N, 15.75 (15.90%); by University College Dublin.

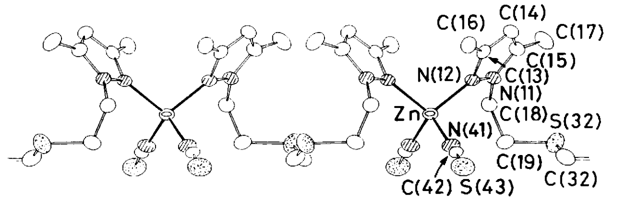


Figure 1. ORTEP drawing of $Zn(bddo)(NCS)_2$ with the atom-labelling scheme. Hydrogen atoms are omitted for clarity. Atoms are represented by their ellipsoids at the 50% probability level

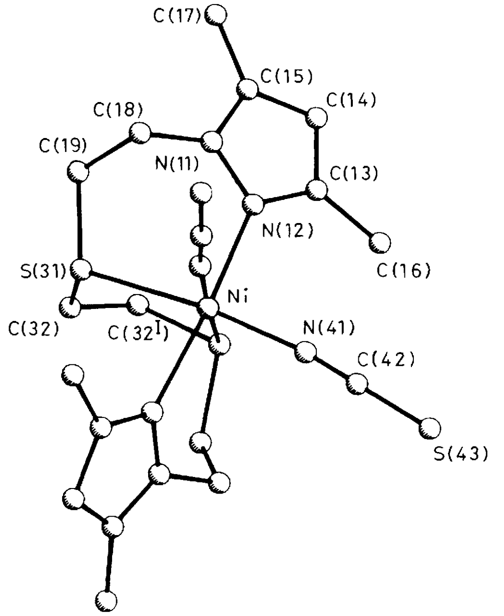


Figure 2. PLUTO drawing of $Ni(bddo)(NCS)_2$ with the atom-labelling scheme. Hydrogen atoms are omitted for clarity

ture of this compound (see Figure 1) consists of chains of zinc ions linked by the ligand molecules. The chains are parallel to the *a* axis and have normal van der Waals contacts. The zinc ions lie on a two-fold axis resulting in an asymmetric unit equal to half a formula unit. The zinc ion is co-ordinated by four N atoms: two N atoms of the pyrazole units and two N atoms of the thiocyanate anions in a tetrahedral geometry. The Zn^{II} to pyrazole N and thiocyanate N distances are 2.016(6) and 2.018(8) Å respectively, which can be regarded as normal.[3,7] The sulphur atoms do not participate in the co-ordination. The ethylene bridge between the two sulphur atoms of the ligand is disordered. A satisfactory description of this disorder is found in an equal occupancy of two positional configurations. There is also a slight disorder in the position of thiocyanate anion, which is limited, remarkably, to the nitrogen and sulphur atoms of the anion.

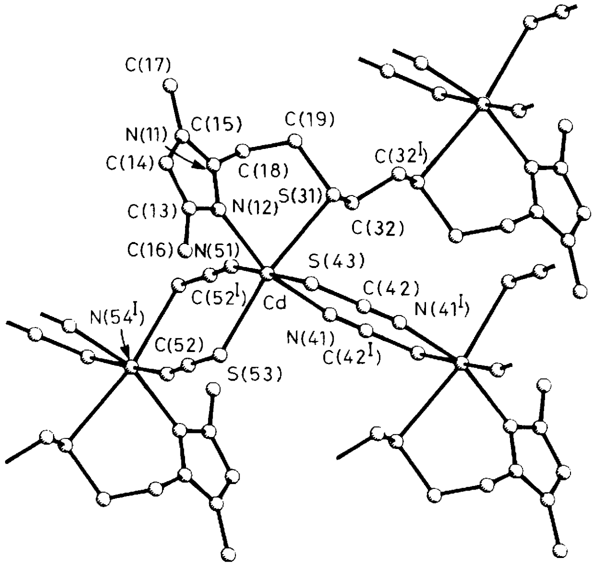


Figure 3. PLUTO drawing of $Cd_2(bddo)(NCS)_4$ with the atom-labelling scheme. Hydrogen atoms are omitted for clarity

