Coordination behaviour of the ligand 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn) towards first-row transition metals. X-ray structure of $[Cu(bddn)(H_2O)](BF_4)_2$

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Abstract

The synthesis and characterization of the ligand 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn) and its coordination compounds, viz. $[M(L)(X)_2]$ where M is Co^{2+}, Zn^{2+}; X is Cl^-, Br^-, NCS^-, and $[Cu(L)(H_2O)](BF_4)_2$ are described. The X-ray structure of $[Cu(bddn)(H_2O)](BF_4)_2$ has been determined. The compound crystallizes from ethanol in the monoclinic space group $P2_1/c$ with unit-cell parameters $a=18.508(5)$, $b=9.253(3)$, $c=15.743(5)$ Å, $\beta=107.91(3)°$, $V=2565.5$ Å^3, $D_{calc}=1.57$ g/cm^3 for $Z=4$. The structure was refined to $R=0.099$ and $R_w=0.116$ for 1841 unique reflections with $I>\sigma(I)$. The copper(II) ion is coordinated by two pyrazole nitrogen donors, two thioether donors and a water molecule in a trigonal bipyramidal environment, with the two pyrazoles in an unusual *cis* position. The donor atoms at the axial positions are a nitrogen and a sulfur, the equatorial plane donors are nitrogen, sulfur and the oxygen atom. From the ligand field spectra, the infrared patterns and the X-ray powder patterns it was concluded that the structures of the cobalt(II)- and zinc(II)-containing compounds are structurally similar to $Zn(bddo)(NCS)_2$, a previously reported chain like structure with an $MN_2N'_2$ chromophore, in which the ligand S atoms do not bind to the metal ion.

Introduction

In recent years the use of low-molecular weight coordination compounds as models for the active site in metalloproteins has gained much attention [1]. One of our approaches is dealing with models for the active site of type I copper proteins [2]. In the active site of such proteins a copper atom is coordinated by two nitrogen (His) donors, one thioether (Met) donor and one thiolate (Cys) donor, forming the distorted tetrahedral N_2SS^* chromophore [3]. In the active site of the type I copper protein azurin [4] an oxygen (carbonyl) donor is present at about 3 Å from the metal. The role of these proteins is that of an electron carrier. The unusually high reduction potential leads to a relatively stable Cu(I) state. The very small superhyperfine coupling in the EPR spectrum and the high molar extinction coefficient for the 600 nm electronic absorption are properties which make this class of metalloproteins interesting subjects for modelling.

In our program towards models for the N_2SS^* active site the ligand 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn) was developed [5], which contains an N_2S_2 donor set, with pyrazoles as the nitrogen donor atoms. To obtain a better understanding of the coordination behaviour of this type of ligands not only Cu(I) and Cu(II) compounds, but also coordination compounds of bddn with Ni(II), Co(II) and Zn(II), with the anions Cl^-, Br^-, NCS^- and BF_4^- have been obtained. This paper describes the results of this study, including an X-ray structure determination of $[Cu(bddn)(H_2O)](BF_4)_2$ and molecular mechanics calculations on the structure of its cation.

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Experimental

Synthesis of the ligand bddn

The ligand bddn was prepared by the condensation of tosylated 1-(2′-hydroxyethyl)-3,5-dimethyl-pyrazole(ptos-N-hed) [5] and 1,3-propanedithiol. A mixture of 3.2 ml 1,3-propanedithiol, 20 g ptos-N-hed, 3.3 g NaOH and about 100 ml of water was refluxed and stirred for 5 h. After standing overnight at room temperature, the crude ligand bddn had precipitated as a white substance. The ligand was recrystallized from diethyl ether. The yield after drying *in vacuo* was 9.6 g (85% relative to thiol). The ligand was characterized by ^1H NMR spectroscopy (m.p. 60 °C; ^1H NMR, solvent $CDCl_3$: 5.44(s, 2H), 3.80(t, 4H), 2.60(t, 4H), 2.16(t, 4H), 1.92(d, 12H), 1.48(q, 2H) ppm).

