Appendix 3

The Crystal Structures and Electronic Properties of Bis(di-2-pyridylamine)copper(II) Bis(tetrafluoroborate) and Bis[bis-aquabis(di-2-pyridylamine)copper(II)] Sulfate Heptahydrate

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Abstract

In the $[Cu(C_{10}H_9N_3)_2][BF_4]_2$ **1** complex, the Cu(II) ion is in a compressed tetrahedral environment of four N atoms from two di-2-pyridylamine ligands, with an average Cu-N distance of 1.962(7) Å; the dihedral angle between the N-Cu-N planes of the two ligands is 55.0(2)°. The asymmetric unit of $[Cu(C_{10}H_9N_3)_2(H_2O)_2][SO_4].7H_2O$ **2** contains two units of one-half $[Cu(dpyam)_2]$ moieties (the other halfs inversion related), one sulfate and nine water molecules. Each Cu(II) ion involves the elongated rhombic octahedral CuN_4O_2 chromophore, and is surrounded by four N atoms from the two inversion related dpyam ligands, with an average Cu-N distance of 2.019(2) Å . The axial positions of Cu(1) are occupied by the centrosymmetrically related O atoms of the two water molecules at 2.496(3) Å, giving it a tetragonally distorted $Cu(1)N_4O_2$ octahedron; similarly the inversion related water oxygens at 2.465(3) Å give a $Cu(2)N_4O_2$ chromophore . The electronic and e.s.r spectra of **1** and **2** are consistent with the compressed tetrahedral and

the elongated rhombic octahedral stereochemistries, respectively as reported for other related complexes.

Keywords : Crystal structure; Copper complexes ; Bipyridylamine complexes

1. Introduction

The $[Cu(chelate)_2(OXO)]^+$ cations, where chelate is di-2-pyridyl (bpy), 1,10-*O*-phenanthroline (phen) or di-2-pyridylamine (dpyam) and OXO is ONO^-, $CH_3CO_2^-$, HCO_2^- or $CH_3CH_2CO_2^-$, have been well known and characterized as having cis-distorted octahedral copper(II) stereochemistry [1,2]. The copper(II) complexes of $Cu(chelate)_2(OXO).nH_2O$ and $Cu(chelate)_2X_2$, where OXO is divalent $S_4O_6^{2-}$, $S_3O_6^{2-}$ or $S_2O_6^{2-}$ oxyanions and X is monovalent polyatomic ClO_4^-, BF_4^-, PF_6^- or NO_3^- anions, show different geometries with four- , five- and six-fold co-ordination. These complexes can crystalline as monomeric or polymeric chain structures. Previous work led to the characterisation of a number of phen , bpy and dpyam ligands represented a sequence of increasingly flexible chelate nitrogen ligands. The four-coordinate $[Cu(phen)_2][PF_6]_2$ [3], $[Cu(bpy)_2][PF_6]_2$ [4] and $[Cu(dpyam)_2][ClO_4]_2$ [5], the five-coordinate $[Cu(bpy)_2(OH_2)][S_2O_6]$ [6] and six-coordinate $[Cu(dpyam)_2(ONO_2)_2]$ [7] complexes belong to the mononuclear compounds, whereas the ligand bridged $[Cu(bpy)_2(S_4O_6)]$ [8], $[Cu(bpy)_2(S_3O_6)]$ [8], $[Cu(phen)_2(S_4O_6)]$ [9], $[Cu(bpy)_2(O_2ClO_2)][ClO_4]$ [10] and $[Cu(bpy)_2(F_2BF_2)][BF_4]$ [10] complexes correspond to the polymeric infinite chain structure.

Among these types of copper(II) complexes with the dpyam ligand, only one crystal structure has been crystallographically and spectroscopically characterised, namely bis(di-2-pyridylamine)copper(II) perchlorate [5]. Because of the interest in the more flexible dpyam ligand and also because of the variety of geometries and co-ordination numbers displayed by the copper(II) ion, an atttempt has been made to prepare the copper(II) dpyam complexes involving the bridging BF_4^- and SO_4^{2-} anions. The complexes of bis(di-2-pyridylamine)copper(II) bis(tetrafluoroborate) **1** and diaqua-bis(di-2-

pyridylamine)copper(II) sulfate heptahydrate **2** were prepared and their crystal structures determined crystallographically. Their i.r. , e.s.r. and electronic spectra have also been investigated and discussed, along with structural and spectral comparisons with those of other relevant complexes.

