Copper coordination compounds of the ligand 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh). X-ray structures of $[Cu(bddh)]_2(BF_4)_2$, $[Cu(bddh)Cl]_2CuCl_4$ and $[Cu(bddh)(3,5\text{-dimethylpyrazole})](BF_4)_2$

W. G. Haanstra, W. L. Driessen*, R. A. G. de Graaff, J. Reedijk
Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden (The Netherlands)

Y. F. Wang and **C. H. Stam**
Laboratory for Crystallography, J. H. van 't Hoff Institute, University of Amsterdam, 1018 WV Amsterdam (The Netherlands)

(Received February 20, 1991; revised April 16, 1991)

Abstract

The new ligand 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh) rendered the following coordination compounds with copper(I) and copper(II) salts: $Cu(bddh)(NO_3)_2$, $[Cu(bddh)(H_2O)](BF_4)_2$, $[Cu(bddh)Cl]_2CuCl_4$, $[Cu(bddh)(Hdmpz)](BF_4)_2$ (Hdmpz = 3,5-dimethylpyrazole), $[Cu(bddh)Cl]BF_4$, $[Cu(bddh)]_2(BF_4)_2$, Cu(bddh)Cl and Cu(bddh)Br. The compound $[Cu(bddh)Cl]_2CuCl_4$ crystallizes from ethanol in the monoclinic space group *Cc*, with $a = 19.018(4)$, $b = 14.840(3)$, $c = 14.963(3)$ Å, $\beta = 100.24(2)$, $V = 4158$ Å^3, $Z = 4$ and $D_{calc} = 1.63$ g cm^{-3}. The refinement using 5145 measured and 1826 observed ($F > 2\sigma(F)$) reflections resulted in the *R* values 0.062 (*R*) and 0.068 (R_w). The asymmetric unit consists of two $[Cu(bddh)Cl]^+$ cations and a $CuCl_4^{2-}$ anion. The copper(II) atom in $[Cu(bddh)Cl]^+$ cation is coordinated by two pyrazole nitrogen atoms in *trans* position (1.991(9) and 1.98(1) Å), two thioether atoms in *cis* position (2.422(3) and 2.480(3) Å) and one chloride atom (2.249(4) Å) in a distorted trigonal bipyramid with the nitrogen donors on axial positions and the two sulfurs and chloride in the equatorial plane. The tetrahedral $CuCl_4^{2-}$ anion lies in disorder. The compound $[Cu(bddh)(Hdmpz)](BF_4)_2$ crystallizes from ethanol in the monoclinic space group $P2_1/c$, with $a = 18.360(3)$, $b = 9.419(3)$, $c = 16.068(2)$ Å, $\beta = 100.29(1)$, $V = 2734$ Å^3, $Z = 4$ and $D_{calc} = 1.55$ g cm^{-3}. The refinement using 6883 measured and 2326 observed ($F > 2\sigma(F)$) reflections resulted in the *R* values 0.055 (*R*) and 0.061 (R_w). The asymmetric unit consists of a $[Cu(bddh)(Hdmpz)]^{2+}$ cation and two tetrafluoroborate anions. The copper(II) atom is coordinated by three pyrazole nitrogen atoms (1.987(6) and 1.962(6) Å; Hdmpz: 1.977(6) Å) and two sulfur atoms (2.478(2) and 2.404(3) Å) in a distorted trigonal bipyramid, with the ligand pyrazole groups on axial positions. The copper(I) compound $[Cu(bddh)]_2(BF_4)_2$ crystallizes from ethanol in the monoclinic space group *C*2/*c*, with $a = 22.679(2)$, $b = 12.766(2)$, $c = 14.213(2)$ Å, $\beta = 106.69(1)$, $V = 3942$ Å^3, $Z = 8$ and $D_{calc} = 1.55$ g cm^{-3}. The refinement using 1495 observed ($F > 2.5\sigma(F)$) reflections resulted in the *R* values 0.049 (*R*) and 0.082 (R_w). The cationic part of the compound is dinuclear with C_2 symmetry. The copper(I) ions are 4.603(3) Å apart. Each copper(I) ion is coordinated by a pyrazole nitrogen atom at 2.067(6) Å and two thioether atoms at 2.426(2) and 2.333(3) Å from one ligand and by a pyrazole nitrogen at 1.980(8) Å of another ligand in a strongly distorted tetrahedral fashion. Spectroscopic results strongly suggest that the compounds $[Cu(bddh)(H_2O)](BF_4)_2$ and $[Cu(bddh)Cl]BF_4$ contain the trigonal bipyramidal [Cu(bddh)A] unit (A = anion), as present in $[Cu(bddh)Cl]_2CuCl_4$ and $[Cu(bddh)(Hdmpz)](BF_4)_2$. The compounds Cu(bddh)Cl and Cu(bddh)Br are IR and X-ray isomorphous.

Introduction

An increasing number of coordination compounds of low molecular weight is being designed and synthesized in order to obtain a better insight into the structure and nature of the active sites of metalloproteins [1]. The research presented in this paper, is inspired by the interest in the active site of the so-called blue-copper proteins [2]. These blue-copper proteins are known for their interesting and remarkable spectroscopic and chemical properties [2]. The structures of some examples of this class of

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

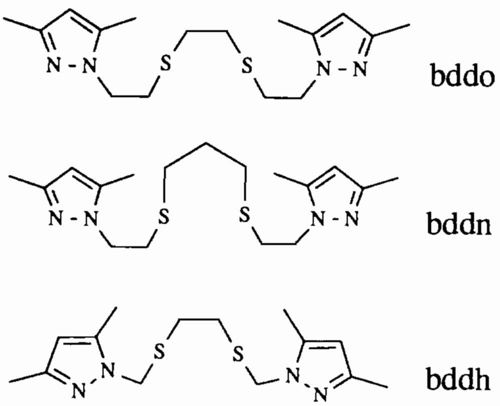

Fig. 1. The ligands bddo, bddn and bddh.

proteins have been determined using X-ray crystallography [2]. The results show that the active sites consist of a copper ion coordinated by two imidazoles, one thioether and one thiolate. The coordination geometry can be interpreted as a distorted, flattened tetrahedron. The bonding distances of the imidazole rings and the thiolate function can be regarded as normal, whereas the thioether function is long [3], approximately 2.9 Å.