Synthesis and characterization of the coordination compounds

The compounds of the divalent metals were prepared by adding a hot solution of 2 mmol of the appropriate metal salt in 10 ml of absolute ethanol to a stirred hot solution of 2 mmol bddn in about 20 ml of absolute ethanol. The thiocyanate compounds were prepared by adding a stoichiometric amount of NH_4NCS in warm ethanol to an ethanolic solution of bddn and the metal nitrate. About 2 ml of triethylorthoformate was then added for dehydration. Subsequent cooling to room temperature resulted in the crystallization of some of the coordination compounds in sufficient yields for analysis. For the metal salts $Ni(Cl, Br, NCS, BF_4)I_2$, $(Co, Zn)(BF_4)_2$ and $Cu(Cl, Br, NCS)_2$ no solid coordination compounds could be obtained using this method. Reducing the volume of the solvent, cooling and addition of diethyl ether did not invoke crystallization. Also, changing the solvent to acetonitrile or methanol was not successful.

The experiments with copper(I) were performed under a dinitrogen atmosphere, using degassed and carefully dried acetonitrile [6]. No solid copper(I) containing coordination compound could be obtained, however.

Infrared spectra in the 4000–300 cm^{-1} range of the ligand bddn and of the coordination compounds pelleted in KBr were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a PE data station. Electronic spectra (270–2000 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 Kα radiation. After destruction with nitric acid, metal analyses were carried out complexometrically with edta [7]. The X-band EPR spectrum of a powdered sample of $[Cu(bddn)(H_2O)](BF_4)_2$ was recorded on a Varian E3 spectrophotometer at liquid nitrogen temperature.

Crystal structure determination of $[Cu(bddn)(H_2O)](BF_4)_2$

Crystals of $[Cu(bddn)(H_2O)](BF_4)_2$ suitable for X-ray analysis were obtained directly from the reaction mixture.

Crystal data: $CuC_{17}N_4H_{30}OB_2F_8$, $M = 607.75$, monoclinic, space group $P2_1/c$, $a = 18.508(5)$, $b = 9.253(3)$, $c = 15.743(5)$ Å, $\beta = 107.91(3)°$, $V = 2565.5$ Å^3 (as determined by 25 independent reflections), $\lambda = $ Mo Kα (0.710730 Å), $D_{calc} = 1.57$ g/cm^3, $Z = 4$, green parallelepiped shaped crystal, μ(Mo Kα) = 9.65 cm^{-1}.

Data collection: CAD-4 diffractometer, $\omega/2\theta$ scan mode. Data collection range $1.5° < \theta < 21.5°$, $-19 < h < 18$, $-9 < k < 0$ and $0 < l < 16$. A total of 3063 reflections was measured, of which 1841 were significant ($I > \sigma(I)$) and used in the refinement.

Structure analysis and refinement: the structure was solved using Patterson methods and refined by Fourier difference maps. All non-hydrogen atoms were refined anisotropically, except for those of the BF_4^- anions which were refined isotropically with the B atoms constrained to the centres of the groups of fluorines. While examination of difference maps did not suggest split tetrafluoroborate groups there was clearly extensive rotational disorder present which was difficult to model satisfactorily. Hydrogen atom positions were calculated for all carbons except the methyl groups and were included in the final calculations. The water molecule hydrogens were not located. Because of the above-mentioned disorder in the position of the BF_4^- anions some electron density remained near the F atoms ($\sigma_{max} = 0.85$ e/Å^3). Final values for R and R_w are 0.099 and 0.116, respectively. These relatively high values are most likely caused by the inadequate modelling of the disorder in the tetrafluoroborate anions. Final coordinates and B_{eq} values for the non-hydrogen atoms and a selection of the relevant bond lengths and bond angles are listed in Tables 1 and 2, respectively. See also 'Supplementary material'.

Molecular mechanics calculations

Molecular mechanics (MM) calculations were performed with a version of the MM2 program [8] modified to allow for coordination numbers greater than four [9] and to include periodicity at metal angles. Computations were carried out on the Amdahl 5870 computer at the University of Reading and on the Amdahl V7B computer of Leiden University.