2. Experimental

Di-2-pyridylamine and $NaBF_4$ were obtained from Fluka Chemika Co. and used without further purification. The compound $CuSO_4.5H_2O$ obtained from Farmitalia Carlo Erba Co., $Ba(OH)_2.8H_2O$ from Riedel-de Haen Co., were used as received.The known $[Cu(dpyam)_2][ClO_4]_2$ **3** [5] and $[Cu(dpyam)_2(NO_3)_2]$ **4** [7] complexes were reprepared in our laboratory to compare their electronic spectra with those of **1** and **2**. Elemental analyses(C,H,N) were carried out by the Microanalytical Service of Science and Technological Research Equipment Centre, Chulalongkorn University on Perkin–Elmer PE2400 CHNS/O Analyser. The metal content was determined on a Shimazu AA-6501F atomic absorption spectrophotometer.

2.1 Preparations

$[Cu(dpyam)_2][BF_4]_2$ **1**. This compound was prepared by mixing a boiling solution of $CuSO_4.5H_2O$ (0.12 g, 0.5 mmol), $Ba(OH)_2.8H_2O$(0.22 g, 0.7 mmol), $NaBF_4$ (0.11 g, 1 mmol) in water (60 ml), and dpyam (0.17 g, 1 mmol) in hot methanol (20 ml); a deposited white precipitate of $BaSO_4$ was separated by filtration. On slow evaporation of the solvent compound **1** crystallised as dark purple crystals. Found: C, 41.25 ; H, 3.09 ; N, 14.41 ; Cu, 10.88 %. Calculated for $C_{20}H_{18}CuN_6B_2F_8$: C, 41.45 ; H, 3.13 ; N, 14.50 ; Cu, 10.96 %.

$[Cu(dpyam)_2(H_2O)_2][SO_4].7H_2O$ **2**. This compound was prepared by adding a boiling solution of $CuSO_4.5H_2O$ (0.75 g, 3 mmol) in water (10 ml), to a warm solution of dpyam (0.34 g, 2 mmol) in methanol (25 ml). Yellowish green crystals of **2** were deposited after a week. Found: C, 36.03 ; H, 5.38 ; N, 12.49 ; Cu, 9.50 %. Calculated for $C_{20}H_{36}CuN_6O_{13}S$: C, 36.17 ; H, 5.46 ; N, 12.65 ; Cu, 9.57 %.

$[Cu(dpyam)_2][ClO_4]_2$ **3**. This complex was prepared by adding a hot solution of $Cu(ClO_4)_2.6H_2O$ (0.37 g, 1 mmol) in 30 ml water to a boiling solution of dpyam (0.34 g, 2 mmol) in 20 ml methanol. After standing for 5 days, purple crystals of **3** were obtained. Found: C, 39.79; H, 3.00; N, 13.94; Cu, 10.60%. Calculated for $C_{20}H_{18}N_6CuCl_2O_8$: C, 39.72 ; H, 3.00 ; N, 13.89 ; Cu, 10.51 %.

$[Cu(dpyam)_2(NO_3)_2]$ **4**. This complex was prepared by adding a hot solution of $Cu(NO_3)_2.3H_2O$ (0.24 g, 1 mmol) in 20 ml water to a boiling solution of dpyam (0.34 g, 2 mmol) in 20 ml ethanol. On slow evaporation of the solution, **4** was deposited as green crystals after a few days. These crystals were filtered off and air dried. Found: C, 45.37; H, 3.39; N, 21.10; Cu, 12.08%. Calculated for $C_{20}H_{18}CuN_8O_6$: C, 45.33 ; H, 3.42 ; N, 21.14 ; Cu, 11.99 %.

