Unusual Behaviour of the Thioether Function of the Ligand 1,8-Bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) towards Transition-metal Salts. *X*-Ray Structures of a Green and a Red Modification of $[Cu(bddo)Cl_2]$†

Willem G. Haanstra, Wilfred A. J. W. van der Donk, Willem L. Driessen,* and Jan Reedijk
Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
John S. Wood
Department of Chemistry, Lederle Graduate Research Centre, University of Massachusetts at Amherst, Amherst, MA 01003, U.S.A.
Michael G. B. Drew
Department of Chemistry, The University, Whiteknights, Reading, RG6

Co-ordination compounds of the new ligand 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) with MCl_2 (M = Fe, Mn, Ni, Co, Zn, Cu, or Cd), MBr_2 (M = Mn, Co, Ni, or Zn), $Cu(BF_4)_2$, and CuX (X = BF_4, NCS, Cl, Br, or I) are described. The general formula for the divalent metal is $[M(bddo)X_2]$ and for copper(I), $[Cu_2(bddo)X_2]$. With $CuCl_2$ two modifications were obtained. The green modification of $[Cu(bddo)Cl_2]$ crystallises in space group $P2_1/n$ with a = 9.019(2), b = 28.671(5), c = 8.431(2) Å, β = 113.65(2)°, R = 0.055, and R' = 0.066 for 1 578 unique reflections [$I > 2\sigma(I)$]. The compound consists of $Cu(bddo)Cl_2$ units. The copper atom is co-ordinated by two pyrazole nitrogens and two chloride atoms, in *trans* positions, in a distorted square-planar geometry. The red modification of $[Cu(bddo)Cl_2]$ crystallises in space group *Pbcn* with a = 9.397(4), b = 15.093(4), c = 15.142(4) Å, Z = 4, R = 0.069, and R' = 0.089 for 864 unique reflections [$I > \sigma(I)$]. This compound consists of $CuCl_2$ units linked together by ligand molecules, thus forming chains with distinct C_2 symmetry perpendicular to the chain axis. The copper atom is co-ordinated in a distorted-tetrahedral geometry by two pyrazole nitrogens and two chloride atoms in *cis* positions. The sulphur atoms do not participate in the co-ordination, although molecular-mechanics calculations show that the ligand bddo is not sterically hindered to form tetradentate mononuclear chelates, *i.e.* with a MN_2S_2 chromophore. The structures of the other divalent metal halides were established as being very similar to that of the red modification. For $[Cu(bddo)(BF_4)_2]$ semi-co-ordination of one or both tetrafluoroborates is indicated by the i.r. spectrum. Solid-state ^{13}C n.m.r. spectra of the copper(I) compounds indicate that the S atoms show significant shifts, suggesting co-ordination. In the thiocyanate and iodide compounds both thioether sulphurs co-ordinate in an identical manner, whereas in the chloride and bromide compounds they co-ordinate in a different manner.

To obtain insight into the correlation between the structure and nature of metalloproteins, low-molecular-weight co-ordination compounds may be used to model these metalloproteins.[1,2] In our programme directed towards modelling the N_2SS^* active site of type (blue) I copper proteins we developed a synthetic route to a set of N_2S_2 ligands.[3] These ligands contain pyrazole groups and thioether sulphur atoms to mimic the donor set of the active site. The set consists of similar ligands differing only in the number of methylene units between the donor functions. By studying the co-ordination behaviour of these ligands towards transition-metal salts a better understanding can be gained about the factors that determine the co-ordination geometry, thus providing a good base for studies of more complex chelating systems.

A previous report[3] described the unusual chelating properties of the ligand 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) towards the divalent zinc, cobalt, nickel, and cadmium thiocyanates. The co-ordination behaviour of bddo towards the metal salts MX_2 (M = Fe, Mn, Ni, Co, Zn, Cu, or Cd), X = Cl; M = Mn, Co, Ni, or Zn, X = Br), $Cu(BF_4)_2$, and CuX (X = BF_4, NCS, Cl, Br, or I) is reported here. With $CuCl_2$ two differently coloured modifications, a red and a green one, were obtained. For both compounds a single-crystal structure determination has now been performed. This paper also describes a detailed study of the spectroscopic properties of the compounds. Solid-state ^{13}C n.m.r. spectroscopy of the copper(I) compounds was undertaken because of insolubility of these compounds. To understand better the unusual co-ordination behaviour and to investigate possible steric constraints of the ligand bddo towards $CuCl_2$, molecular mechanics calculations were performed on the species $[Cu(bddo)]^{2+}$, $[Cu(bddo)Cl]^+$, and $[Cu(bddo)Cl_2]$ in a variety of co-ordination geometries.

Results and Discussion

General and Spectroscopy.—The compounds obtained with the divalent metal salts all have formula $[M(bddo)X_2]$ while copper(I) salts form compounds $[Cu_2(bddo)X_2]$ (X = Cl, Br, I, or BF_4). Analytical results for the co-ordination compounds were satisfactory. Colour, melting point, analytical data, i.r. and *X*-ray powder type, and electronic absorption maxima are

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. units employed: cal = 4.184 J, dyn = 10^{-5} N.