TABLE 1. Fractional coordinates and B_{eq} (Å^2) of the non-hydrogen atoms of $[Cu(bddn)(H_2O)](BF_4)_2$ with standard deviations in parentheses

Atom	x	y	z	B_{eq}[a]
Cu(1)	0.2382(1)	0.1207(3)	0.0467(1)	3.69(5)
S(31)	0.2474(3)	−0.1160(6)	0.1059(3)	4.9(1)
S(35)	0.1083(3)	0.0680(6)	0.0202(4)	5.4(1)
O(11)	0.2598(6)	0.026(2)	−0.0695(7)	6.4(4)
N(11)	0.3871(7)	0.094(1)	0.1890(8)	3.8(4)
N(12)	0.3247(6)	0.182(1)	0.1518(8)	3.6(3)
N(21)	0.1586(7)	0.402(2)	−0.0299(9)	5.2(4)
N(22)	0.2229(7)	0.313(2)	−0.0123(9)	4.7(4)
C(13)	0.3326(8)	0.293(2)	0.211(1)	3.9(4)
C(14)	0.3965(8)	0.277(2)	0.282(1)	4.3(5)
C(15)	0.4314(8)	0.149(2)	0.2708(9)	4.3(5)
C(16)	0.2766(9)	0.418(2)	0.195(1)	5.0(5)
C(17)	0.5023(9)	0.062(2)	0.320(1)	5.4(5)
C(18)	0.3999(9)	−0.033(2)	0.142(1)	4.5(5)
C(19)	0.3493(9)	−0.159(2)	0.144(1)	5.8(6)
C(23)	0.2771(9)	0.398(2)	−0.0266(9)	4.6(5)
C(24)	0.2480(9)	0.533(2)	−0.054(1)	4.7(5)
C(25)	0.1731(10)	0.537(2)	−0.056(1)	6.0(5)
C(26)	0.3558(8)	0.338(2)	−0.017(1)	5.6(5)
C(27)	0.112(1)	0.656(2)	−0.075(2)	7.4(7)
C(28)	0.088(1)	0.347(3)	−0.012(2)	15(1)
C(29)	0.0605(9)	0.228(2)	−0.032(2)	11.0(9)
C(32)	0.224(1)	−0.078(2)	0.208(1)	6.2(6)
C(33)	0.136(1)	−0.066(3)	0.184(1)	8.7(7)
C(34)	0.104(1)	0.074(3)	0.135(1)	7.4(6)
B(41)[b]	0.580	0.195	0.088	13.1(6)*
F(42)	0.5538(9)	0.249(2)	0.012(1)	15.9(6)*
F(43)	0.535(1)	0.185(2)	0.137(1)	16.2(6)*
F(44)	0.604(1)	0.054(2)	0.081(1)	16.4(6)*
F(45)	0.636(1)	0.263(3)	0.133(1)	20.2(8)*
B(51)[b]	0.080	0.521	0.234	20.4(8)*
F(52)	0.1476(8)	0.600(2)	0.284(1)	11.2(4)*
F(53)	0.0758(9)	0.548(2)	0.157(1)	13.3(5)*
F(54)	0.028(1)	0.554(2)	0.265(1)	16.5(6)*
F(55)	0.110(1)	0.391(2)	0.258(1)	16.3(6)*

[a] Defined as $B_{eq} = (8/3)\pi^2 \text{trace } U_{ij}$ where the U_{ij} are referred to orthogonal axes. Starred atoms were refined isotropically. [b] Boron atoms constrained to centres of F_4-tetrahedra.

TABLE 2. Selected bond distances (Å) and angles (°) of $[Cu(bddn)(H_2O)](BF_4)_2$ with standard deviations in parentheses