In previous reports [4–6] we described the interesting coordination behaviour of ligands incorporating two pyrazole groups, to mimic the imidazole function present in the proteins, and two thioether functions. To avoid practical problems such as disulfide formation, a thioether function is used to mimic the protein thiolate function. These pyrazole containing ligands form a set in which the ligands differ by the number of methylene units between the donor functions. A remarkable feature was observed with the previously described ligands bddo and bddn (see Fig. 1), as they form several coordination compounds in which the thioethers do not coordinate to the metal ion [4–6]. It was suggested that the long bridge between the pyrazole and thioether function is too flexible to ensure thioether coordination [4–6]. To investigate this phenomenon in more detail, the new ligand 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh) was synthesized. Its coordination behaviour towards copper(I) and copper(II) salts is described in this report. In a separate paper, coordination compounds with transition metals other than copper will be described [7].

Experimental

Synthesis of the ligand bddh

The materials used in the synthesis were all commercially available and were used without purification. The synthesis of 3,5-dimethylpyrazole (Hdmpz) and 1-hydroxymethyl-3,5-dimethylpyrazole (nhdp) is described elsewhere [8].

1-(Chloromethyl)-3,5-dimethyl-pyrazole (ncdp.HCl)

To a cooled solution ($T<5$ °C) of 30 g (0.24 mol) of nhdp in carefully dried chloroform 30.3 g (0.26 mol) of thionyl chloride was added dropwise. The temperature of the reaction mixture was not allowed to exceed 10 °C. Stirring was prolonged for 30 min, while the reaction mixture was allowed to warm up to room temperature. The solvent was stripped *in vacuo* and the resulting yellow oil was solidified by the addition of dry diethylether while stirring vigorously. The product (yield 43 g) contains additional HCl (*c*. 5%), but is sufficiently pure to proceed with the synthesis, as was concluded from NMR spectroscopy. The compound hydrolyzes when exposed to air and must be stored under inert atmosphere. ^{1}H NMR (solvent $CDCl_3$): 2.52 (s, 3H), 2.56 (s, 3H), 5.76 (s, 2H), 6.32 (s, 1H) ppm.

1,6-Bis(3′, 5′-dimethyl-1′-pyrazolyl)-2,5-dithiahexane (bddh)

46 g (190 mmol, 80% purity) ncdp·HCl was solved in 100 ml of dry dmf. To this solution was added dropwise 8 ml (95 mmol) of 1,2-ethanedithiol dissolved in *c*. 10 ml of dmf. When the addition of the thiol was completed the reaction mixture was heated to 90–100 °C and after 15 min at this temperature a solution of 14 g KOH in 50 ml water was added. Heating was stopped and after 15 min 200 ml of water was added to the mixture. After cooling to room temperature the reaction mixture was extracted four times with 100 ml of chloroform. The collected layers of chloroform were dried and stripped *in vacuo*. The yellowish oil (yield 22 g, 76%) was crystallized from thf. ^{1}H NMR (solvent $CDCl_3$): 2.20 (s, 6H), 2.28 (s, 6H), 2.76 (s, 4H), 5.04 (s, 4H), 5.80 (s, 2H) ppm.

When no base or water was added to the reaction mixture a small amount of white crystalline solid was obtained from the mixture. This product proved to be the hydrochloric salt of the ligand bddh. ^{1}H NMR (solvent $CDCl_3$): 2.46 (s, 12H), 3.20 (s, 4H), 5.66 (s, 4H), 6.20 (s, 2H) ppm.

Synthesis of the coordination compounds

The coordination compounds were prepared by dissolving 2 mmol of the appropriate hydrated metal salts in 7–10 ml of warm ethanol, methanol or acetonitrile and adding this solution to a warm solution of the ligand in the same solvent. For the preparation of the mixed-anion coordination compounds a combination of the appropriate hydrated metal salts was used. Triethylorthoformate (*c.* 1 ml) was added for dehydration in all cases. After cooling to room temperature usually crystalline products were obtained. When the product precipitated as a powder, different solvents were tried. The synthesis of the copper(I) compounds were performed in an inert dinitrogen atmosphere and with the use of carefully dried solvents. In most cases cooling to room temperature, or cooling to −23 °C, or adding diethyl ether yielded crystalline products.

Characterization procedures

Metal contents were determined by EDTA titration, after destruction of the compound by heating with concentrated nitric acid. C, H and N elements were analyzed at the Microanalytical Laboratory of University College (Dublin). IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a P. E. data station. Samples were prepared as KBr pellets or as nujol mulls. Vis–near-IR spectra were recorded on a Perkin-Elmer 330 spectrophotometer in the diffuse reflectance mode with MgO as reference. X-band EPR spectra were recorded on a Jeol JES-RE2X spectrophotometer equipped with a Jeol Esprit 330 data system at 77 K for powdered samples. ^{1}H NMR spectra were recorded on a JNM-FX 200 spectrometer (200 MHz, Fourier transform).

X-ray data collection and structure refinement

The crystals were isolated from the reaction mixtures. The data collected for the three structures are listed in Table 1. Scattering factors and anomalous dispersion corrections were taken from the literature [9].

Crystal structure determination of $[Cu(bddh)]_2(BF_4)_2$

The structure was solved by means of the heavy-atom method. Refinement proceeded by means of block-diagonal least-squares calculations, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms. An empirical absorption correction was applied (DIFABS [10]) and a weighting scheme $w = 1/(6.1 + F_o + 0.023F_o^2)$ was employed. The calculations were carried out with the program XRAY76 [11]. Fractional coordinates with isotropic thermal parameters and selected bond lengths and bond angles are collected in Tables 2 and 3, respectively.

Crystal structure determination of $[Cu(bddh)Cl]_2CuCl_4$

The determination of the structure was started using the space group *Cc*. The coordinates of the three copper atoms were determined using the Patterson function. The remaining non-hydrogen atoms were located using Fourier difference maps. The

TABLE 1. Crystallographic data for the structures of $[Cu(bddh)]_2(BF_4)_2$ (**I**), $[Cu(bddh)Cl]_2CuCl_4$ (**II**) and $[Cu(bddh)(N\text{-}3,5\text{-dimethyl-pyrazole})](BF_4)_2$ (**III**)