2.2 Crystallography

Reflection data for both crystals of **1** and **2** were measured at 20°C using graphite monochromated MoKα radiation (λ = 0.71073 Å) with a detector distance of 4cm and swing angle of -35°. A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0,88,180°) and each exposure of 30s covered 0.3° in ω. The collected data were reduced by using the program SAINT [1] and empirical absorption correction was done by using the SADABS [2] program. Both structures were solved by direct methods and refined by least squares method on F_{obs}^2 by using the SHELXTL [3] software package. All non–H atoms were anisotropically refined. Except the water hydrogens, all hydrogen atoms were geometrically fixed and allowed to ride on the attached atoms. For **1**, the final conventional R(F)=0.033 and *w*R(F^2)=0.081 for 4160 reflections with I > 2σ(I); the weighting scheme, $w=1/[\sigma^2(F_0^2)+(0.0346P)^2+1.59P]$, where $P=(F_0^2)+2Fc^2)/3$. For **2**, R(F)=0.054 and *w*R(F^2)=0.092 for 4665 reflections with I > 2σ(I); the weighting scheme,

$w=1/[\sigma^2(F_o^2)+(0.0303P)^2+1.35P]$, where $P=(F_o^2)+2Fc^2)/3$. The molecular graphics were created by using SHELXTL.

The crystal and refinement details for complexes **1** and **2** are listed in Table 1. Selected bond lengths and angles and the geometry of hydrogen bonds are given in Table 2-5. Figure 1 illustrates the structure of **1**, Figure 2 the structure of **2**, and the atom numbering scheme used.

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

2.3 Physical measurements

The infrared spectra were recorded on a Biorad FTS-7/PC FTIR Spectrometer as KBr pellets in the 4 000-450 cm^{-1} region. The electronic reflectance spectra were measured as polycrystalline samples on a Perkin-Elmer Lambda2S spectrometer, over the range 9 090-30 000 cm^{-1}. The electron spin resonance spectra were recorded at room temperature on a Jeol ESR JES-RE2X spectrometer, operating at X band by the service of Science and Technological Research Equipment Centre Chulalongkorn University. Figure 3 shows the electronic reflectance spectra of the complexes **1-4.**

3. Results and discussion.

3.1 Crystal structures

The structure of complex **1** is made up of a $[Cu(dpyam)_2]^{2+}$ cation and two independent BF_4^- anions, Figure 1. The structure of the cation involves a four coordinate CuN_4 chromophore, with a compressed tetrahedral stereochemistry and with the point-group symmetry being nearly C_{2v} or D_2 [14] if only the atoms bonded to the metal are considered. The copper atom is bonded in a bidentate fashion to two dpyam ligands. There is no indication for

semi-coordination of the tetrafluoroborate groups to the Cu atom [15], the closest fluorine-copper distance being 3.548(5) Å, The four Cu-N distances are somewhat different with a mean value of 1.962(7) Å. They involve bite angles [N(1)-Cu-N(2) and N(4)-Cu-N(5)] of 93.3(2) and 95.4(2)°, respectively, slightly more than 90°. The dihedral angle between the planes defined by N(1), Cu, N(2) and N(4), Cu, N(5) is 55.0(2)°, the dihedral angle between the mean planes of two dpyam ligands is 56.29(5)°. The former dihedral angle is somewhat closer to the 90° angle expected for the tetrahedral geometry than the 0° angle expected for the square planar configuration. The pyridine rings are essentially planar (r.m.s.d. 0.006-0.012 Å) but the ligand as a whole is not, with 9.9(2) and 10.8(2)° dihedral angles between the plans defined by two pyridine rings of N(1)/N(2) and N(4)/N(5) dpyam ligands, respectively.

Both tetrafluoroborate anions of **1** involve approximately tetrahedral stereochemistry with an acceptable mean B-F distance of 1.375(10) Å and mean F-B-F angle of 109.5(7)°, which were as expected and normally found in the tetrahedral BF_4^- anion [16]. There is however significant variation of the B-F distances, 1.341(10) to 1.416(8) Å and 1.311(10) to 1.417(10) Å and the F-B-F angles, 105.2(6) to 117.9(7) °, and 101.9(6) to 115.7(7) °, respectively for the $B(1)F_4^-$ and $B(2)F_4^-$ anion. This distortion from expected regular tetrahedral BF_4^- species, which has near C_{3v} symmetry, is due to the involvement of F atoms in strong N-H...F and weak C-H...F hydrogen bonds (Table 3). This could also be indicated from the splitting of ν_3 mode in the i.r. spectrum of **1**.