$Ni(bddo)(NCS)_2$. The nickel ion is in a distorted octahedral $N_2N'_2S_2$ geometry (see Figure 2). The nickel ion and the centre of the ethylene bridge lie on a two-fold axis, so the asymmetric unit consists of half the formula unit. The ligand co-ordinates through two pyrazole N atoms in a *trans* position and the two S atoms in a *cis* position. The thiocyanate anions co-ordinate through their N atoms in a *cis* position. The distortion from octahedral symmetry is not very large considering that the relevant angles lie between 85.1 and 96.7°. The Ni–N(12) distance [2.193(4) Å] is slightly, but not exceptionally, longer than normal.[8–10] The other bonding distances can be regarded as normal.[11,12] The packing of the co-ordination units in the crystal lattice proceeds *via* normal van der Waals contacts.

$Cd_2(bddo)(NCS)_4$. The cadmium ions are chained together by double thiocyanate bridges, these chains being further linked together by ligand molecules, forming a two-dimensional sheet structure. The sheets are parallel to the *a,c* plane (see Figures 3 and 4). Each cadmium ion (see Figure 3) is co-ordinated by three N and three S atoms in a fashion close to octahedral. The co-ordination distances can be regarded as normal for a cadmium compound.[13] The co-ordination angle of the thiocyanates to the metal ion is in the case of S co-ordination (Cd–S–C) close to 90° [97.0(1) and 102.1(1)°] and in the case of N co-ordination close to 180° [165.6(3) and 162.3(3)°].

This type of co-ordination of cadmium is not extraordinary.[14,15] Examples of double thiocyanate bridges with cadmium atoms are present in the literature, *catena*-di-μ-thiocyanato-*N*,*S*-bis(1*H*-1,2,4-triazole-N^4)cadmium, reported by Haasnoot *et al.*,[14] shows a two-dimensional sheet structure, where cadmium

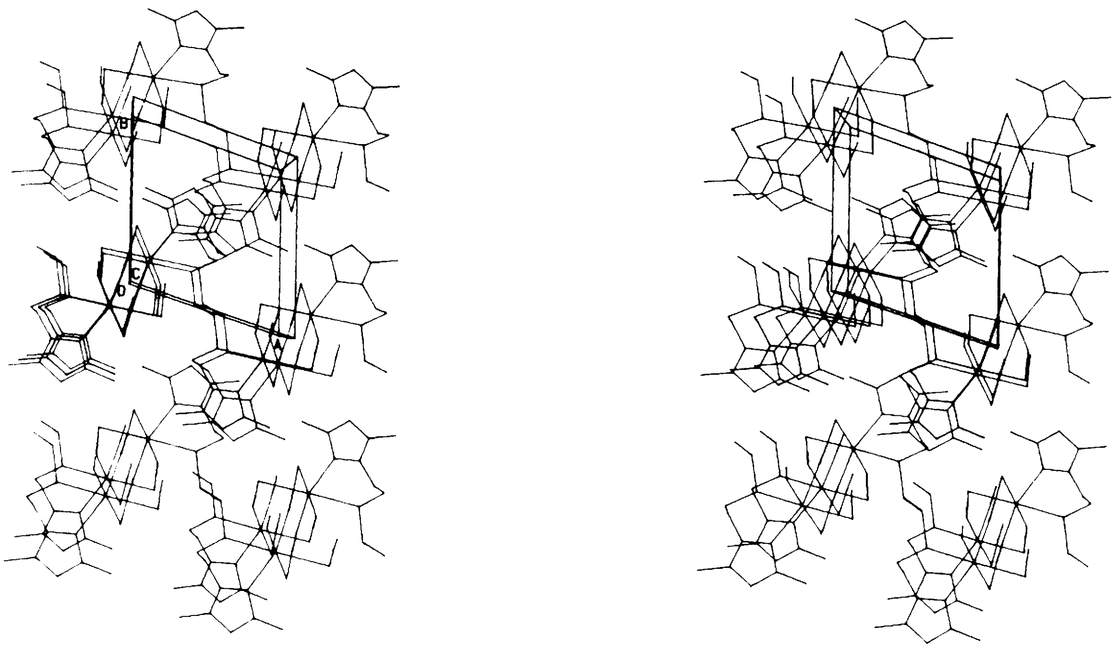
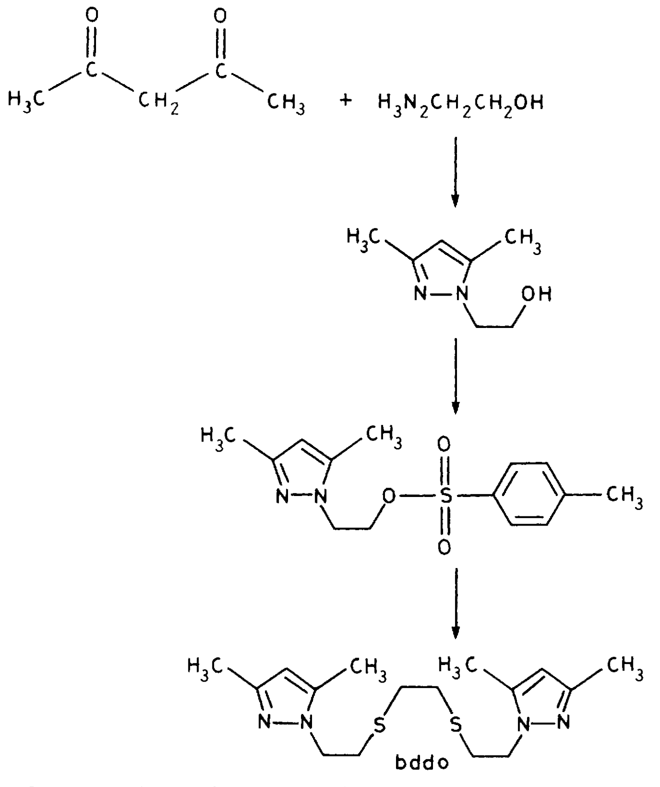