Cu(1)–N(12)	2.00(1)	C(13)–C(16)	1.52(2)
Cu(1)–N(22)	1.99(1)	C(15)–C(17)	1.53(2)
Cu(1)–O(11)	2.17(1)	N(11)–C(18)	1.44(2)
Cu(1)–S(31)	2.366(6)	C(18)–C(19)	1.51(3)
Cu(1)–S(35)	2.363(5)	C(19)–S(31)	1.84(2)
S(35)–C(29)	1.79(2)	N(21)–N(22)	1.40(2)
S(35)–C(34)	1.83(2)	N(22)–C(23)	1.34(2)
B(41)–F(42)	1.24(2)	C(23)–C(24)	1.38(2)
B(41)–F(43)	1.31(2)	C(24)–C(25)	1.39(3)
B(41)–F(44)	1.40(2)	C(25)–N(21)	1.36(3)
B(41)–F(45)	1.23(2)	C(23)–C(26)	1.52(2)
B(51)–F(52)	1.45(1)	C(25)–C(27)	1.53(3)
B(51)–F(53)	1.21(2)	N(21)–C(28)	1.50(3)
B(51)–F(54)	1.25(2)	C(28)–C(29)	1.21(3)
B(51)–F(55)	1.33(2)	C(29)–S(35)	1.79(2)
N(11)–N(12)	1.39(2)	S(31)–C(32)	1.83(2)
N(12)–C(13)	1.37(2)	C(32)–C(33)	1.56(3)
C(13)–C(14)	1.36(2)	C(33)–C(34)	1.54(3)
C(14)–C(15)	1.39(3)	C(34)–S(35)	1.83(2)
C(15)–N(11)	1.39(2)		
S(31)–Cu(1)–S(35)	79.9(2)	C(19)–S(31)–C(32)	105(1)
S(31)–Cu(1)–N(12)	89.7(4)	S(31)–C(32)–C(33)	108(1)
S(31)–Cu(1)–O(11)	87.0(4)	N(12)–N(11)–C(18)	120(1)
S(35)–Cu(1)–N(12)	135.8(5)	C(15)–N(11)–C(18)	129(1)
N(12)–Cu(1)–O(11)	120.3(5)	C(32)–C(33)–C(34)	113(2)
S(35)–Cu(1)–N(22)	96.4(4)	N(21)–N(22)–C(23)	105(1)
N(22)–Cu(1)–O(11)	90.4(5)	N(22)–C(23)–C(24)	110(1)
N(12)–Cu(1)–N(22)	95.5(5)	C(23)–C(24)–C(25)	109(2)
S(35)–Cu(1)–O(11)	102.0(3)	C(24)–C(25)–N(21)	105(2)
S(31)–Cu(1)–N(22)	174.9(3)	C(25)–N(21)–N(22)	111(1)
N(11)–N(12)–C(13)	105(1)	N(22)–C(23)–C(26)	121(2)
N(12)–C(13)–C(14)	111(1)	C(24)–C(23)–C(26)	129(2)
C(13)–C(14)–C(15)	108(1)	N(21)–C(25)–C(27)	122(2)
C(14)–C(15)–N(11)	106(1)	C(24)–C(25)–C(27)	134(2)
C(15)–N(11)–N(12)	111(1)	N(21)–C(28)–C(29)	125(3)
N(12)–C(13)–C(16)	122(1)	C(28)–C(29)–S(35)	122(2)
C(14)–C(13)–C(16)	127(2)	C(29)–S(35)–C(34)	105(1)
N(11)–C(15)–C(17)	116(2)	S(35)–C(34)–C(33)	110(2)
C(14)–C(15)–C(17)	138(1)	N(22)–N(21)–C(28)	120(2)
N(11)–C(18)–C(19)	114(2)	C(25)–N(21)–C(28)	128(2)
C(18)–C(19)–S(31)	114(1)		

Force field parameters used for C, H, N, O and S were taken from values in the MM2 program. Van der Waals parameters for the copper ion were taken from the literature [10]. The torsional parameters M–X–Y–Z were given the same values as C(sp^3)–X–Y–Z and for the torsion parameters X–M–Y–Z free rotation around the M–Y bond was assumed. The stretching parameters involving the metal were fitted to match the X-ray structure of [Cu(bddn)(H_2O)]. Because X-ray structures cannot yield reliable coordinates for the hydrogen atoms, all the coordinates for the hydrogen atoms were calculated. It was found that all metal parameters were non-critical, which means that a small variation in parameter does not result in a great deviation in the minimized structure.

Results and discussion

General and spectroscopy

The compounds obtained with the Co(II) and Zn(II) salts all have the formula $M(bddn)X_2$, while copper(II) tetrafluoroborate forms the compound $[Cu(bddn)(H_2O)](BF_4)_2$. Analytical results of the coordination compounds were satisfactory, see 'Supplementary material'. Colour, melting point, infrared type, X-ray powder type and electronic absorption maxima of the compounds are collected in Table 3. The ligand field maxima of the cobalt compounds

TABLE 3. Colour, X-ray and IR types, and electronic absorption maxima of the coordination compounds of bddn