	I	**II**	**III**
Formula	$CuC_{14}H_{22}N_4S_2BF_4$	$Cu_3C_{28}H_{44}N_8S_4Cl_6$	$CuC_{19}H_{30}N_6S_2B_2F_8$
Formula weight	460.84	1024.33	643.66
Space group	*C*2/*c*	*Cc*	*P*2$_1$/*c*
a (Å)	22.679(2)	19.018(4)	18.360(3)
b (Å)	12.766(2)	14.840(3)	9.419(3)
c (Å)	14.213(2)	14.963(3)	16.068(2)
α (°)	90	90	90
β (°)	106.69(1)	100.24(2)	100.29(1)
γ (°)	90	90	90
V (Å^3)	3942	4158	2734
Z	8	4	4
D_{calc} (g cm^{-3})	1.55	1.63	1.55
μ (Mo Kα) (cm^{-1})	13.5	21	10
Crystal size (mm^3)	0.2×0.23×0.45	0.50×0.25×0.25	0.43×0.38×0.13
Data collection	CAD4	CAD4	CAD4
Range (2θ) (°)	1.1–22	2.2–27	2.3–27
Scan method	ω–2θ	ω–2θ	ω–2θ
h, *k*, *l* range	−23–23, 0–13, 0–14	−24–24, 0–19, 0–19	−23–23, 0–12, 0–20
No. measured data	2270	5145	6883
No. unique data	1495[a]	1826[b]	2326[b]
R	0.049	0.062	0.055
R_w	0.082	0.068	0.061

[a] $F > 2.5\sigma(F)$. [b] $F > 2\sigma(F)$.

TABLE 2. Fractional coordinates and equivalent thermal parameters of the non-hydrogen atoms of $[Cu(bddh)]_2(BF_4)_2$

Atom	x	y	z	U_{eq}
Cu(1)	0.41219(5)	0.31213(8)	0.11912(8)	0.0443(6)
S(2)	0.30528(9)	0.2822(2)	0.1114(2)	0.042(1)
S(5)	0.4379(1)	0.3121(2)	0.2903(2)	0.047(1)
B(30)	0.3170(7)	−0.0215(10)	0.1999(9)	0.068(8)
F(31)	0.2571(4)	0.007(1)	0.1641(8)	0.172(9)
F(32)	0.3492(5)	0.0477(6)	0.1667(9)	0.155(9)
F(33)	0.3308(4)	−0.0129(7)	0.2996(6)	0.124(7)
F(34)	0.3295(5)	−0.1192(5)	0.1751(6)	0.130(7)
N(11)	0.3268(3)	0.4916(5)	0.0935(5)	0.039(4)
N(12)	0.3860(3)	0.4673(5)	0.0957(5)	0.040(4)
N(21)	0.4944(3)	0.1886(5)	0.4482(5)	0.045(4)
N(22)	0.5495(3)	0.2375(6)	0.4705(5)	0.043(4)
C(3)	0.3104(4)	0.2828(7)	0.2411(6)	0.043(5)
C(4)	0.3632(4)	0.3427(8)	0.3064(7)	0.056(6)
C(10)	0.2776(4)	0.4125(7)	0.0708(7)	0.048(6)
C(13)	0.4156(4)	0.5595(7)	0.1051(6)	0.048(6)
C(14)	0.3757(5)	0.6403(7)	0.1072(7)	0.053(6)
C(15)	0.3195(4)	0.5936(6)	0.1007(6)	0.044(5)
C(16)	0.4819(5)	0.5629(10)	0.108(1)	0.084(9)
C(17)	0.2591(5)	0.6417(8)	0.0955(9)	0.072(8)
C(20)	0.4566(4)	0.1832(7)	0.3470(7)	0.049(6)
C(23)	0.5736(4)	0.2256(7)	0.5669(7)	0.046(5)
C(24)	0.5342(4)	0.1662(7)	0.6047(6)	0.049(6)
C(25)	0.4839(4)	0.1442(7)	0.5282(7)	0.045(5)
C(26)	0.6340(5)	0.2746(10)	0.6196(8)	0.068(7)
C(27)	0.4273(5)	0.0828(8)	0.5253(8)	0.064(7)

TABLE 3. Relevant bond lengths (Å) and bond angles (°) of $[Cu(bddh)]_2(BF_4)_2$

Cu(1)–S(2)	2.426(2)
Cu(1)–S(5)	2.333(3)
Cu(1)–N(12)	2.067(6)
Cu(1)–N(22)	1.980(8)
S(2)–Cu(1)–S(5)	89.68(9)
S(2)–Cu(1)–N(12)	84.6(2)
S(2)–Cu(1)–N(22)	120.8(2)
S(5)–Cu(1)–N(12)	98.2(2)
S(5)–Cu(1)–N(22)	130.3(2)
N(12)–Cu(1)–N(22)	121.1(3)
Cu(1)–S(2)–C(3)	100.5(3)
Cu(1)–S(2)–C(10)	96.9(3)
C(3)–S(2)–C(10)	103.6(4)
Cu(1)–S(5)–C(4)	99.7(3)
Cu(1)–S(5)–C(20)	114.6(3)
C(4)–S(5)–C(20)	104.2(5)

TABLE 4. Fractional coordinates[a] ($\times 10^5$ for Cu(1); $\times 10^4$ for others) and isotropic temperature factor ($Å^2 \times 10^2$ for Cu, Cl(1) and S; $Å^2 \times 10$ for all C, for Cl(21) to Cl(24) and all N) of the non-hydrogen atoms of $[Cu(bddh)Cl]_2CuCl_4$

Atom	x	y	z	B_{iso}
Cu(1)	−22098(5)	1771(7)	7892(7)	290(4)
Cl(1)	−1863(2)	−599(3)	2083(2)	510(11)
N(11)	−1160(5)	84(6)	−437(5)	25(3)
N(12)	−1526(5)	−419(6)	114(6)	28(3)
C(13)	−1309(6)	−1259(8)	26(8)	34(4)
C(14)	−820(6)	−1289(9)	−549(8)	34(4)
C(15)	−729(6)	−432(9)	−828(8)	34(4)
C(16)	−1605(6)	−2019(8)	496(9)	47(4)
C(17)	−252(6)	−58(9)	−1428(8)	45(4)
C(18)	−1245(6)	1045(7)	−515(8)	32(3)
N(21)	−3631(5)	956(7)	821(6)	29(3)
N(22)	−2931(5)	924(6)	1252(6)	31(3)
C(23)	−2873(6)	1501(8)	1929(8)	30(3)
C(24)	−3541(7)	1884(9)	1945(9)	41(4)
C(25)	−4006(7)	1520(9)	1248(9)	41(4)
C(26)	−2188(6)	1668(9)	2568(8)	45(4)
C(27)	−4787(7)	1669(10)	956(9)	64(5)
C(28)	−3905(6)	374(9)	61(8)	39(4)
S(31)	−2011(2)	1474(2)	−117(2)	303(8)
C(32)	−2737(6)	1320(7)	−1052(7)	35(4)
C(33)	−3023(6)	395(7)	−1281(7)	40(4)
S(34)	−3253(2)	−288(2)	−356(2)	335(9)
Cu(2)	5041(7)	1726(2)	7445(8)	991(14)
Cl(21)	5632(9)	2584(11)	8541(11)	62(5)
Cl(22)	4426(9)	2494(9)	6374(9)	55(4)
Cl(23)	4843(6)	393(7)	7890(7)	119(5)
Cl(24)	5934(6)	1298(6)	6447(7)	96(3)