Figure 4. Stereoview of $Cd_2(bddo)(NCS)_4$



Scheme. Synthesis of 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo)

atoms are linked by strong hydrogen bridges between two ligand molecules. In that example the packing of the sheets is determined by additional weak hydrogen bridges and van der Waals forces. In the case of $Cd_2(bddo)(NCS)_4$ the sheets are connected only by van der Waals forces.

Conclusions

The potential quadridentate ligand bddo shows a remarkable flexibility in its co-ordination behaviour towards the thiocyanates of zinc, cobalt, nickel, and cadmium. In the compounds $Zn(bddo)(NCS)_2$ and $Co(bddo)(NCS)_2$ the thioether functions do not co-ordinate, whereas they do in the nickel compound. Considering the configuration of the ligand in the compounds $Ni(bddo)(NCS)_2$ and $Cd_2(bddo)(NCS)_4$ it is not likely that steric factors prevent the ligand bddo from co-ordinating in a quadridentate chelating N_2S_2 fashion.

An $N_2N'_2S_2$ octahedral co-ordination of nickel(II) thiocyanate by a related N_2S_2 ligand has been reported by Bouwman *et al.*[4] That ligand, 1,6-bis(4-imidazolyl)-2,5-dithiahexane (abbreviated bidhx), contains imidazolyl instead of pyrazolyl groups. The bite between the thioether donor and the nitrogen donor of the azolyl ring is one methylene unit greater in the case of bddo than with bidhx. This difference results in a greater bond angle, respectively 92 and 80.5°, and a much smaller distortion from octahedral geometry. The metal–donor distances in the compounds $Ni(bddo)(NCS)_2$ and $Ni(bidhx)(NCS)_2$ are similar.

Considering the structures of the zinc and cadmium compounds, the relatively large bite may be the origin of the opening up of the chelate ring. As, apparently, steric factors are not involved, the donor strength of the thioether S atoms may be too weak to impose a quadridentate co-ordination with the thiocyanates of Zn and Co.