	Melting point (°C)	IR[a]	X-ray[b]	Colour	LF absorptions (10^3 cm^{-1})
Co(bddn)Cl_2[c]	210	A	I	blue	17.1(sh), 15.5, 8.3, 6.9, 5.7
Co(bddn)Br_2[c]	212	A	II	blue	17.0, 15.4, 14.8, 8.0, 6.7, 5.4
Co(bddn)$(NCS)_2$[c]	148	B	III	blue	16.2, 9.0(very broad)
Zn(bddn)Cl_2	211	A	I	white	
Zn(bddn)Br_2	212	A	II	white	
Zn(bddn)$(NCS)_2$	154	B	III	white	
[Cu(bddn)(H_2O)]$(BF_4)_2$[d]	194	C	IV	green	25.0, 12.9

[a] Infrared type based on similarity of infrared spectra. [b] Structural isomorphism based on powder diffraction patterns. [c] LF absorptions of the corresponding bddo containing compounds, see ref. 5. [d] EPR data: $g_1=2.01$, $g_2=2.09$, $g_3=2.18$.

clearly show that the Co(II) ion is tetrahedrally coordinated by four donor atoms [11]. The infrared spectra and the X-ray powder patterns of the corresponding zinc compounds are identical; this implies that the Co(II) and Zn(II) compounds are structurally isomorphous.

In a previous report [5] several compounds with the related ligand bddo were described. The ligand bddo differs from bddn in having only two methylene units between the thioether atoms instead of three in bddn. In that report the structure of polymeric Zn(bddo)$(NCS)_2$ is described. The Zn atoms are coordinated by two pyrazole nitrogen atoms from different ligands and two thiocyanate nitrogen atoms in a tetrahedral geometry. The sulfur atoms of the ligand bddo do not participate in the coordination. Because of the structural isomorphism in the group (Co, Zn)(bddo)((NCS, Cl, Br)$_2$ and the strong resemblance of the ligand field spectra of Co(bddn)(Cl, Br, NCS)$_2$ with Co(bddo)(Cl, Br, NCS)$_2$ it is clear that the compounds (Co, Zn)(bddn)(Cl, Br, NCS)$_2$ have structures which are very similar to the structure of Zn(bddo)$(NCS)_2$, viz. a chain like structure with MN_2X_2 chromophores.

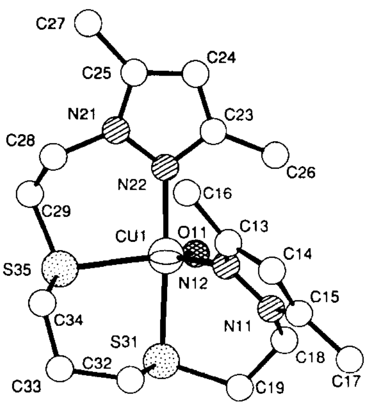

Fig. 1. Structure of [Cu(bddn)(H_2O)]$(BF_4)_2$. Hydrogen atoms and anions are omitted for clarity.

The ligand field spectrum of [Cu(bddn)(H_2O)]$(BF_4)_2$ shows a broad absorption at 12.9×10^3 cm^{-1} and a charge-transfer absorption Cu(II) $\leftarrow$ S(σ) at 25×10^3 cm^{-1} [11, 12]. The rhombic powder EPR spectrum of the compound ($g_1=2.01$, $g_2=2.09$, $g_3=2.18$) shows a low g_1 value. According to Hathaway and coworkers [13] this would agree with a d_{z^2}-based ground state and thus with a trigonal bipyramidal coordination geometry.

Description of the X-ray structure of [Cu(bddn)(H_2O)]$(BF_4)_2$

In [Cu(bddn)(H_2O)]$(BF_4)_2$ (see Fig. 1) the copper atom is coordinated by two pyrazole nitrogen donors, two thioether donors and a water molecule. The bond lengths of the nitrogen donors are equivalent within experimental error (Cu–N(12) = 2.00(1) and Cu–N(22) = 1.99(1) Å), as are the thioether sulfur to copper bond lengths, Cu–S(31) = 2.366(5) and Cu–S(35) = 2.363(5) Å. The water molecule coordinates to the copper atom at a distance of 2.17(1) Å. These bonding distances can all be regarded as normal [14]. The coordination geometry is not a perfect trigonal bipyramid. To distinguish between a trigonal bipyramid and a square pyramid Addison *et al.* [15] defined the τ parameter, being an index which equals zero in the case of a perfect square pyramid and equals unity in the case of a perfect trigonal bipyramid. The τ parameter for [Cu(bddn)(H_2O)]$(BF_4)_2$ is 0.65, indicating that the structure can best be described as a distorted trigonal bipyramid. The axial positions are thus occupied by a nitrogen and a sulfur donor. The equatorial plane is made up of one nitrogen, one sulfur and an oxygen atom. To the best of our knowledge this is the second example of an azole thioether ligand having the nitrogen donors in a *cis* position, i.e. one axial and one equatorial. The distortion from a perfect trigonal