[a]Because of constraints mimicking two-fold symmetry only the coordinates of one $[Cu(bddh)Cl]^+$ cation are provided.

coordinates and thermal parameters were refined using a locally developed least-squares program. The refinement of the model was not satisfactory, partly caused by the unfavourable data to variables ratio. Inspection of the errors in the coordinates and unsatisfactory bond lengths in the ligands suggested the presence of additional pseudo-symmetry, corresponding with the space group *C2/c*. Refinement based on the *C2/c* space group greatly improved the refinement of the model for the $[Cu(bddh)Cl]^+$ unit. However the refinement of the tetrahedral $CuCl_4^{2-}$ anion appeared impossible because of disorder which could not be described satisfactory in this space group. Thus it was decided to refine the structure in *Cc* with two $[Cu(bddh)Cl]^+$ units constrained according to *C2/c* symmetry, decreasing the number of variables considerably. This approach rendered the best fit. The refinement of $CuCl_4^{2-}$ improved but remained unsatisfactory, as can be deduced from the bond lengths, bond angles and the large values for the thermal parameters ($CuCl_4^{2-}$ is coded Cu(2), Cl(21) to Cl(24) in Table 4). Clear indications of disorder in the $CuCl_4^{2-}$ anion remain. The maximum values for remaining electron density in the final difference Fourier are located in the neighbourhood of the $CuCl_4^{2-}$ unit (+0.84 and −0.58 e $Å^3$).

Absorption correction was applied using the program DIFABS [10]. The coordinates of the hydrogen

TABLE 5. Relevant bond lengths (Å) and bond angles (°) of $[Cu(bddh)Cl]_2CuCl_4$

Cu(1)–Cl(1)	2.249(4)
Cu(1)–N(12)	1.991(9)
Cu(1)–N(22)	1.98(1)
Cu(1)–S(31)	2.422(3)
Cu(1)–S(34)	2.480(3)
Cu(2)–Cl(21)	2.22(2)
Cu(2)–Cl(22)	2.14(2)
Cu(2)–Cl(23)	2.14(1)
Cu(2)–Cl(24)	2.53(2)
Cl(1)–Cu(1)–N(12)	95.2(3)
Cl(1)–Cu(1)–N(22)	95.8(3)
Cl(1)–Cu(1)–S(31)	146.9(1)
Cl(1)–Cu(1)–S(34)	122.0(1)
N(12)–Cu(1)–N(22)	168.9(4)
N(12)–Cu(1)–S(31)	83.6(3)
N(12)–Cu(1)–S(34)	92.3(2)
N(22)–Cu(1)–S(31)	86.4(3)
N(22)–Cu(1)–S(34)	83.0(3)
S(31)–Cu(1)–S(34)	91.1(1)
Cu(1)–S(31)–C(18)	97.0(4)
Cu(1)–S(31)–C(32)	99.2(4)
Cu(1)–S(34)–C(28)	97.2(4)
Cu(1)–S(34)–C(33)	95.7(4)
Cl(21)–Cu(2)–Cl(22)	112.7(6)
Cl(21)–Cu(2)–Cl(23)	113.2(7)
Cl(21)–Cu(2)–Cl(24)	105.9(7)
Cl(22)–Cu(2)–Cl(23)	128.5(7)
Cl(22)–Cu(2)–Cl(24)	91.6(7)
Cl(23)–Cu(2)–Cl(24)	97.2(5)

atoms were calculated at a distance of 0.95 Å from the parent atom. The coordinates of the hydrogen atoms were coupled to the coordinates of the parent atom during refinement. Fractional coordinates with isotropic thermal parameters and selected bond lengths and bond angles are collected in Tables 4 and 5, respectively.

Crystal structure determination of $[Cu(bddh)(Hdmpz)](BF_4)_2$

The coordinates of the copper atom were determined using a Patterson map. The remaining non-hydrogen atoms were located using Fourier difference maps. The positions of the hydrogen atoms were calculated at a distance of 0.95 Å from the parent atom, and coupled to the parent atom during refinement. A locally developed least-squares program was used for the refinement. Absorption correction was applied using the program DIFABS [10]. Disorder was found for one of the tetrafluoroborate anions, which was described by two independent orientations of the anion and refined with isotropic thermal parameters. Fractional coordinates with isotropic thermal parameters and selected bond lengths and bond angles are collected in Tables 6 and 7, respectively.

Results and discussion

General and IR spectroscopy

Analytical data, melting point, colour, electronic absorption maxima and *g* values of the coordination compounds of bddh are collected in Table 8. The isolated copper(I) compounds appeared to be stable in air for several months.

The elemental analysis of $Cu(bddh)(NO_3)_2$ excludes the presence of water, which is confirmed by IR spectroscopy [12]. In a nujol mull of the compound the $\nu_1 + \nu_4$ overtone region of the N–O vibrations shows two sharp vibrations at 1720 and 1750 cm^{-1}. The relative sharpness indicates that only one type of nitrate is present in the compound. The pattern is in good agreement with two monodentate coordinating nitrate anions [13]. Thus, the coordination geometry of the copper atom in $Cu(bddh)(NO_3)_2$ is most likely an octahedron, made up by two nitrogens, two sulfurs and two monodentate coordinating nitrates.

The compound formed from bddh and $CuCl_2$ must be formulated, according to crystal structure determination, as $[Cu(bddh)Cl]_2CuCl_4$. A possible Cu–Cl vibration [12] is located at 320 cm^{-1}. The same vibration is also present in the IR spectrum of $[Cu(bddh)Cl](BF_4)$. The ν_3 of the tetrafluoroborate anion is relatively sharp and in agreement with the hypothesis that the tetrafluoroborate anion is not involved in (semi)-coordination [14]. Ligand vibrations make it impossible to identify the ν_1 and ν_2 vibrations of a BF_4^- anion involved in (semi)-coordination.