Experimental

Synthesis and Characterisation of the Ligand.—The synthesis of bddo is depicted in the Scheme. All reagents were commercially available and were of sufficient purity. Proton n.m.r. spectra were recorded on a JEOL PS-100 instrument at 99.5 MHz, with $SiMe_4$ as internal standard.

N-(2-*Hydroxyethyl*)-3,5-*dimethylpyrazole*. A solution of 2-hydroxyethylhydrazine (109 g) in absolute ethanol (100 cm^3) was added dropwise to a stirred solution of 2,4-pentanedione (140 g) in absolute ethanol (300 cm^3). The temperature of the reaction mixture was kept below 15 °C with an ice–salt mixture. After the addition of the hydrazine the reaction mixture was allowed to warm to room temperature and stirred for another 30 min. The solvent was then removed at low pressure. Diethyl ether (*ca.* 250 cm^3) was added to the resulting yellow oil, and

Table 2. Crystal data for Zn(bddo)$(NCS)_2$ (**1**), Ni(bddo)$(NCS)_2$ (**2**), and Cd_2(bddo)$(NCS)_4$ (**3**)

	(1)	(2)	(3)
Formula	$C_{18}H_{26}N_6S_4Zn$	$C_{18}H_{26}N_6NiS_4$	$C_{20}H_{26}Cd_2N_8S_6$
M	520.08	513.39	795.67
Space group	$Pbcn$	$P4_12_12$	$P\bar{1}$
a/Å	9.521(1)	9.370(3)	8.695(3)
b/Å	14.835(5)	9.370(3)	9.083(5)
c/Å	16.840(4)	26.524(7)	10.008(3)
α/°	90	90	91.10(3)
β/°	90	90	99.34(3)
γ/°	90	90	108.23(2)
U/Å^3	2 378	2 329	738.7
Z	4	4	1
D_c/g cm^{-3}	1.45	1.464	1.788
Crystal size/mm	0.15 × 0.18 × 0.50	0.10 × 0.20 × 0.20	0.20 × 0.30 × 0.30
μ(Mo-K_α) cm^{-1}	14.17	12.1	18.2
Lorentz and polarization correction applied	Yes	Yes	Yes
Absorption correction applied	No	No	Yes (φ scan)
F(000)	1 083	1 072	394
Diffractometer	CAD4	Nicolet P3	Nicolet P3
Radiation (λ/Å)	0.710 73	0.710 69	0.710 69
Orientation reflection	24	18	18
2θ range/°	9.99—11.88	8.4—21.8	9.5—24.6
Temperature/°C	22	20	20
Scan method	ω—θ	ω—θ	ω—θ
Data collection range/°	2—25	2—25	2—27
Range h	−11 to 11	−7 to 7	−11 to 10
k	0—17	0—11	−11 to 11
l	0—20	0—31	0—12
No. of unique data	1 072[a]	1 441[b]	2 794[b]
$R = \Sigma F/\Sigma F_o$	0.058	0.041	0.029
$R' = [\Sigma F^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$	0.069	0.034	0.033

[a] $I > 2\sigma(I)$. [b] $I > 3\sigma(I)$.

after cooling to room temperature the crude product precipitated (153 g, 76%). The purity, checked by n.m.r. spectroscopy, was satisfactory. δ (solvent $CDCl_3$) 5.76 (1 H, s), 4.44 (1 H, br s), 3.92 (4 H, m), and 2.20 (6 H, d).

Tosylation. Acetone (300 cm^3) and water (300 cm^3) were added to a mixture of the above product (60 g) and toluene-*p*-sulphonyl chloride (90 g). While stirring, a solution of NaOH (20.0 g) in water (*ca.* 75 cm^3) was then added dropwise. The temperature of the reaction mixture was kept below 10 °C with an ice–salt mixture. After addition of the base the mixture was heated until about one third of the solvent was evaporated. It was then allowed to cool and was stirred until the tosylated product started to precipitate. The yield, after drying in a desiccator, was 105 g (83%) of *N*-(2-toluene-*p*- sulphonyloxyethyl)-3,5-dimethylpyrazole. The purity was checked by n.m.r. spectroscopy, and found satisfactory for further synthetic purposes. δ (solvent $CDCl_3$) 7.60 (2 H, d), 7.04 (2 H, d), 5.68 (1 H, s), 4.20 (4 H, m), 2.44 (3 H, s), and 2.16 (6 H, d).