The asymmetric unit of **2** contains two crystallographically independent units of one-half [Cu(II)$(dpyam)_2$] moieties (the other half being inversion related), one sulfate and nine water molecules. The two copper atoms are in an octahedral environment with four nitrogen atoms from the two inversion related dpyam ligands occupying the basal plane (exactly planar) of each copper atom. The axial positions in Cu(1) are occupied by the centrosymmetrically related water oxygens O(1W) and O(1W)(-x,-y,-z) at 2.496(3) Å on either side and those in Cu(2) are occupied by the inversion related O(2W) and O(2W)(1-x, 1-y, -z) at 2.465(3) Å giving the elongated rhombic octahedral CuN_4O_2 chromophores with tetragonalities (T = mean in-

plane Cu-N distance/mean out-of-plane Cu-O distance) of 0.807 and 0.821 for the Cu(1) and Cu(2) chromophores, respectively. The Cu-N distances are not significantly different, 2.004(2) and 2.025(2) Å; and 2.021(2) and 2.027(2) Å for the Cu(1) and Cu(2) chromophores, respectively. The mean value of Cu-N distances is 2.019(2) Å. The pyridine rings of the two dpyam ligands in the asymmetric units are planar; the dihedral angle between N(1),C(1)-C(5) and N(2), C(6)-C(10) planes is 35.6(2)° and that for N(4), C(11)-C(15) and N(5), C(16)-C(20) planes is 38.9(1)°. The N(1)-Cu(1)-N(2), N(4)-Cu(2)-N(5) bite angles for the dpyam ligands are 85.93(8) and 85.40(8)°, respectively, which are clearly less than those of **1**; 93.3(2) and 95.4(2)°. The crystal structure is stabilised by a number of O-H...O hydrogen bonds involving the water molecules (Table 5).

The ionic SO_4^{2-} anion exhibits a nearly tetrahedral geometry. The four S-O distances vary from 1.458(2) to 1.473(2) Å with a mean value of 1.465(3) Å and these values are within the range normally found for the uncoordinated sulfate [19]. The six O-S-O angles vary from 108.2(2) to 111.2(2)° and have an average value of 109.5(3)°.

*3.2 Comparison of complexes **1** and **2** with their relevant complexes of known structure.*

The molecular structure of **1** is comparable to those of the complexes, namely $[Cu(bpy)_2][PF_6]_2$ [4] and $[Cu(phen)_2][PF_6]$ [3], all of which have clearly compressed tetrahedral geometry around copper with CuN_2 plane dihedral angles of 42.1 and 40.1°, respectively. Closer similarity is also observed with a deprotonated dpyam complex, $[Cu(DPA)_2]$ [17] and a deprotonated dpyam derivative $[Cu(MPA)_2]$ [18] which have the CuN_2 dihedral angles of 58.8 and 57.4°, respectively. The most similarity to **1** is observed in $[Cu(HDPA)_2][ClO_4]$[5] where HDPA=dpyam, which is the only known tetrahedral copper(II) structure with a neutral dpyam ligand, dihedral angle 56.6°. The present structure with a dihedral angle of 55.0° suggests that the chelate function of the dpyam ligand is significantly different from those of the less flexible bpy and phen ligands and that of the phen ligand is comparable

to that of the bpy ligand. However, despite the more flexibility of the neutral undeprotonated dpyam ligand compared to the deprotonated DPA^- and MPA^-, the dihedral angles of both complexes **1** and $[Cu(HDPA)_2][ClO_4]$ [5], 55.0 and 55.6° are less than those of the more aromatic deprotonated complexes $[Cu(DPA)_2]$ [17]and $[Cu(MPA)_2]$ [18], 58.5 and 57.4°.