The IR spectrum of the compound $[Cu(bddh)(dmpz)](BF_4)_2$ clearly shows the presence of the Hdmpz molecule (1575 cm^{-1}) and the presence of a hydrogen bridge [12].

The presence of water in the compound $[Cu(L)(H_2O)](BF_4)_2$ was deduced from elemental analysis and IR spectroscopy [12]. The relatively sharp H–O stretch vibration at 3430 cm^{-1} suggests that the water molecule coordinates to the metal ion or is located in a cavity of the crystal lattice, and may also be involved in a weak hydrogen bridge. The tetrafluoroborate anion may be the acceptor of the hydrogen bridge, but ligand vibrations make it impossible to identify the ν_1 and ν_2 vibrations of a BF_4^- anion involved in a hydrogen bridge [14]. Considering the structures of $[Cu(bddh)Cl]_2CuCl_4$ and $[Cu(bddh)(Hdmpz)](BF_4)_2$ it is likely that the water molecule coordinates to the copper(II) atom

TABLE 6. Fractional coordinates ($\times 10^5$ for Cu; $\times 10^4$ for others) and isotropic temperature factor (Å$^2\times 10^2$ for Cu and S; Å$^2\times 10$ for others) of [Cu(bddh)(*N*-3,5-dimethylpyrazole)]$(BF_4)_2$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso}
Cu(1)	24771(5)	42966(11)	64414(6)	329(3)
N(11)	1067(3)	5759(7)	6088(4)	40(2)
N(12)	1565(3)	5002(7)	5714(4)	34(2)
C(13)	1397(4)	5307(8)	4888(5)	34(2)
C(14)	792(5)	6197(8)	4735(6)	45(3)
C(15)	594(4)	6481(10)	5495(7)	43(3)
C(16)	1834(4)	4722(10)	4274(5)	50(3)
C(17)	−20(4)	7381(11)	5738(6)	64(3)
C(18)	1023(4)	5531(11)	6969(6)	55(3)
S(41)	3100(1)	6631(2)	6446(1)	452(7)
C(42)	2620(5)	7458(11)	7216(6)	63(3)
C(43)	2390(5)	6589(11)	7888(6)	66(3)
S(44)	1876(1)	4996(3)	7589(1)	464(7)
N(21)	3960(3)	4725(6)	7460(4)	35(2)
N(22)	3363(3)	3826(6)	7273(4)	34(2)
C(23)	3544(4)	2680(10)	7765(5)	38(2)
C(24)	4242(4)	2837(10)	8242(5)	39(3)
C(25)	4500(4)	4144(10)	8040(5)	38(2)
C(26)	3027(5)	1461(10)	7727(6)	59(3)
C(27)	5224(4)	4890(10)	8334(6)	57(3)
C(28)	3974(4)	6087(8)	7032(6)	50(3)
N(31)	2054(3)	1602(7)	5578(4)	38(2)
N(32)	2594(3)	2618(6)	5739(4)	32(2)
C(33)	3161(4)	2149(10)	5388(5)	38(3)
C(34)	2988(4)	825(10)	5024(5)	44(3)
C(35)	2286(5)	496(10)	5153(5)	43(3)
C(36)	3854(4)	3000(10)	5421(6)	50(3)
C(37)	1793(5)	−766(10)	4929(6)	69(3)
B(40)	5949(6)	1928(13)	641(7)	45(3)
F(41)	5656(3)	1343(7)	1291(4)	100(3)
F(42)	6655(3)	1475(8)	702(4)	104(3)
F(43)	5963(4)	3334(6)	791(5)	99(3)
F(44)	5553(3)	1648(7)	−113(4)	79(2)
B(50)	671(5)	1119(16)	6860(7)	73(3)
F(51)	729(7)	1732(13)	7644(7)	88(2)
F(52)	889(6)	2250(14)	6427(8)	88(2)
F(53)	1123(6)	−56(13)	6885(8)	88(2)
F(54)	−62(5)	818(14)	6561(7)	88(2)
B(50A)[a]	658(7)	1130(24)	6852(8)	73(3)
F(51A)	664(8)	789(17)	6035(9)	102(3)
F(52A)	667(9)	70(17)	7402(10)	102(3)
F(53A)	−16(8)	1719(18)	6884(11)	102(3)
F(54A)	1218(8)	2091(17)	7111(11)	102(3)

[a] Alternative position of the disordered tetrafluoroborate anion.

and also bridges to one or two tetrafluoroborate anions.

The powder diffraction patterns and the IR spectra of the compounds Cu(bddh)Cl and Cu(bddh)Br are identical, indicating that both compounds have similar structures.

Crystal structure of [Cu(bddh)]$_2(BF_4)_2$

The structure of the dication is depicted in Fig. 2. The compound is dinuclear with C_2 symmetry. The copper(I) ions are separated by 4.603(3) Å. Each copper(I) ion is coordinated by a pyrazole nitrogen atom at 2.067(6) Å (see Table 3) and two thioether atoms at 2.426(2) and 2.333(3) Å from one ligand and by a pyrazole nitrogen at 1.980(8) Å of another ligand in a strongly distorted tetrahedral fashion. These distances are common [16]. The small ligand bites, forming five-membered chelate rings, are clearly the source of a large part of the distortion from perfect tetrahedral geometry. This may also explain the differences in bond lengths between the two pyrazole heterocycles. The dinuclear nature of the compound suggests that the ligand bddh is unable to form, in a tetradentate chelating conformation, the tetrahedral coordination which is preferred by copper(I). The present structure offers an elegant solution to the steric constraints imposed by the ligand.

Crystal structure of [Cu(bddh)Cl]$_2$CuCl$_4$

The asymmetric unit of [Cu(bddh)Cl]$_2$CuCl$_4$ consists of two [Cu(bddh)Cl]$^+$ cations and a CuCl$_4^{2-}$ counter anion. The copper(II) atom in the [Cu(bddh)Cl]$^+$ cation (see Fig. 3) is coordinated by two pyrazole nitrogen atoms in *trans* position, two thioether atoms in *cis* position and one chloride atom. The coordination geometry is a distorted trigonal bipyramid with the nitrogen donors on axial positions and the two sulfurs and chloride in the equatorial plane. The geometry is distorted, due to the small ligand bites of the ligand. The bond lengths of the nitrogens (1.991(9) and 1.98(1) Å, Table 5), thioethers (2.422(3) and 2.480(3) Å) and chloride (2.249(4) Å) can be regarded as normal [16]. The CuCl$_4^{2-}$ anion is disordered, which can be deduced from the bond lengths and angles (Table 5). The coordination geometry of the anion is tetrahedral. Copper to copper distances are above 6.4 Å. The molecules are packed according to normal van der Waals forces.