Condensation with 1,2-*ethanedithiol.* A mixture of 1,2-ethanedithiol (3.0 g), the above product (20 g) NaOH (3.3 g), and water (*ca.* 100 cm^3) was refluxed and stirred for 5 h. After standing overnight at room temperature, the crude ligand bddo precipitated as a white substance. It was recrystallized from absolute ethanol. The yield after drying *in vacuo* was 8.8 g, m.p. 78 °C. The ligand was characterized by ^{1}H n.m.r. spectroscopy: δ (solvent $CDCl_3$) 5.76 (2 H, s), 4.12 (4 H, t), 2.96 (4 H, t), 2.52 (4 H, s), and 2.24 (12 H, d).

Synthesis and Characterization of the Co-ordination Compounds.—The co-ordination compounds were prepared by adding a hot solution of NH_4SCN (2 mmol) in absolute ethanol (*ca.* 10 cm^3) to a stirred hot solution of bddo (1 mmol) and the appropriate metal(II) nitrate (1 mmol) in absolute ethanol (*ca.* 20 cm^3). Triethyl orthoformate (*ca.* 2 cm^3) was then added for dehydration. Subsequent cooling to room temperature resulted in the crystallization of the co-ordination compounds.

Infrared spectra in the 4 000—300 cm^{-1} range of the ligand bddo and of the co-ordination compounds pelleted in KBr were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a PE data station. Electronic spectra (270—2 000 nm), using the diffuse reflectance method with MgO as reference, were obtained with a PE 330 spectrophotometer, also equipped with a PE data station. *X*-Ray powder diagrams of the compounds were obtained with a Guinier type camera using Cu-K_α radiation. After destruction with nitric acid, metal analyses were carried out complexometrically with ethylenediaminetetra-acetate.[16]

Data Collection and Structure Refinement.—The data collected for the three structures are listed in Table 2. Scattering factors and anomalous dispersion corrections were taken from the literature.[17]

Zn(bddo)$(NCS)_2$. The structure was solved by direct methods and refined by block-matrix least squares calculations using a local set of computer programs on the Leiden University Amdahl V7B computer. A few hydrogen atoms were located from Fourier difference maps; others were placed at 0.95 Å from the parent atoms. The thermal parameters of the hydrogen atoms were refined, while coupled to each other, to a final value of 8.27 Å^2. The positional parameters of the hydrogen atoms were refined with the atoms coupled to their parent atom. The thermal parameters of the non-hydrogen atoms were refined anisotropically. The disordered ethylene bridge between the sulphur atoms of the ligand could best be described by two equally occupied positions C(32) and C(32′). After the last refinement stage there was still some additional electron density close to the sulphur atom of the thiocyanate anion.

Table 3. Fractional co-ordinates (Zn, × 10^5; others, × 10^4) of Zn(bddo)(NCS)$_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Zn	0(0)	45 270(7)	25 000(0)
N(11)	2 413(7)	5 408(4)	1 562(4)
N(12)	1 611(6)	5 356(4)	2 233(4)
C(13)	2 053(8)	6 041(5)	2 696(5)
C(14)	3 099(9)	6 535(6)	2 316(5)
C(15)	3 324(9)	6 113(6)	1 601(6)
C(16)	1 480(11)	6 213(7)	3 507(6)
C(17)	4 359(10)	6 311(7)	959(6)
C(18)	2 250(11)	4 754(6)	939(6)
C(19)	2 855(12)	3 841(7)	1 127(6)
S(31)	4 751(3)	3 817(2)	1 200(1)
C(32)	513(3)	346(1)	220(1)
C(32′)	518(3)	418(1)	220(1)
N(41)	773(10)	3 761(6)	3 389(5)
C(42)	973(10)	3 597(6)	3 894(6)
S(43)	1 237(4)	3 240(2)	4 846(2)

Atoms C(32) and C(32′) describe the disorder in the ethylene bridge. See text for further details.