Table 1. Colour, melting point, analytical data (calculated values in parentheses), i.r., and *X*-ray type, electronic absorption maxima, and proposed chromophore of the bddo (L) compounds

			Analysis/%				
Compound	Colour	M.p. (°C)	M	Cl/Br	I.r. type	*X*-Ray type	Ligand-field maxima (10^3 cm^{-1})
[Fe(L)Cl_2]	Brown	250 (decomp.)	12.8 (12.0)	14.7 (15.2)	A	II	30.3, 7.1
[Mn(L)Cl_2]	White	>260	11.9 (11.8)	15.1 (15.3)	A	I	
[Co(L)Cl_2][a]	Blue	>260	12.6 (12.6)	14.4 (15.1)	A	I	17.4, 15.6(sh), 8.7, 7.1, 5.8
[Ni(L)Cl_2][b]	Purple	>260	11.7 (12.5)	13.8 (15.1)	A	II	17.9, 14.8, 9.9
[Cu(L)Cl_2]	Red	201 (decomp.)	13.2 (13.4)	15.3 (15.1)	A	I′	24.0, 11.2
[Cu(L)Cl_2][c]	Green	175 (decomp.)	13.3 (13.4)	15.4 (15.1)	C	III	26.1, 16.5, 13.9
[Zn(L)Cl_2]	White	>260	13.5 (13.8)	14.2 (14.9)	A	I	
[Cd(L)Cl_2]	White	236	21.5 (21.5)		A	I	
[Mn(L)Br_2]	White	>260	9.93 (9.93)		A	I	
[Co(L)Br_2]	Blue	>260	10.7 (10.6)	27.4 (28.7)	A	I	16.7(sh), 15.2, 7.9, 6.8, 5.6
[Ni(L)Br_2]	Purple	258	10.7 (10.5)	26.3 (28.7)	A	II	29.0, 17.4, 14.4, 9.8
[Zn(L)Br_2]	White	>260	11.8 (11.6)	30.0 (28.3)	A	I	
[Cu(L)$(BF_4)_2$][d]	Green	152	11.0 (11.0)		B	IV	28.6, 16.1, 13.2, 10.2
[Cu_2(L)$(NCS)_2$][e]	White	207	21.5 (21.9)		D	VI	
[Cu_2(L)Cl_2]	White	196	22.6 (23.7)	13.2 (13.2)	E	V	
[Cu_2(L)Br_2]	White	179	19.8 (20.3)		E′	V	
[Cu_2(L)I_2]	White	178	17.4 (17.7)		F	VII	

[a] S, 12.7 (13.7); C, 41.2 (41.0); H, 5.6 (5.6); and N, 11.8 (12.0%). [b] C, 41.1 (41.0); H, 5.8 (5.6); and N, 11.9 (12.0%). [c] C, 40.2 (40.6),; H, 5.4 (5.5); and N, 11.6 (11.8%). [d] C, 32.6 (33.4); H, 4.9 (4.6); and N, 9.5 (9.7%). [e] S, 22.2 (22.0%).

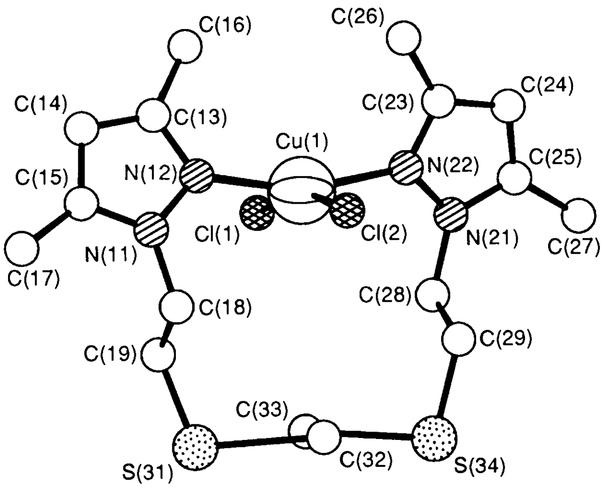

Figure 1. PLUTO (W. D. S. Motherwell and W. Clegg, University of Cambridge, 1978) drawing of [Cu(bddo)Cl_2] (**1**) with the atom labelling scheme. Hydrogen atoms are omitted for clarity

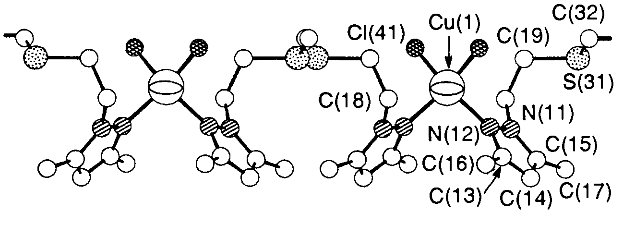

Figure 2. PLUTO drawing of [Cu(bddo)Cl_2] (**2**) with the atom labelling scheme. Hydrogen atoms are omitted for clarity

summarised in Table 1. The ligand-field maxima of the nickel(II) and cobalt(II) halide compounds show clearly that the metals are tetrahedrally surrounded by four strong donor atoms,[4] *viz.* two pyrazole nitrogens and two halide ions. The i.r. spectra and *X*-ray powder patterns were assigned a type, which enhances the recognisability of isomorphous compounds in Table 1. The i.r. and *X*-ray powder patterns of the group [M(bddo)Cl_2] (M = Mn, Co, Zn, or Cd) and [M(bddo)Br_2] (M = Mn, Co, or Zn) are almost identical, only small differences in *d* values for the bromides being observed. This means that these compounds are structurally isomorphous, possessing the same MN_2X_2 chromophore. The compounds [M(bddo)Cl_2] (M = Fe or Ni) and [Ni(bddo)Br_2] show the same i.r. patterns and characteristic ligand-field spectra for tetrahedrally surrounded metal ions, thus indicating a similar MN_2X_2 chromophore. No detailed assignment of the electronic absorptions was undertaken because the chromophores contain donors of different types in distorted geometries.