Crystal structure of [Cu(bddh)(Hdmpz)]$(BF_4)_2$

The copper(II) atom in [Cu(bddh)(Hdmpz)]$(BF_4)_2$ is coordinated by three pyrazole nitrogen atoms and two sulfur atoms (see Fig. 4). The coordination geometry is a distorted trigonal bipyramid, with the ligand pyrazole groups in axial positions. The bonding distances for the nitrogen donors (bddh: 1.987(6) and 1.962(6) Å, Table 7; Hdmpz: 1.977(6) Å) and of the thioether sulfurs (2.478(2) and 2.404(3) Å) can be regarded as normal [16]. The coordination geometry resembles the geometry of the

TABLE 7. Relevant bond lengths (Å) and bond angles (°) of [Cu(bddh)(N-3,5-dimethylpyrazole)](BF$_4$)$_2$

Cu(1)–N(12)	1.978(6)	B(50)–F(52)	1.37(2)
Cu(1)–S(41)	2.478(2)	B(50)–F(53)	1.38(2)
Cu(1)–S(44)	2.404(3)	B(50)–F(54)	1.37(1)
Cu(1)–N(22)	1.962(6)	B(50A)–F(51A)	1.35(2)
Cu(1)–N(32)	1.977(6)	B(50A)–F(52A)	1.33(3)
N(31)–H(311)	0.95	B(50A)–F(53A)	1.37(2)
B(40)–F(41)	1.37(1)	B(50A)–F(54A)	1.38(2)
B(40)–F(42)	1.35(1)	F(52)–H(311)	1.91(1)
B(40)–F(43)	1.35(1)	F(51A)–H(311)	2.01(2)
B(40)–F(44)	1.32(1)	F(52)–N(31)	2.80(1)
B(50)–F(51)	1.37(2)	F(51A)–N(31)	2.88(2)
N(12)–Cu(1)–S(41)	92.6(2)	F(51A)–B(50A)–F(52A)	118(2)
N(12)–Cu(1)–S(44)	84.6(2)	F(51A)–B(50A)–F(53A)	107(1)
N(12)–Cu(1)–N(22)	171.7(3)	F(51A)–B(50A)–F(54A)	108(1)
N(12)–Cu(1)–N(32)	95.6(2)	F(52A)–B(50A)–F(53A)	101(1)
S(41)–Cu(1)–S(44)	91.67(9)	F(52A)–B(50A)–F(54A)	112(1)
S(41)–Cu(1)–N(22)	82.6(2)	F(53A)–B(50A)–F(54A)	111(2)
S(41)–Cu(1)–N(32)	127.9(2)	S(44)–Cu(1)–N(22)	88.7(2)
S(44)–Cu(1)–N(32)	140.3(2)	N(22)–Cu(1)–N(32)	92.7(2)
Cu(1)–S(41)–C(42)	95.9(3)	Cu(1)–S(41)–C(28)	96.8(3)
Cu(1)–S(44)–C(18)	97.3(3)	Cu(1)–S(44)–C(43)	98.3(4)
F(41)–B(40)–F(42)	108.5(9)	F(41)–B(40)–F(43)	105(1)
F(41)–B(40)–F(44)	113.1(9)	F(42)–B(40)–F(43)	108.0(9)
F(42)–B(40)–F(44)	111(1)	F(43)–B(40)–F(44)	110.6(9)
F(51)–B(50)–F(52)	99(1)	F(51)–B(50)–F(53)	111(1)
F(51)–B(50)–F(54)	109(1)	F(52)–B(50)–F(53)	114(1)
F(52)–B(50)–F(54)	110(1)	F(53)–B(50)–F(54)	113(1)

TABLE 8. Melting point, colour, electronic absorption maxima (in 10^3 cm^{-1} and *g* values of the coordination compounds with bddh (denoted by L)

Compound	Melting point (°C)	Colour	Maxima	*g* values
Cu(L)(NO$_3$)$_2$[a]	175	green	14.5, 11.1	2.21, 2.11, 2.01
[Cu(L)(H$_2$O)](BF$_4$)$_2$[b]	190d	green	14.5, 10.8	2.21, 2.11, 2.01
[Cu(L)Cl]$_2$CuCl$_4$[c]	139	green	14.8, 10.4	2.23, 2.12, 2.06
[Cu(L)(Hdmpz)](BF$_4$)$_2$[d]	186	green	15.5, 12.8	2.09[i]
[Cu(L)Cl]BF$_4$[e]	163	green	14.5, 10.6	2.20, 2.09
[Cu(L)]$_2$(BF$_4$)$_2$[f]	207	white		
CuLCl[g]	169	white		
CuLBr[h]	207d	white		

[a] %M = 12.7(12.8), %C = 33.3(33.8), %H = 4.48(4.45), %N = 16.8(16.9), calculated values in parentheses. [b] %M = 11.6(11.5), %C = 29.2(29.7), %H = 4.17(4.28), %N = 9.70(9.91). [c] %M = 18.8(18.6), %C = 31.4(32.8), %H = 4.37(4.33), %N = 10.6(10.9). EPR spectrum at room temperature is isotropic with *g* = 2.08. [d] %M = 9.87(9.84), %C = 35.0(35.5), %H = 4.58(4.70), %N = 12.6(13.1). [e] %M = 12.8(12.8). [f] %M = 13.5(13.5), %C = 36.0(36.5), %H = 4.66(4.81), %N = 11.9(12.2). [g] %M = 15.1(15.5), %Cl = 8.8(8.7), %C = 41.5(41.0), %H = 5.26(5.37), %N = 13.9(13.7); This compound is X-ray and IR isomorphous with Cu(L)Br. [h] %M = 13.6(14.0). [i] Exchange narrowed.

[Cu(bddh)Cl]$^+$ in [Cu(bddh)Cl]$_2$CuCl$_4$, as can be deduced from the bonding distances and angles collected in Tables 5 and 7.

Although the position of the hydrogen H(311) attached to N(31) of Hdmpz was calculated at 0.95 Å, the hydrogen bridge to one of the tetrafluoroborate anions can be recognized from the distances in Table 7. This tetrafluoroborate anion is disordered, however, both orientations used for the description of the disorder show the presence of the hydrogen bridge, N(31)–F(52) = 2.80(1) and N(31)–F(51a) = 2.88(2). The second tetrafluoroborate anion is not disordered and shows no other contacts than normal van der Waals contacts.