Table 4. Distances (Å) and angles (°) of Zn(bddo)(NCS)$_2$ with e.s.d.s in parentheses

Zn–N(12)	2.016(6)	C(14)–C(15)	1.37(1)
Zn–N(41)	2.018(8)	C(15)–C(17)	1.49(1)
N(11)–N(12)	1.367(7)	C(18)–C(19)	1.51(1)
N(11)–C(15)	1.360(9)	C(19)–S(31)	1.81(1)
N(11)–C(18)	1.44(1)	S(31)–C(32)	1.81(2)
N(12)–C(13)	1.349(9)	N(41)–C(42)	0.905(9)
C(13)–C(14)	1.39(1)	C(42)–S(43)	1.71(1)
C(13)–C(16)	1.49(1)		
N(12)–Zn–N(41)	103.4(3)	C(13)–C(14)–C(15)	106.0(8)
N(12)–N(11)–C(15)	111.1(6)	N(11)–C(15)–C(14)	107.0(7)
N(12)–N(11)–C(18)	120.3(6)	N(11)–C(15)–C(17)	122.5(8)
C(15)–N(11)–C(18)	128.6(7)	C(14)–C(15)–C(17)	130.5(8)
Zn–N(12)–N(11)	130.1(5)	N(11)–C(18)–C(19)	114.4(8)
Zn–N(12)–C(13)	124.6(5)	C(18)–C(19)–S(31)	114.4(7)
N(11)–N(12)–C(13)	105.1(6)	C(19)–S(31)–C(32)	106(1)
N(12)–C(13)–C(14)	110.8(7)	Zn–N(41)–C(42)	158(1)
N(12)–C(13)–C(16)	123.0(8)	N(41)–C(42)–S(43)	176(1)
C(14)–C(13)–C(16)	126.3(8)		

Table 5. Fractional co-ordinates of Ni(bddo)(NCS)$_2$

Atom	x	y	z
Ni	0.193 5(1)	0.193 5(1)	0.0000
S(43)	0.647 8(2)	0.256 8(2)	0.080 7(1)
S(31)	0.172 6(2)	−0.062 6(2)	0.024 2(1)
N(41)	0.389 2(5)	0.210 8(6)	0.031 4(2)
N(11)	0.101 3(5)	0.179 1(5)	0.114 2(2)
N(12)	0.100 9(5)	0.263 7(5)	0.071 8(1)
C(42)	0.497 0(6)	0.230 2(6)	0.051 8(2)
C(13)	0.015 3(6)	0.373 1(6)	0.083 1(2)
C(14)	−0.035 5(7)	0.359 1(7)	0.132 4(2)
C(15)	0.019 5(6)	0.236 5(7)	0.151 1(2)
C(16)	−0.019 3(11)	0.491 9(10)	0.048 3(4)
C(17)	0.001 9(12)	0.164 3(9)	0.201 4(3)
C(18)	0.191 8(8)	0.055 2(7)	0.118 9(2)
C(19)	0.135 1(8)	−0.073 6(7)	0.091 4(3)
C(32)	−0.002 3(7)	−0.111 6(7)	−0.003 2(3)

The refinement was done by minimizing the function $\Sigma w(\Delta F)^2$ with $w = 1/\sigma(F)$. Atomic co-ordinates are presented in Table 3 and relevant bonding distances and angles in Table 4.