X-Ray Structure of the Green Modification of [Cu(bddo)Cl_2] (**1**).—The structure of this compound (see Figure 1) consists of discrete Cu(bddo)Cl_2 units, packed by normal van der Waals interactions. The copper atom is co-ordinated by two pyrazole nitrogens and two chloride atoms in a distorted square-planar geometry. The pyrazole groups are in *trans* position to each other. The Cu-N bonding distances are 2.002(9) and 2.026(9) Å, which are normal for copper–pyrazole-nitrogen distances.[5] The Cu-Cl bonding distances are 2.235(3) and 2.240(3) Å, which are also normal Cu-Cl interactions.[5] The tetrahedral distortion of the square-planar geometry is clearly demonstrated by the angles N(12)-Cu-N(22) and Cl(1)-Cu-Cl(2), which are respectively 161.0(2) and 160.4(1)°. The dihedral angle, as computed using the two CuNCl planes, is 27°. The copper atom is not co-ordinated to the sulphur atoms, as the Cu-S distances (4.97 and 5.01 Å) are far too large. The bridge segment SCH_2CH_2S is disordered in the crystal. Examination of the packing of the molecules did not reveal any other than normal intermolecular van der Waals interactions. Relevant bond distances and angles are listed in Table 2.

X-Ray Structure of the Red Modification of [Cu(bddo)Cl_2] (**2**).—The structure of this compound, depicted in Figure 2, consists of $CuCl_2$ units linked together by ligand molecules,

Table 2. Bond distances (Å) and angles (°) of $[Cu(bddo)Cl_2]$ (**1**)

Cu–Cl(1)	2.235(3)	S(31)–C(33)*	2.305(18)
Cu–Cl(2)	2.240(3)	C(32)–C(33)*	1.349(23)
Cu–N(12)	2.002(9)	N(21)–N(22)	1.363(12)
Cu–N(22)	2.026(9)	N(22)–C(23)	1.330(13)
N(11)–N(12)	1.386(12)	C(23)–C(24)	1.403(13)
N(12)–N(13)	1.337(13)	C(24)–C(25)	1.373(13)
C(13)–C(14)	1.380(13)	C(25)–N(21)	1.353(13)
C(14)–C(15)	1.410(13)	C(23)–C(26)	1.483(15)
C(15)–N(11)	1.343(13)	C(25)–C(27)	1.513(14)
C(13)–C(16)	1.498(13)	N(21)–C(28)	1.473(14)
C(15)–C(17)	1.476(14)	C(28)–C(29)	1.481(15)
N(11)–C(18)	1.446(13)	C(29)–S(34)*	1.831(13)
C(18)–C(19)	1.504(14)	S(34)–C(33)*	2.296(18)
C(19)–S(31)*	1.782(13)	S(34)–C(32)*	2.266(18)
S(31)–C(32)*	2.293(18)		
Cl(1)–Cu–Cl(2)	160.4(1)	N(22)–C(23)–C(24)	108.3(9)
N(12)–Cu–N(22)	161.0(2)	C(23)–C(24)–C(25)	106.8(1)
Cl(1)–Cu–N(12)	89.6(2)	C(24)–C(25)–N(21)	107.3(9)
Cl(1)–Cu–N(22)	92.2(2)	C(25)–N(21)–N(22)	109.4(9)
Cl(2)–Cu–N(12)	93.3(2)	N(22)–C(23)–C(26)	121.9(1)
Cl(2)–Cu–N(22)	91.3(2)	C(24)–C(23)–C(26)	129.9(1)
N(11)–N(12)–C(13)	105.2(8)	N(21)–C(25)–C(27)	122.6(1)
N(12)–C(13)–C(14)	111.5(8)	C(24)–C(25)–C(27)	130.1(1)
C(13)–C(14)–C(15)	105.5(9)	N(22)–N(21)–C(28)	122.3(1)
C(14)–C(15)–N(11)	106.6(9)	C(25)–N(21)–C(28)	128.1(1)
C(15)–N(11)–N(12)	111.2(8)	N(21)–C(28)–C(29)	109.7(1)
N(12)–C(13)–C(16)	119.8(11)	C(28)–C(29)–S(31)	111.2(8)
C(14)–C(13)–C(16)	128.6(11)	C(19)–S(31)–C(32)*	107.5(1)
N(11)–C(15)–C(17)	122.8(11)	C(19)–S(31)–C(33)*	99.2(11)
C(14)–C(15)–C(17)	130.5(12)	S(31)–C(32)–C(33)*	73.4(14)
N(12)–N(11)–C(18)	121.0(10)	S(31)–C(33)–C(32)*	72.4(14)
C(15)–N(11)–C(18)	127.2(11)	C(29)–S(34)–C(33)*	101.2(1)
N(11)–C(18)–C(19)	113.1(12)	C(29)–S(34)–C(32)*	98.4(12)
C(18)–C(19)–S(31)	112.9(7)	S(34)–C(33)–C(32)*	71.6(14)
N(21)–N(22)–C(23)	108.2(8)	S(34)–C(32)–C(33)*	74.0(14)

* Disordered SCH_2CH_2S bridge.