TABLE 4. Metal stretching parameters (mdyne Å^{-1}), the metal bonding distances (Å) of the X-ray structure and the MM structure for $[Cu(bddn)(H_2O)]^{2+}$

Distance	r_0	k_s	X-ray	MM A	MM B	MM C
Cu–N	1.99	2.0	1.99, 2.00	2.00, 2.01	2.00, 2.01	2.00, 2.01
Cu–S	2.36	2.0	2.37, 2.36	2.33, 2.31	2.32, 2.31	2.32, 2.31
Cu–O	2.17	2.0	2.17	2.17	2.17	2.17

TABLE 5. Bending parameters (mdyne Å^{-1} rad^{-2}) at the metal atom, bond angles (°) and O(11)–H(261) distance (Å) in X-ray and MM structures for $[Cu(bddn)(H_2O)]^{2+}$

Angle/Distance	X-ray	MM A[a]	MM B[b]	MM C[c]
S(31–Cu–N(22)	174.8	174.0	174.8	174.9
S(35)–Cu–N(12)	135.8	128.9	130.8	131.3
O(11)–Cu–S(35)	102.1	108.7	95.0	76.4
O(11)–Cu–N(12)	120.3	120.0	131.8	150.4
O(11)–H(281)	2.64[d]	2.66	2.78	3.16

[a] k_b = 0.1 mdyne Å^{-1} rad^{-2}. [b] k_b = 0.01 mdyne Å^{-1} rad^{-2}. [c] k_b = 0.0 mdyne Å^{-1} rad^{-2}. [d] C(28)–O(11) = 3.4 Å and C(28)–H(281)–O(11) = 120°.

TABLE 6. Steric energy (kcal/mol) of MM structures for $[Cu(bddn)(H_2O)]^{2+}$ after minimization

	MM A	MM B	MM C	MM D
Compressing	1.37	1.23	1.19	2.48
Bending	7.39	6.99	6.68	10.22
Stretch-bend	−1.08	−0.92	−0.87	−3.39
van der Waals				
1,4	4.84	4.86	4.87	5.20
other	−10.2	−10.5	−10.5	−8.82
Torsion	−0.30	−0.20	−0.17	0.95
Dipole	1.34	1.33	1.32	0.94
Final	3.35	2.79	2.47	7.59

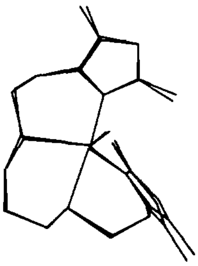

Fig. 2. Superposition of the MM structure A and the X-ray structure of $[Cu(bddn)(H_2O)]^{2+}$.

bipyramid is less than is observed for the related compound $[Cu(bmdhp)(H_2O)]^{2+}$, in which bmdhp is a benzimidazole thioether N_2S_2 ligand, having τ equal to 0.48 [15].

The water molecule is not coordinated symmetrically relative to S(35) and N(12), with the O(11)–Cu–S(35) angle at 102.1(4)° and the O(11)–Cu–N(12) angle at 120.3(5)°. The two tetrafluoroborate anions are located close to the water molecule (O(11)–F(44) = 2.69(2) and O(11)–F(52) = 2.84(2) Å). These oxygen fluorine distances are in the range usually observed for weak hydrogen bonds (2.7–3.0 Å) [16]. That the interaction must be weak can also be observed in the high B_{eq} of both the tetrafluoroborate anions.