Table 6. Distances (Å) and angles (°) of Ni(bddo)(NCS)$_2$ with e.s.d.s in parentheses

Ni–S(31)	2.492(2)	N(11)–C(18)	1.443(7)
Ni–N(41)	2.021(5)	N(11)–C(15)	1.355(6)
Ni–N(12)	2.193(4)	C(18)–C(19)	1.507(9)
S(43)–C(42)	1.627(6)	C(13)–C(14)	1.396(7)
S(31)–C(32)	1.812(7)	C(13)–C(16)	1.482(9)
S(31)–C(19)	1.820(7)	C(14)–C(15)	1.353(8)
N(41)–C(42)	1.160(8)	C(15)–C(17)	1.505(8)
N(12)–C(13)	1.336(6)	C(32)–C(32$^{\rm I}$)	1.518(13)
N(12)–N(11)	1.377(5)		
S(31)–Ni–S(31$^{\rm I}$)	85.1(1)	S(31)–C(32)–C(32$^{\rm I}$)	112.7(5)
S(31)–Ni–N(41)	170.6(1)	S(31)–C(19)–C(18)	111.1(5)
S(31)–Ni–N(41$^{\rm I}$)	92.4(1)	N(12)–N(11)–C(18)	122.4(4)
S(31)–Ni–N(12)	92.0(1)	N(12)–N(11)–C(15)	111.1(5)
S(31)–Ni–N(12$^{\rm I}$)	82.3(1)	N(12)–C(13)–C(16)	124.6(6)
N(12)–Ni–N(12$^{\rm I}$)	172.2(2)	N(12)–C(13)–C(14)	110.1(5)
N(12)–Ni–N(41)	88.7(2)	N(11)–N(12)–C(13)	105.0(4)
N(41)–Ni–N(12$^{\rm I}$)	96.7(2)	N(11)–C(18)–C(19)	113.3(5)
N(41)–Ni–N(41$^{\rm I}$)	91.5(2)	N(11)–C(15)–C(17)	121.5(7)
Ni–S(31)–C(32)	102.1(2)	N(11)–C(15)–C(14)	106.7(5)
Ni–S(31)–C(19)	108.8(3)	C(19)–S(31)–C(32)	102.0(4)
Ni–N(41)–C(42)	174.1(5)	C(15)–N(11)–C(18)	126.2(5)
Ni–N(12)–N(11)	122.4(4)	C(14)–C(15)–C(17)	131.7(6)
Ni–N(12)–C(13)	131.6(4)	C(14)–C(13)–C(16)	125.3(7)
S(43)–C(42)–N(41)	179.5(4)	C(13)–C(14)–C(15)	107.1(6)

Symmetry equivalent position: I = $y, x, -z$.

Table 7. Fractional co-ordinates of Cd$_2$(bddo)(NCS)$_4$

Atom	x	y	z
Cd	0.122 26(3)	0.169 54(2)	−0.229 04(2)
S(43)	0.033 3(1)	0.313 6(1)	−0.028 1(1)
S(53)	0.179 9(1)	−0.136 6(1)	0.367 0(1)
S(31)	0.411 3(1)	0.201 3(1)	−0.034 9(1)
N(41)	−0.037 2(4)	0.066 7(3)	0.138 5(3)
N(51)	0.193 1(4)	0.040 1(4)	−0.397 9(3)
N(11)	0.450 9(3)	0.444 6(3)	−0.294 7(3)
N(12)	0.288 7(3)	0.411 5(3)	−0.283 0(3)
C(42)	−0.008 0(4)	0.166 0(3)	0.068 1(3)
C(52)	0.185 7(4)	−0.033 7(4)	0.506 2(3)
C(13)	0.251 5(4)	0.541 5(3)	−0.313 3(3)
C(14)	0.389 6(5)	0.653 3(4)	−0.344 4(3)
C(15)	0.513 5(4)	0.590 7(4)	−0.330 9(3)
C(16)	0.084 3(6)	0.554 1(5)	−0.310 5(5)
C(17)	0.689 6(6)	0.656 4(6)	−0.350 7(5)
C(18)	0.539 1(5)	0.334 8(5)	−0.259 4(5)
C(19)	0.577 5(6)	0.322 9(5)	−0.107 9(7)
C(32)	0.442 8(6)	0.013 9(5)	−0.058 0(5)

Ni(bddo)(NCS)$_2$. The structure was solved by direct and Fourier methods using SHELX 76[18] and SHELX 86 programs.[19] Least-squares refinement, minimizing $\Sigma(\Delta F)^2$, employed anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms located from difference Fourier synthesis. Atomic co-ordinates are listed in Table 5 and relevant bonding distances and angles in Table 6.