Table 3. Bond distances (Å) and angles (°) of $[Cu(bddo)Cl_2$ (**2**)

Cu–Cl(41)	2.228(3)	C(15)–C(17)	1.54(2)
Cu–N(12)	1.985(9)	N(11)–C(18)	1.46(1)
N(11)–N(12)	1.36(1)	C(18)–C(19)	1.53(2)
N(12)–C(13)	1.32(1)	C(19)–S(31)	1.79(1)
C(13)–C(14)	1.37(2)	S(31)–C(32)	1.88(2)
C(14)–C(15)	1.39(2)	S(31)–C(33)*	1.93(2)
C(15)–N(11)	1.36(1)	C(32)–C(33)	1.56(3)
C(13)–C(16)	1.50(2)		
Cl(41)–Cu–Cl(41)*	105.7(1)	N(12)–C(13)–C(16)	122(1)
Cl(41)–Cu–N(12)	130.6(2)	C(14)–C(13)–C(16)	127(1)
Cl(41)–Cu–N(12)*	98.7(2)	C(13)–C(14)–C(15)	107(1)
N(12)–Cu–N(12)*	96.5(2)	N(11)–C(15)–C(14)	105(1)
C(19)–S(31)–C(32)	101(1)	N(11)–C(15)–C(17)	123(1)
C(19)–S(31)–C(33)*	103(1)	C(14)–C(15)–C(17)	132(1)
N(12)–N(11)–C(15)	110.7(9)	N(11)–C(18)–C(19)	114(1)
N(12)–N(11)–C(18)	121.1(8)	S(31)–C(19)–C(18)	114.8(8)
C(15)–N(11)–C(18)	128(1)	S(31)–C(32)–C(33)	102(1)
N(11)–N(12)–C(13)	106.5(9)	S(31)–C(33)*–C(32)*	103(1)
N(12)–C(13)–C(14)	111(1)		

* Symmetry-related atoms: $-x, y, \frac{1}{2} - z$.

thus forming chains with distinct C_2 axes perpendicular to the chain axis. A study of the packing of the chains indicated that the packing is governed by normal van der Waals interactions. The copper atom is co-ordinated by two pyrazole nitrogens and two chloride atoms, in a normal distorted-tetrahedral fashion with the angles N(12)–Cu–N(12′) 96.5(2)° and Cl(41)–Cu–Cl(41′) 105.7(1)° and the dihedral angle, defined by the planes $CuCl_2$ and CuN_2, 65.0°. The bond distances of copper to the nitrogen and chloride are respectively 1.985(9) and 2.228(3) Å, which are considered as normal.[5] The ethylene bridge between the sulphur atoms is disordered and can be described satisfactorily by two equally half-occupied positions, C(32) and C(33). Relevant bond distances and angles are listed in Table 3.

Table 4. E.p.r. data for the copper(II) compounds of bddo

Compound	Method	T/K	g
$[Cu(bddo)Cl_2]$ (green)[a]	Q-Band	56	2.244, 2.043, 2.024
$[Cu(bddo)Cl_2]$ (red)	X-Band	77	2.44, 2.10
$[Cu(bddo)(BF_4)_2]$[b]	Q-Band	55	2.224, 2.099, 2.004

[a] X-Band, 77 K, g 2.06. [b] X-Band, 77 K, g 2.22, 2.11, and 2.01

E.P.R. and Electronic Spectroscopy of the Copper(II) *Compounds.*—The e.p.r. and electronic absorption data for compounds (**1**) and (**2**) and also those of $[Cu(bddo)(BF_4)_2]$ are listed in Tables 1 and 4. Battaglia *et al.*[6] observed a correlation between the electronic spectra of $[CuCl_4]^{2-}$ anions and the corresponding dihedral angle. Although the present compounds have an N_2Cl_2 chromophore, the blue shift of the absorption envelope with decreasing dihedral angle (= flattening of the tetrahedron) is also observed for the present two modifications. The e.p.r. spectrum of (**2**) is remarkable, showing a g value as high as 2.44, which can be explained as resulting from the weak tetrahedrally based ligand field of the N_2Cl_2 donor set.[7]

The donor set of the compound $[Cu(bddo)(BF_4)_2]$ cannot be determined exactly. The analytical results show clearly that the compound does not contain additional solvent or water molecules. The hypothesis that the tetrafluoroborate anion is also (semi)-co-ordinating is supported by the occurrence of the ν_1 vibration of the BF_4^- in the i.r. spectrum[8] at 765 cm^{-1}. From the available data it is not established whether there are one or two (semi)-co-ordinating BF_4^- anions, so the chromophore for the $[Cu(bddo)(BF_4)_2]$ compound is proposed to be either N_2S_2F or $N_2S_2F_2$.

Solid-state ^{13}C *N.M.R. Spectroscopy.*—Because of the limited number of spectroscopic techniques which can give structural information about copper(I) compounds, and also because of the poor solubility of the compounds in the common deuteriated solvents, solid-state ^{13}C n.m.r. spectroscopy was undertaken. From the shifts of the resonances relative to the free ligand conclusions may be derived concerning the co-ordination of the thioethers. The results are collected in Table 5. No effort was made to specify which pyrazole-ring carbon resonance belongs to which carbon.