Molecular mechanics investigation of $[Cu(bddn)(H_2O)](BF_4)_2$

Angles in the equatorial plane of the X-ray structure deviate considerably from the ideal 120° expected in a trigonal bipyramid. A rather small distance of 2.64 Å was found between a hydrogen H(261) (attached to C(26)) and O(11). To investigate the influence of this contact, MM calculations were performed in which the angle bending constant of the angles O(11)–Cu–N(12) and O(11)–Cu–S(35) was varied. Although the position of H(261) was calculated to have the methyl group eclipsed according to H(241) on the pyrazole ring, the relevant torsion angles do not change more then 10° during minimalization, thus indicating that the correct orientation of the methyl group was calculated.

The X-ray coordinates provided the starting model for the MM calculations. Bond angles (θ_0) around the metal were set at ideal trigonal bipyramidal values. The stretching parameters (r_0, k_s, Table 4) involving the metal were adjusted to obtain a good fit between the MM minimized structure and the observed X-ray structure. The MM minimized structures will be referred to as MM structures A, B, C or D. In MM structure A the bending constants of the angles O(11)–Cu–N(12) and O(11)–Cu–S(35) were comparable to those established by previous MM calculations on copper compounds [10, 17], i.e. 0.1 mdyne $Å^{-1}$ rad^{-2}. In the MM structures B and C these bending constants were reduced to 0.01 and 0.0 mdyne $Å^{-1}$ rad^{2}, thus increasing the positional freedom of O(11) in the equatorial plane.

The relevant angles and the distance between H(261) and O(11) are included in Table 5. The corresponding final steric energies obtained after minimalization are collected in Table 6. The results clearly show that by releasing O(11), the deviation between an ideal trigonal bipyramidal environment and the minimized structure becomes greater and the distance between H(261) and O(11) increases. Apparently the force field of the MM2 program can very well account for the deviation without incorporating crystal-lattice effects or H bonding of the water molecule with the two BF_4^- anions. The MM structure A, in which realistic angle bending constants were used, and the observed X-ray structure have been studied using the superimposing facility of a graphics system. This superposition, shown in Fig. 2, demonstrates the good fit of the observed and calculated structures.

Another interesting detail of the structure is the fact that the axial positions are occupied by a strong nitrogen donor and a weak thioether donor. More frequently a structure is encountered with the axial positions both occupied by the two strong nitrogen donors [15, 18]. Minimizing a model with the nitrogen atoms in the axial positions and two thioether groups and a water molecule in the equatorial positions, using MM structure A parameters, rendered an MM structure (D) with a considerably higher steric energy of 7.59 kcal/mol (see Table 6). When this figure is compared with the final steric energy of MM structure A (3.35 kcal/mol), it is clear that the MM structure A is less strained. The difference in energy between the two models is primarily caused by the angle bending energy terms of Cu–S–C and S–Cu–S, and the stretching energy terms of Cu–S, C–S, C–C in the propyl bridge. In MM structure A the Cu–S–C–C–C–S–Cu ring has a chair configuration, whereas in MM structure D this ring is at best a distorted chair.

Conclusions

In our previous report [5] it was noted that the coordination behaviour of the ligand bddo is unusual. The ligand bddn is structurally related to bddo and also shows the same unusual coordinational behaviour towards the cobalt and zinc salts, viz. in having non-coordinating thioether functions. Several X-ray structures of coordination compounds of bddo have made it clear that intramolecular steric effects do not prevent the ligand from coordinating in a tetradentate fashion. This is, most likely, also the case for bddn, considering the strutural similarity with bddo and the fact that the thioether atoms of bddn are bound to the central metal ion in $[Cu(bddn)(H_2O)](BF_4)_2$. The MM calculations performed on $[Cu(bddn)(H_2O)]^{2+}$ show that the chelate type conformation is not sterically unfavourable and that the deviations from ideal trigonal bipyramidal coordination can be explained by intraligand interactions taken up into the MM2 force field.

In the literature many examples [15, 19] can be found of coordination compounds with ligands with shorter bridges between azole nitrogen and sulfur donor atoms. In most cases the thioether atoms do coordinate. This leads to the assumption that the donor strength of the thioether functions alone is not sufficient to form chelates with a tetradentate coordination mode in combination with the relative long 'bridges' between the donor atoms of the ligands bddn and bddo.

Supplementary material

Tables of anisotropical parameters of the non-hydrogen atoms, fractional coordinates and B_{eq} values for the hydrogen atoms; observed and calculated structure factors; and analytical results are available from the authors.

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