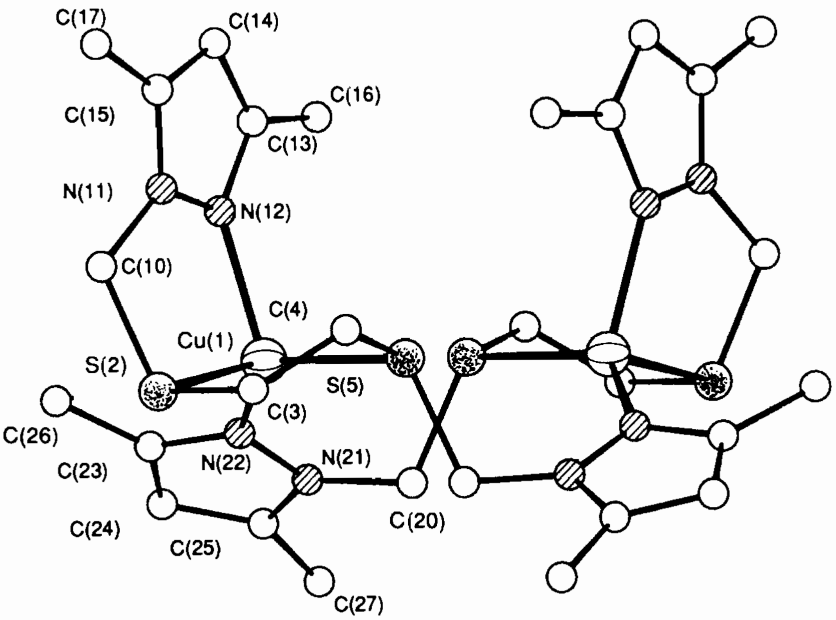

Fig. 2. PLUTO [15] drawing of $[Cu(bddh)]_2(BF_4)_2$. The hydrogens and the tetrafluoroborate anions are omitted for clarity.

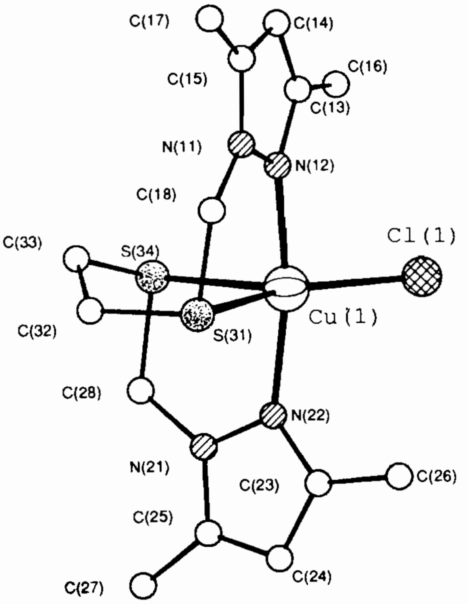

Fig. 3. PLUTO [15] drawing of $[Cu(bddh)Cl]_2CuCl_4$. The hydrogens and the $CuCl_4^{2-}$ anion are omitted for clarity.

EPR and electronic spectroscopy

All copper(II) compounds show two absorption maxima in the ligand field spectrum (Table 8). Except for the compound $[Cu(bddh)(Hdmpz)](BF_4)_2$ the values for the absorptions are very alike.

The compounds $Cu(bddh)(NO_3)_2$ and $[Cu(bddh)(H_2O)](BF_4)_2$ show an orthorhombic type EPR spectrum with similar *g* values (Table 8). The EPR spectrum of $[Cu(bddh)(Hdmpz)](BF_4)_2$ is isotropic, most likely due to extensive exchange narrowing as a result of lattice packing effects. In contrast the compound $[Cu(bddh)Cl]BF_4$ shows an axial type EPR spectrum [17].

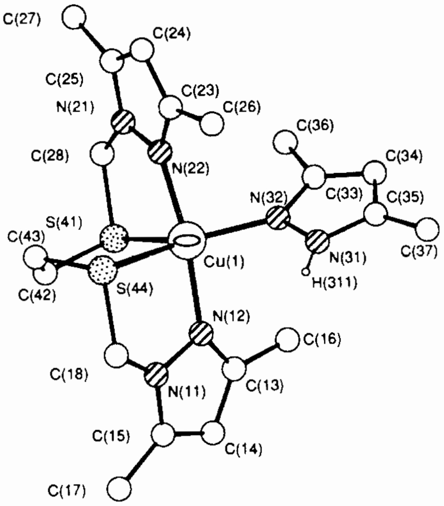

Fig. 4. PLUTO [15] drawing of $[Cu(bddh)(Hdmpz)](BF_4)_2$.The hydrogens and the tetrafluoroborate anions are omitted for clarity.

The $CuCl_4^{2-}$ unit in the compound $[Cu(bddh)Cl]_2CuCl_4$ should result in clear effects in the EPR and ligand field spectra [18]. However, the orthorhombic EPR spectrum indicates that the three copper species in the asymmetric unit are exchange coupled and as a result the presence of separate species cannot be detected in the EPR spectrum. The d–d transitions of the tetrachlorocuprate anion are known [18] to fall in the range 15 to 8×10^3 cm^{-1} and are related to the flattening of the $CuCl_4^{2-}$ tetrahedron. The ligand field spectrum of $[Cu(bddh)Cl]_2CuCl_4$ resembles the spectrum of $[Cu(bddh)Cl]BF_4$, both showing two absorption maxima. However, no additional absorptions below 25×10^3 cm^{-1}, due to a $CuCl_4^{2-}$ anion, could be identified; they are probably obscured by the absorptions of the cationic species.

Discussion and concluding remarks

The results of the present investigations show that the ligand bddh is capable of forming coordination compounds both with copper(II) and copper(I) salts. The formation of the tetrachlorocuprate anion suggests that the $[Cu(bddh)Cl]^+$ molecule, with a trigonal bipyramidal geometry, is favoured by the ligand bddh when coordinating to copper(II) atoms. Experiments directed towards the synthesis of this stable $[Cu(bddh)A]^+$ cation, with A = coordinating anion or molecule, resulted in the formation of the mixed-anion compound $[Cu(bddh)Cl]BF_4$ and the compound $[Cu(bddh)(Hdmpz)](BF_4)_2$. The presence of the $[Cu(bddh)Cl]^+$ cation in the compound $[Cu(bddh)Cl]BF_4$ could be deduced by IR spectroscopy. The crystal structure of $[Cu(bddh)(Hdmpz)](BF_4)_2$ illustrates the possibility of substituting the chloride by a neutral nitrogen donor molecule (Hdmpz), without introducing major changes in the coordination. The compound $[Cu(bddh)(H_2O)](BF_4)_2$ is likely to contain the same trigonal bipyrimidal unit. As a matter of fact such a trigonal bipyramidal geometry has been found for several other $[CuN_2S_2A]$ chromophores with imidazole and benzimidazole thioether ligands [2, 19].