Cd$_2$(bddo)(NCS)$_4$. The structure was solved by direct and by Fourier methods using SHELX 76 and SHELXS 86 programs. Least-squares refinement, minimizing $\Sigma(\Delta F)^2$, employed anisotropic thermal parameters for non-hydrogen atoms and fixed (U = 0.07 Å^2) isotropic thermal parameters for hydrogen atoms located from Fourier difference synthesis. Atomic co-ordinates are given in Table 7 and relevant bonding distances and angles in Table 8.

Table 8. Distances (Å) and angles (°) of $Cd_2(bddo)(NCS)_4$ with e.s.d.s in parentheses

Cd–S(31)	2.849(1)	N(12)–C(13)	1.346(5)
Cd–S(43)	2.719(1)	C(13)–C(14)	1.393(5)
Cd–S(53$^{\mathrm{I}}$)	2.686(1)	C(14)–C(15)	1.357(7)
Cd–N(12)	2.350(1)	C(15)–N(11)	1.349(4)
Cd–N(41$^{\mathrm{I}}$)	2.296(3)	C(13)–C(16)	1.499(8)
Cd–N(51)	2.309(4)	C(15)–C(17)	1.507(6)
S(43)–C(42)	1.647(3)	C(18)–N(11)	1.454(6)
C(42)–N(41)	1.146(5)	C(18)–C(19)	1.512(9)
S(53)–C(52)	1.648(4)	S(31)–C(19)	1.794(6)
C(52)–N(51)	1.141(5)	S(31)–C(32)	1.823(5)
N(11)–N(12)	1.372(5)	C(32)–C(32$^{\mathrm{II}}$)	1.482(7)
S(31)–Cd–S(43)	84.5(1)	S(53)–C(52)–N(51)	178.4(3)
S(31)–Cd–N(12)	81.0(1)	N(11)–N(12)–C(13)	105.3(3)
S(31)–Cd–N(41$^{\mathrm{I}}$)	81.4(1)	N(12)–C(13)–C(14)	109.3(4)
S(31)–Cd–N(51)	95.7(1)	C(13)–C(14)–C(15)	107.4(4)
S(43)–Cd–S(53$^{\mathrm{I}}$)	85.3(1)	C(14)–C(15)–N(11)	106.6(3)
S(43)–Cd–N(12)	90.0(1)	C(15)–N(11)–N(12)	111.3(3)
S(43)–Cd–N(41$^{\mathrm{I}}$)	92.0(1)	C(16)–C(13)–N(12)	122.2(3)
N(51)–Cd–N(12)	91.7(1)	C(17)–C(15)–C(14)	131.4(4)
N(51)–Cd–N(41$^{\mathrm{I}}$)	86.4(1)	C(17)–C(15)–N(11)	122.0(4)
N(51)–Cd–S(53$^{\mathrm{I}}$)	94.3(1)	C(15)–N(11)–C(18)	127.1(3)
S(53$^{\mathrm{I}}$)–Cd–N(41$^{\mathrm{I}}$)	93.1(1)	N(12)–N(11)–C(18)	121.4(3)
S(53$^{\mathrm{I}}$)–Cd–N(12)	104.9(1)	N(11)–C(18)–C(19)	112.8(5)
Cd–S(43)–C(42)	97.0(1)	C(18)–C(19)–S(31)	115.4(3)
Cd–S(53$^{\mathrm{I}}$)–C(52)	102.1(1)	C(19)–S(31)–C(32)	100.1(3)
Cd–N(41$^{\mathrm{I}}$)–C(42)	165.6(3)	C(16)–C(13)–C(14)	128.4(4)
Cd–N(51)–C(52)	162.3(3)	S(31)–C(32)–C(32$^{\mathrm{II}}$)	111.9(3)
S(43)–C(42)–N(41)	177.6(4)		

[a] Symmetry equivalent positions: I $1 - x, 1 - y, 1 - z$; II $1 - x, -y, -z$.

Additional material available from the Cambridge Crystallographic Data Centre comprises the atom co-ordinates and thermal parameters.

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