The stereochemistry of **2** can be distinguished from that of a trigonal distorted square pyramidal CuN_4O chromophore of $[Cu(bpy)_2(OH_2)][S_2O_6]$ [6] and a tetrahedral CuN_4 chromophore of $[Cu(bpy\ or\ phen)_2][PF_6]_2$ [3,4] and $[Cu(dpyam)_2]X_2$ [5] where X= ClO_4^- **3** and BF_4^- **1**. The elongated rhombic octahedral CuN_4O_2 chromophore in **2** is comparable to those of the infinite chain structure of the elongated rhombic octahedral complexes [Cu(bpy or phen)$_2$(OXO)] [8,9] and $[Cu(bpy)_2X]X$ [10], where OXO = $S_4O_6^{2-}$ or $S_3O_6^{2-}$ and X = ClO_4^- or BF_4^-, but in which the Cu(II) centres are bridged by the coordinated OXO^{2-} and X^- anions. However, these chain structure complexes exhibits a marked tetrahedral twist of the basal plane compared to the exactly planar basal planes of **2**. Additionally, the tetragonalities of these complexes , T = 0.71-0.76, are much lesser than that of **2**, corresponding to the more elongated distortion in these complexes. The most relevant complex to **2** is found in the tetragonally, distorted CuN_4O_2 octahedron of monomeric complex $[Cu(dpyam)_2(NO_3)_2]$ [7], in which the axial positions are weakly coordinated by two unidentate oxygen donor nitrate anions at 2.477(2) Å and with the comparable tetragonality of 0.811 compared to those of **2** (0.807 and 0.821). This is an example of structure change associated with the different coordinating ability of the counter ion.

There are no unusual features in either the bond lengths or bond angles of the dpyam ligand in both complexes **1** and **2** [20-22]. The steric hindrance between the two dpyam ligaands in both complexs is relieved in a quite different manner. In **2**, the ligand twists such that the dihedral angle between the pyridine rings reaches 35.6(2) and 38.9(1)°, while in **1** this dihedral angle is much smaller [9.9(3) and 10.8(3)°] because the dpyam ligands try to define a tetrahedral environment around the copper atom.

3.3 Electronic properties

The polycrystalline e.s.r. spectrum [23] of **1** recorded at room temperature involves axial spectrum with $g_{//} = 2.29$ and $g_{\perp} = 2.17$ The trend exhibited by the g values, $g_{//} >> g_{\perp} > 2.0$, points towards a $d_{x^2-y^2}$ ground state [2,23], consistent with the compressed tetrahedral CuN_4 chromophore as discussed earlier [4]. The $d_{x^2-y^2}$ ground state for **1** is also consistent with the $d_{x^2-y^2}$ ground state previously reported for $[Cu(dpyam)_2][ClO_4]_2$ [14] which has a compressed tetrahedral CuN_4 chromophore with comparable dihedral angle of 55.6°. The tetrahedral complex $[Cu(dpyam)_2][ClO_4]_2$ **3** was also prepared in our laboratory, to compare its reflectance spectrum with that of **1**. The comparability in the molecular structure of **1** and **3** is reflected in the similarity of their electronic reflectance spectra, namely, 18 180, 15 630 (sh), 13 330(sh),10 370 and 18 350, 15 750(sh), 13 510(sh), 10 440 cm^{-1}, respectively, values which agree closely with those previously reported for **3** [14,24]. Both of which are significant different from the three d-d bands observed in the polarized single-crystal spectrum of **3** [14] at 10 400, 13 500 and 15 700 cm^{-1}. Using the tentative one-electron orbital squence $d_{x^2-y^2} > d_{xy} > d_{xz} > d_{z^2} > d_{yz}$ which is assigned for a preferable C_{2v} symmetry [4,14] which a $d_{x^2-y^2}$ ground state, three transitions at 10 370, 13 330(sh) and 15 630(sh) in **1** correspond to d_{xz} $\overline{\quad}$ $d_{x^2-y^2}$,; d_{z^2} $\overline{\quad}$ $d_{x^2-y^2}$ and d_{yz} $d_{x^2-y^2}$ transitions, respectively. A very intense band at 18 180 and 18 350 cm^{-1} for **1** and **3**, respectively is most likely to be a ligand charge transfer band [4]. A week band at ca. 7 500 cm^{-1} previously reported in **3** corresponds to the d_{xy} $d_{x^2-y^2}$ transition , but it is not in the spectral range recorded for **1**. However, the assignment of four spin allowed ligand-field transitions in pseudo-tetrahedral bis(bidentate ligand)copper complexes have been made as a function of the dihedral angles ranging from 53.8 to 58.8°, showing the splitting of the tetrahedral $^2T_2$ ground state and the ^2E excited state with increasing flattening (decreasing dihedral angle) of the tetrahedron [18]. The electronic reflectance spectra of **1** and **3** are at significant lower energy than those of