The most important differences between the compounds listed in Table 5 concern the resonances 3 and 4. For all four copper(I) compounds resonance 3 shifts downfield (1.1 to 4.9 p.p.m.) compared to the free ligand. Resonance 4 shifts upfield in the case of $[Cu_2(bddo)(NCS,I)_2]$ (*ca.* 7.2 p.p.m.), whereas in the case of $[Cu_2(bddo)(Cl,Br)_2]$ a second resonance appears at *ca.* 2.3 p.p.m. upfield. This behaviour leads to the assumption that in case of the thiocyanate and iodide complexes both thioether ligand atoms co-ordinate to the copper(I) atom in an identical manner. For both the chloride and the bromide compounds the chemical surroundings of the thioether atoms are inequivalent, and therefore the thioether atoms do not co-ordinate in the same way. The number of donating atoms available for each copper(I) atom might appear to be limited to three. However, when a bridging role of the anions or the thioethers is assumed the co-ordination number could be larger.

Molecular Mechanics (m.m.) *investigation of bddo.*—In the green modification of [Cu(bddo)Cl_2] (**1**), see Figure 1, the thioether atoms do not co-ordinate to the copper atom. It is clear that the lone pairs of the thioether atoms are not directed towards the copper atom. To investigate the possibility of steric hindrance restraining the ligand bddo from co-ordinating in a tetradentate fashion, m.m. calculations were performed on various conformations of the [Cu(bddo)Cl_2] molecule. The models which were considered as possible co-ordination geometries are summarised in Table 6. The *X*-ray structure of [Cu(bddo)Cl_2] (**1**) has also been included as a model (*SP*-N_2Cl_2) in the calculations.

The metal parameters used for the calculation of a MM2 force field are listed in Table 7 (for further details see Experimental section). Co-ordinates used for the starting conformations were taken from *X*-ray structures containing the ligand, or a very similar pyrazole-containing ligand, in the desired conformation. This process reduces the chance of finding a local minimum when minimising.

The results of the calculations are listed in Table 6. The SCH_2CH_2S bridge segment in the minimised structure of (**1**), code *SP*-N_2Cl_2, deviates significantly from the *X*-ray structure. This is also the part of the *X*-ray structure that is disordered. Although the values of the final steric energy do not represent the formation enthalpies it is clear that all studied conformations are relatively unstrained, thus indicating that there is no evident steric reason why the ligand bddo would not co-ordinate to copper(II) chloride in a tetradentate chelate fashion.

The angles Cu–S–C ($\Theta_0 = 100°$) in the models, where the sulphur atoms co-ordinate, fall in the range 102—115°. Although this is slightly greater than usually found (93—105°),* this is not likely to be the origin of the unusual co-ordination behaviour of bddo.

Conclusion

In a previous report[3] the structures of the compounds [Zn(bddo)$(NCS)_2$], [Co(bddo)$(NCS)_2$], [Ni(bddo)$(NCS)_2$], and [Cd_2(bddo)$(NCS)_4$] were described. The ligand sulphur atoms co-ordinate to the Ni^{II} and Cd^{II}, but in case of Zn^{II}, and the present isomorphous Co^{II}, the sulphurs do not co-ordinate and the structures of these compounds are very similar to that of the present polymeric compound (**2**). The compounds [M(bddo)Cl_2] (M = Fe, Mn, Co, Ni, Zn, or Cd) and [M(bddo)Br_2] (M = Mn, Co, Ni, or Zn) show spectroscopic properties indicating that they are structurally very similar to the polymeric compounds [Cu(bddo)Cl_2] (**2**) and [M(bddo)$(NCS)_2$] (M = Zn or Co) and must therefore have very similar polymeric structures with non-co-ordinating sulphur atoms. Experiments undertaken to prepare divalent metal tetrafluoroborates were only successful in the case of $Cu(BF_4)_2$. The thioether donor atoms are very likely to be co-ordinating in this compound, together with one or two weakly co-ordinating tetrafluoroborate anions. The m.m. calculations on the bddo–$CuCl_2$ system show also that this is sterically possible. Of the investigated divalent first-row transition-metal salts only $Cu(BF_4)_2$ and $Ni(NCS)_2$ form complexes in which the sulphurs co-ordinate. So, in principle, the ligand is capable of donating all its donor atoms to the metal ion. With ligands having shorter bridges between the azole nitrogen and the thioether sulphur atom full tetradentate chelation occurs in most cases.[9,10] The non-co-ordinating behaviour of the thioether sulphurs seems therefore to be due to its rather poor donor properties in combination with the large flexible bite between the thioether

Table 5. ^{13}C N.m.r. chemical shifts (p.p.m.) for the solid copper(I) bddo compounds

Compound	1[a]	2[a]	3[a]	4[a]
bddo (solid)	11.5 13.3	103.8 142.2 147.3	44.1	28.7[b]
[Cu_2(bddo)$(NCS)_2$][c]	12.6 16.5	104.7 141.2 147.2	49.0	34.8
[Cu_2(bddo)I_2]	12.5 14.9	106.1 140.2 146.7	47.0	35.9
[Cu_2(bddo)Br_2]	10.6 16.0	106.2 141.1 150.7	46.5	28.9 31.9
[Cu_2(bddo)Cl_2]	10.9 15.4	106.1 140.8 150.7	45.2	28.5 32.0

[a] 1 = Methyl-group carbons, 2 = pyrazole-ring carbons, 3 = carbons adjacent to pyrazole ring, and 4 = carbons adjacent to thioether sulphur. [b] Two resonances lying close together. [c] Because of background noise no identification of the C(NCS) resonance was possible.