Although the copper atom in $Cu(bddh)(NO_3)_2$ is probably coordinated by the ligand and two monodentate coordinating nitrate anions in an octahedron, most likely the conformation of bddh in this compound is very similar to the conformation in the above described trigonal bipyrimidal $[Cu(bddh)A]^+$ cation.

Brubaker *et al.* [20] described the coordination chemistry of the ligand 1,8-bis(2-pyridyl)-3,6-dithiaoctane (abbreviated as pdto) towards copper(I) and copper(II) atoms. In $[Cu(pdto)]PF_6$ the copper(I) atom is tetrahedrally coordinated by two pyridyl nitrogen donors and two thioether donor atoms at distances comparable to those found in $[Cu(bddh)]_2(BF_4)_2$. With divalent copper the ligand pdto formed $[Cu(pdto)(ClO_4)]ClO_4$, which consists of CuN_2S_2O chromophores in a square planar geometry. The ligand bddh forms a dinuclear coordination compound with copper(I) tetrafluoroborate, in which the copper atoms are coordinated by two pyrazole nitrogen donors and two thioether donors. The ligand bddh shows the above described preference towards divalent copper for a [Cu(bddh)A] unit. Although the coordination behaviour of pdto resembles the coordination behaviour of bddh to a certain extent, it is remarkable that the cation in $[Cu(bddh)]_2(BF_4)_2$ is dinuclear. The difference between these ligands is the heterocycle (pyrazolyl versus pyridyl) and the size of the bite between N(heterocycle) and thioether. In the case of pdto this bite results in a six-membered chelate ring and in the case of bddh this chelate ring is five-membered. This difference is likely to be the cause of $[Cu(bddh)]_2(BF_4)_2$ being dinuclear; the distortion from tetrahedral geometry is clearly too large in a mononuclear complex of bddh and copper(I). The structure of the compounds with copper(I) halides cannot be deduced without a single-crystal structure determination. Crystals of Cu(bddh)Cl were obtained, but attempts to solve the crystal structure failed due to twinning of the crystal.

In the report describing the coordination behaviour of bddh towards first-row transition metals other than copper [7], the effect of the bite between pyrazole and thioether upon the coordination behaviour of bddh-type ligands (see Fig. 1) has been discussed. The occurrence of non-coordinating thioether atoms in coordination compounds with bddo and bddn was explained by the long bridge between the pyrazole and thioether functions in these ligands. However, the ligand bddh showed the same non-coordinating thioether atoms in compounds $(Co, Zn)(bddh)Cl_2$, thus pointing out that this effect is less important. The compound $[Cu(bddh)]_2(BF_4)_2$ shows an opposite effect, viz. the bite is too small to form the tetrahedral mononuclear copper(I) complex. The results leads to the conclusion that both bite sizes can lead to opening up of the chelate ring.

Acknowledgement

We want to express our gratitude towards Mr S. Gorter for collecting the diffraction data of two single crystals.

References

1 L. Casella, M. Gulotti, E. Suardi, M. Sisti, R. Pagliarin and P. Zanello, *J. Chem. Soc., Dalton Trans.*, (1990) 2843.

2 J. Reedijk, *Naturwissenschaften, 74* (1987) 71; J. Reedijk, J. van Rijn and W. L. Driessen, in K. D. Karlin and J. Zubieta (eds.), *Biological and Inorganic Copper Chemistry,* Adenine, New York, 1986, p. 143, and refs. therein.

3 A. E. G. Cass and H. A. O. Hill, *Biological Roles of Copper (Ciba Foundation Symposium 1979)* Elsevier, Amsterdam, 1980, p. 71.

4 W. G. Haanstra, W. L. Driessen, J. Reedijk, U. Turpeinen and R. Hämäläinen, *J. Chem. Soc., Dalton Trans.*, (1989) 2309.

5 W. G. Haanstra, W. A. J. W. van der Donk, W. L. Driessen, J. Reedijk, M. G. B. Drew and J. S. Wood, *Inorg. Chim. Acta, 176* (1990) 299.

6 W. G. Haanstra, W. A. J. W. van der Donk, W. L. Driessen, J. Reedijk, J. S. Wood and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, (1990) 3123.

7 W. G. Haanstra, W. L. Driessen, J. Reedijk, R. Frohlich and B. Krebs, *Inorg. Chim. Acta, 185* (1991) 175.

8 W. L. Driessen, *Recl. Trav. Chim. Pays-Bas, 101* (1982) 441.

9 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch Press, Birmingham, U.K., 1974.

10 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1984) 158.

11 J. M. Stewart, The Xray76 system, *Tech. Rep. TR446,* Computer Science Centre, University of Maryland, College Park, MD, 1976.

12 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 3rd edn., 1978.

13 G. J. Kleywegt, W. G. R. Wiesmeijer, G. J. van Driel, W. L. Driessen, J. Reedijk and J. H. Noordik, *J. Chem. Soc., Dalton Trans.*, (1985) 2177; A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, *Can. J. Chem., 49* (1971) 1957.

14 W. L. Driessen and P. H. van der Voort, *Inorg. Chim. Acta, 21* (1977) 217.

15 W. D. S. Motherwell and W. Clegg, *Pluto*, a program for plotting molecular and crystal structures, University of Cambridge, U.K., 1978.

16 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.,* (1989) S1.

17 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev., 5* (1970) 87; B. J. Hathaway, *Struct. Bonding (Berlin), 57* (1984) 55; A. B. P. Lever, *Inorganic Electronic Spectroscopy,* Elsevier, Amsterdam, 2nd edn., 1984.

18 D. W. Smith, *Coord. Chem. Rev., 21* (1976) 93.

19 E. Bouwman, W. L. Driessen and J. Reedijk, *Coord. Chem. Rev., 104* (1990) 143.

20 G. R. Brubaker, J. N. Brown, M. K. Yoo, R. A. Kinsey, T. M. Kutchan and E. A. Mottel, *Inorg. Chem., 18* (1979) 299.