$[Cu(bpy)_2][PF_6]_2$ [4] (15 040 and 16 950(sh) cm^{-1}) and $[Cu(phen)_2][PF_6]_2$ [3] (14 500 and 17 200(sh) cm^{-1}). The lower energy in **1** and **3** is consistent with the significantly higher dihedral angles, 55.0 for **1** and 55.6° for **3**, compared to those of $[Cu(bpy)_2][PF_6]_2$, 40.1° and $[Cu(phen)_2][PF_6]_2$, 42.1°. For the latter two complexes, all four d-d transitions lie within this band envelope, in the range 14 000-18 000 cm^{-1}. It has been known that tetrahedrally distorted complexes of Cu(II) have been of interest as models for copper proteins such as the blue copper proteins.

The axial e.s.r. spectrum of **2** with $g_{//} = 2.28$ and $g_{\perp} = 2.08$ is consistent with the elongated rhombic octahedral CuN_4O_2 chromophore and a $d_{x^2-y^2}$ ground state ($g_{//} >> g_{\perp} > 2.0$) [2,23]. The elongated rhombic octahedral complex $[Cu(dpyam)_2(NO_3)_2]$ **4** whose structure was characterised crystallographically[7], was also prepared in our laboratory , to compare its electronic spectrum with that of **2**. The electronic reflectance spectrum of **2** displays a peak centred at 17 520 cm^{-1} with a poorly resolved shoulder at *ca.* 14 500 cm^{-1} , which correlates well with that of **4** [17 870, 14 700 (sh) cm^{-1}] and previously reported values [7] of complex **4** [18 000, 15 000(sh) cm^{-1}]. These two observed d-d peaks correspond to the d_{z^2} $d_{x^2-y^2}$ and d_{xy}, d_{xz}, d_{yz} $d_{x^2-y^2}$ transitions for the lower-energy shoulder and high-energy peak, respectively. The electronic spectra of complexes **1** and **2** are in the higher energy compared to an observed single peak in the electronic spectra of $[Cu(bpy)_2(F_2BF_2)][BF_4]$[10] and $[Cu(bpy)_2(O_2ClO_2)][ClO_4]$ [10] at *ca.* 15 150 cm^{-1}; and $[Cu(bpy)_2(S_3O_6)]$ [8] and $[Cu(bpy)_2(S_4O_6)]$ [8] at *ca.* 14 800 cm^{-1}, despite the higher tetragonalities of 0.807-0.821 (the lesser elongation in the axial positions). This is a result of the marked tetrahedral twist of the basal planes involved in these bpy complexes as previously reported [25].

Infrared spectra.- Due to overlapping peaks from the dpyam ligands present, only the ν_3 band of a tetrahedral BF_4^- and SO_4^{2-} ions were clearly resolved. Complex **1** displays a broad peak split into two peaks at 1 055 and 1 010 cm^{-1}, while **2** gives a single peak at 1 115 cm^{-1}. These i.r. bands are assigned as the triply degenerate ν_3 mode of vibration of the tetrahedral BF_4^-

and SO_4^{2-} ions, bands which can be resolved into two or three bands when these anions are involved in unidentate co-ordination (C_{3v}) or bidentate co-ordination (C_{2v}) [15,26,27], respectively. A single sharp peak at 1 115 cm^{-1} in **2** suggests that the SO_4^{2-} anions in complex **2** is ionic and not co-ordinated[19]. The splitting into two peaks of the ν_3 band of the BF_4^- ion in **1** suggests the unidentate co-ordination of the BF_4^- ion. This interpretation contrasts with the ionic and non-coordinated BF_4^- anions determined crystallographically in **1**. The distortion of both BF_4^- anions in **1** is most likely a result of a number of hydrogen bonds involving the BF_4^- ions. This type of behavior is also found in $[Cu(I)(FBF_3)(PPh_3)_3]$ [28] which show no evidence for even semi-co-ordination of BF_4^- despite the relatively short Cu-F distance of 2.31 Å. Nevertheless , the failure to obtain any i.r. evidence for the non-coordinated BF_4^- in **1** and co-ordinated BF_4^- in this copper(I) complex suggests caution in the application of i.r. spectra as a criterion of co-ordination of BF_4^- anion.