Table 6. Results* of the molecular-mechanics calculations in kcal mol^{-1}

	SP-N_2Cl_2	*SP*-N_2S_2	*T*-N_2S_2	*TBPY*-N_2S_2Cl	*SPY*-N_2S_2Cl	*OC*-$N_2S_2Cl_2$
Compression	0.56	0.84	0.88	1.49	1.97	2.11
Bending	5.03	4.69	9.58	6.26	7.21	9.01
Stretch bend	0.35	−0.78	−0.56	−1.76	−2.22	−2.14
van der Waals						
1,4	4.44	4.62	1.87	3.47	4.21	3.76
others	−10.32	−7.81	−6.75	−9.01	−8.88	−7.87
Torsion	−2.12	2.10	−0.43	0.09	1.10	0.07
Dipole	0.40	1.31	1.49	1.76	1.60	1.85
Final	−1.64	4.98	6.08	2.31	4.99	6.79

* *SP*-N_2Cl_2 = Square-planar co-ordination, nitrogen donors *trans*, *SP*-N_2S_2 = square-planar co-ordination, nitrogen and sulphur donors *cis* to each other, *T*-N_2S_2 = tetrahedral co-ordination, *TBPY*-N_2S_2Cl = trigonal-bipyramidal co-ordination, nitrogen donors *trans* and sulphurs and chloride in equatorial plane, *SPY*-N_2S_2Cl = square-pyramidal co-ordination, nitrogen and sulphur donors in base plane and chloride in axial position, and *OC*-$N_2S_2Cl_2$ = octahedral co-ordination, nitrogen donors in axial positions, sulphurs and chlorides *cis* to each other.

---

* Distribution analysis on 124 Cu–S–C angles (62 *X*-ray structures with thioethers co-ordinating to Cu, extracted from the CSD file) resulted in the two mean values 102 ± 2 and 99 ± 6° for this angle. This leads to a Cu–S–C angle range of 93—105° at a 95% confidence level.

Table 7. Metal parameters used in the molecular-mechanics calculations: r_0 in Å/k_s in mdyn Å^{-1} for bonds and Θ_0 in °/k_b in mdyn Å^{-1} rad^{-2} for angles

	SP-N_2Cl_2	*SP*-N_2S_2	*T*-N_2S_2	*TBPY*-N_2S_2Cl	*SPY*-N_2S_2Cl	*OC*-$N_2S_2Cl_2$
Cu-N	2.0/2.0	2.0/2.0	2.0/2.0	2.0/2.0	2.0/2.0	2.0/2.0
Cu-S	—	2.3/2.0	2.3/2.0	2.3/2.0	2.3/2.0	2.3/2.0
Cu-Cl	2.24/2.0	—	—	2.24/2.0	2.24/2.0	2.24/2.0
N-Cu-N	180/0.1	90/0.1	109.5/0.1	180/0.1	87/0.1[a]	180/0.1
N-Cu-S	—	90/0.1	109.5/0.1	90/0.1	103—87/0.1	90/0.1
N-Cu-Cl	90/0.1	—	—	90/0.1	99/0.1	90/0.1
S-Cu-S	—	90/0	109.5/0.1	120/0.01[b]	87/0.1	90/0.1
S-Cu-Cl	—	—	—	120/0.01	99/0.1	90/0.1
Cl-Cu-Cl	180/0.1	—	—	—	—	90/0.1

[a] Angles represent a planar base with the metal ion tilted *ca.* 0.3 Å above the base plane. [b] k_b was lowered because the S-C-C-S bridge segment cannot adjust to 120° without excessive strain. With k_b having the value 0.1 mdyn Å rad^{-2} the final steric energy rises to 5.64 kcal mol^{-1}.

Table 8. Crystal data for the green, (**1**) and red, (**2**) modifications of [Cu(bddo)Cl_2] *

	(**1**)	(**2**)
Space group	$P2_1/n$	*Pbcn*
a/Å	9.019(2)	9.397(4)
b/Å	28.671(5)	15.093(4)
c/Å	8.431(2)	15.142(4)
α/°	90	90
β/°	113.65(2)	90
γ/°	90	90
U/Å^3	2 115	2 148
D_c/g cm^{-3}	1.48	1.46
Crystal size/mm	0.40 × 0.20 × 0.15	0.18 × 0.20 × 0.40
Absorption correction	Yes (ψ scan)	No
2θ range/°	9.5—12.0	10.0—14.0
h	−9, to 9	0—10
k	0—29	0—16
l	0—9	0—16
No. measured data	2 415	1 230
No. unique data	1 578 [$I > 2\sigma(I)$]	864 [$I > \sigma(I)$]
No. variables	226	123
$R = \Sigma(F)/\Sigma(F_o)$	0.055	0.069
$R' = [\Sigma(F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$	0.066	0.089

* Details in common: M = 472.98; Z = 4; μ(Mo-K_α) = 15.2 cm^{-1}; Lorentz and polarisation correction applied; CAD4 diffractometer; Mo-K_α radiation (λ = 0.710 73 Å); 25 orientation reflections; 298 K; scan method ω—2θ; data collection range θ 1.5—21.5°; F(000) = 980.

Table 9. Atomic co-ordinates (× 10^4) of non-hydrogen atoms of [Cu(bddo)Cl_2] (**1**)

Atom	x	y	z
Cu	3 706(2)	987(1)	1 892(2)
Cl(1)	2 006(3)	1 497(1)	149(3)
Cl(2)	5 843(3)	703(1)	4 003(3)
S(31)*	7 145(6)	2 375(2)	2 315(5)
S(34)*	4 954(5)	2 332(2)	5 874(5)
N(11)	6 061(9)	1 090(3)	257(9)
N(12)	4 709(9)	870(3)	293(9)
N(21)	1 819(8)	1 258(3)	3 925(10)
N(22)	2 274(9)	916(3)	3 139(9)
C(13)	4 160(11)	598(3)	−1 035(12)
C(14)	5 099(11)	639(3)	−1 926(11)
C(15)	6 313(12)	966(3)	−1 072(13)
C(16)	2 685(11)	304(4)	−1 390(12)
C(17)	7 690(13)	1 140(4)	−1 405(14)
C(18)	6 882(12)	1 455(4)	1 414(12)
C(19)	6 221(13)	1 933(4)	828(13)
C(23)	1 499(12)	526(4)	3 200(12)
C(24)	559(12)	618(4)	4 093(12)
C(25)	789(11)	1 079(4)	4 537(12)
C(26)	1 725(14)	85(3)	2 448(15)
C(27)	124(12)	1 364(4)	5 553(13)
C(28)	2 496(13)	1 733(3)	4 132(13)
C(29)	4 035(12)	1 751(4)	5 606(13)
C(32)*	6 608(18)	2 206(6)	4 554(22)
C(33)*	5 277(18)	2 417(6)	3 462(20)

* SCH_2CH_2S is disordered: the co-ordinates represent the averaged values.

functions and the dominating azole donor functions. On the other hand crystal-packing effects, which have not been included in the m.m. calculations, may also have stabilising effects on certain geometries.

Experimental

Synthesis and Characterisation of the Co-ordination Compounds.—The compounds with metal(II) salts were prepared by adding a hot solution of the appropriate metal salt (2 mmol) in absolute ethanol (10 cm^3) to a stirred hot solution of bddo[3] (2 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 crystallisation of the co-ordination compounds in sufficient yields for analysis. In the case of $CuCl_2$ a mixture of two compounds was obtained using this method. By changing the solvent to acetonitrile the product of the synthesis was, in many cases, either pure red or pure green. No method was found which gave only one of the two compounds in a pure form.

The experiments with copper(I) were performed under a dinitrogen atmosphere and using degassed and dried solvents.[11] The isolated solid compounds were, in contrast to the solutions, air stable. The copper(I) chloride, bromide, and thiocyanate co-ordination compounds were prepared by adding a solution of bddo (2 mmol) in acetonitrile (*ca.* 15 cm^3) to a solution of copper(I) salt (2 mmol) in acetonitrile (*ca.* 30 cm^3). The products precipitated, on standing at room temperature or at −23 °C, overnight. The copper(I) iodide was prepared by first reducing a $Cu(NO_3)_2$ solution (4 mmol) in acetonitrile (30 cm^3) with ascorbic acid dissolved in methanol and subsequently adding bddo (2 mmol) in acetonitrile (15 cm^3), KI (3 mmol) in acetonitrile (10 cm^3), and methanol (10 cm^3). The product starts precipitating after the addition of the methanol.

Infra-red spectra in the 4 000—300 cm^{-1} range for the ligand bddo and for 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 methods with MgO as

Table 10. Atomic co-ordinates ($\times 10^4$) of the non-hydrogen atoms of [Cu(bddo)Cl_2] (**2**)

Atom	*x*	*y*	*z*
Cu	0	2 525(1)	2 500
Cl(41)	−1 147(4)	3 416(2)	1 568(2)
S(31)	4 661(4)	3 190(3)	1 055(2)
N(11)	2 280(10)	1 607(5)	1 519(5)
N(12)	1 540(10)	1 649(6)	2 289(5)
C(13)	1 970(10)	978(7)	2 775(7)
C(14)	2 980(10)	497(7)	2 334(8)
C(15)	3 200(10)	911(7)	1 528(8)
C(16)	1 400(10)	807(9)	3 685(8)
C(17)	4 200(20)	693(9)	750(9)
C(18)	2 090(10)	2 276(8)	833(7)
C(19)	2 750(10)	3 175(8)	1 062(8)
C(32)*	5 050(30)	3 630(20)	2 190(10)
C(33)*	4 850(30)	2 780(10)	2 770(10)

* Refined with occupancy factor equal to 0.5.

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 decomposition with nitric acid, metal analyses were carried out complexometrically with ethylenediaminetetra-acetate.[12] The solid-state ^{13}C n.m.r. spectra were recorded, using noise decoupling, on a Bruker MSL 400 spectrophotometer. The *X*-band e.p.r. spectrum of [Cu(bddo)Cl_2] (red form) was recorded on a Varian E3 spectrophotometer at liquid-nitrogen temperature. The *Q*-band spectra of [Cu(bddo)Cl_2] (green form) and [Cu(bddo)$(BF_4)_2$] were recorded on a Varian E9 spectrophotometer in combination with a Varian E110 microwave bridge and a E266 cavity.

X-Ray Data Collection and Structure Refinement.—The crystals were isolated from batches consisting of the pure form. The data collected for the two structures are listed in Table 8. Scattering factors and anomalous dispersion corrections were taken from ref. 13.

[Cu(bddo)Cl_2] (*green form*) (**1**). The structure was solved by Patterson methods and refined by least-squares calculations. All H atoms except those on C(32) and C(33) were located from difference Fourier maps with reasonable geometries. The positions were not refined and the isotropic thermal parameters of the H atoms were taken as 20% above the value of the adjacent C atoms. The thermal parameters of the non-H atoms were refined anisotropically. Refinement led to large thermal parameters for S(31), S(34), C(32), and C(33) and to unsatisfactory bond distances involving these atoms. It appears that the refined values represent averaged positions for two alternative conformations of the bridge segment. The final discrepancy indices *R* and weighted index *R'* are respectively 0.055 and 0.066. Maximal residual electron density in the final difference Fourier was +0.42 and −0.30 e $Å^{-3}$. Atomic co-ordinates are listed in Table 9 and relevant bond lengths and angles in Table 2.

[Cu(bddo)Cl_2] (*red form*) (**2**). The structure was solved by Patterson methods and refined by least-squares calculations. Some H atoms were located from Fourier difference maps with reasonable geometries, others were placed at 0.95 Å from the parent atom. The positions of the H atoms were coupled to the parent atom and the isotropic thermal parameters were taken as 20% above the value of the adjacent atoms. The thermal parameters of the non-H atoms were refined anisotropically. The ethylene bridge between the two sulphur atoms is statistically disordered and could best be described by two equally occupied positions. The final discrepancy indices *R* and *R'* are respectively 0.069 and 0.089. Maximal residual electron density in the final difference Fourier was +0.56 and −0.45 e $Å^{-3}$. Atomic co-ordinates are listed in Table 10 and relevant bond lengths and angles in Table 3.

Molecular-mechanics Calculations.—Molecular-mechanics calculations were performed with a version of the MM2 program,[14] modified to allow for co-ordination numbers greater than four and to include periodicity at metal angles. Computations were carried out on the Amdahl V7 computer at the University of Reading and on the Amdahl V7B computer at Leiden University. Force-field parameters used for C, H, N, and S were taken from values in the MM2 program. Metal parameters for the trigonal-bipyramidal co-ordination were fitted to match a known structure with the same donor set and co-ordination geometry. Metal parameters for the square-planar type co-ordination were obtained by fitting the *X*-ray structure of complex (**1**). In the case of the octahedral co-ordination type the parameters were assumed equal to those of the square-planar type. It was found that all the metal parameters were non-critical; this means that a small variation in parameter yielded only a small deviation in minimised structure.

Acknowledgements

We are indebted to Dr. R. Day (University of Massachusetts at Amherst) for collecting the diffraction data, to Dr. S. P. J. Albracht (University of Amsterdam) for the recording of the *Q*-band e.p.r. spectra, and to Miss P. D. Verweij (Leiden University) for recording the ^{13}C n.m.r. spectra. We would like to thank the Netherlands Organization for Scientific Research (NWO, grant no. R70-157) for financial support, making it possible for W. G. Haanstra to visit Reading.

References

1 J. Reedijk, W. L. Driessen, and J. van Rijn, in 'Biological and Inorganic Copper Chemistry,' eds. K. D. Karlin and J. Zubieta, Adenine Press, New York, 1986, p. 143 and refs therein.
2 P. J. M. W. L. Birker and J. Reedijk, in 'Copper Coordination Chemistry: Biochemical and Inorganic Perspectives,' eds. K. D. Karlin and J. Zubieta, Adenine Press, New York, 1982, p. 409 and refs therein.
3 W. G. Haanstra, W. L. Driessen, J. Reedijk, U. Turpeinen, and R. Hämäläinen, *J. Chem. Soc., Dalton Trans.*, 1989, 2309.
4 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' 2nd edn, Elsevier, Amsterdam, 1984.
5 B. J. Hathaway, in 'Comprehensive Coordination Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, ch. 53.
6 L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue, and G. C. Pellacani, *Inorg. Chem.*, 1979, **18**, 148.
7 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 87; B. J. Hathaway, *Struct. Bonding (Berlin)*, 1984, **57**, 55.
8 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1978.
9 E. Bouwman, W. L. Driessen, and J. Reedijk. *Acta Crystallogr., Sect. C*, 1984, **40**, 1562.
10 E. Bouwman, J. S. Wood, R. Day, C. J. ten Hove, W. L. Driessen, and J. Reedijk, *Acta Crystallogr., Sect. C*, 1988, **44**, 644.
11 Y. C. M. Pennings, W. L. Driessen, and J. Reedijk, *Polyhedron*, 1988, **17**, 2583.
12 A. I. Vogel, 'Quantitative Inorganic Analysis,' Longmans, London, 1961.
13 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
14 N. L. Allinger and Y. H. Yuh, program no. 423, Quantum Chemistry Program Exchange, Indiana University, Indiana; M. G. B. Drew, S. Hollie, and P. C. Yates, *J. Chem. Soc., Dalton Trans.*, 1985, 1829.

Received 3rd *April* 1990; *Paper* 0/01471K