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References

[1]. B.J. Hathaway, Struct. Bonding (Berlin), 57 (1984) 55.

[2]. B.J. Hathaway, Comprehensive Coordination Chemistry, The Synthesis, Reactions, Properties and Applications of Coordination Compounds. eds, G. Wilkinson, R.D. Gillard and J.A. McCleverty, Pergamon, Oxford, 1987, vol. 5, pp. 533-774.

[3]. K. Amournjarusiri and B.J. Hathaway, Acta Crystallogr., Sect.C, 47 (1991)

1383.

[4]. J. Foley, S. Tyagi and B.J. Hathaway, J. Chem. Soc., Dalton Trans., (1984) 1.

[5]. J. E. Johnson, T.A. Beineke and R.A. Jacobson, J. Chem. Soc. A, (1971) 1371.

[6]. W.D. Harrison and B.J. Hathaway, Acta Crystallogr., Sect.B, 36 (1980) 1069.

[7]. M.C. Munoz, J.M. Lazaro, J. Faus and M. Julve, Acta Crystallo gr., Sect.C, 49 (1993) 1756.

[8]. W.D. Harrison and B.J. Hathaway, Acta Crystallogr., Sect.B, 35 (1997) 2910.

[9]. E. Freire, S. Baggio, R. Baggio and M.T. Garland, Acta Crystallogr., Sect.B, 54 (1998) 464.

[10]. J. Foley, D. Kennefick, D. Phelan, S. Tyagi and B. Hathaway, J. Chem. Soc., Dalton Trans., (1983) 2333.

[11]. Siemens, SAINT v4 Software Reference Manual, Siemens Analytical X-Ray Systems, Inc., Madison, Wisconsin, USA, 1996.

[12]. G. M. Sheldrick, SADABS, Program for Empirical Absorption correction of Area Dectector Data, Univ. of Gottingen, Germany, 1996.

[13]. Siemens, SHELXTL, Version 5 Reference Manual, Siemens Analytical X-Ray Systems, Inc., Madison, Wisconsin, USA, 1996.

[14]. R.J. Dudley, B.J. Hathaway and P.G. Hodgson, J. Chem. Soc., Dalton Trans., (1972) 882.

[15]. I.M. Procter, B.J. Hathaway and P. Nicholls, J. Chem. Soc. A, (1968) 1679.

[16]. B.J. Kilbourne, R.R. Ryan and J.D. Dunitz, J. Chem. Soc. A, (1969) 2407.

[17]. O.R. Rodig, T. Brueckner, B.K. Hurlburt, R.K. Schlatzer, T.L. Venable and E. Sinn, J. Chem. Soc., Dalton Trans., (1981) 196.

[18]. C.E. Baxter, O.R. Rodig, R.K. Schlatzer and E. Sinn, Inorg. Chem.,

18 (1979) 1918.

[19]. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd Ed., Wiley, New York, 1978.

[20]. F.S. Stephens, J. Chem. Soc. A, (1969) 883 and 2081.

[21]. F.S. Stephens, J. Chem. Soc. Dalton Trans., (1972) 1350.

[22]. N.J. Ray and B.J. Hathaway, Acta Crystallogr., Section B, 34 (1978) 3224.

[23]. B.J. Hathaway and D.E. Billing, Coord. Chem. Rev., 5 (1970) 143.

[24]. J.C. Lancuster, W.R. Mcwhinnie and P.L. Welham, J. Chem. Soc. A, (1971) 1742.

[25]. S. Youngme, S. Tonpho, K. Chinnakali, S. Chantrapromma and H.K. Fun, Polyhedron, (1998) in the press.

[26]. C. Belin , M. Chaabouni , J.-L. Pascal , J. Potier and J. Roziere , J. Chem. Soc., Commun., (1980) 105.

[27]. B.J. Hathaway, I.M. Procter, R.C. Slade and A.A.G. Tomlinson, J. Chem. Soc. A, (1969) 2219.

[28]. A.P. Gaughan , Z. Dori and J.A. Ibers , Inorg. Chem., 13 (1974) 1657.

Table 1 Crystal and refinement data for complexes **1** and **2**

Formula	$C_{20}H_{18}B_2CuF_8N_6$	$C_{20}H_{36}CuN_6O_{13}S$
M	579.56	664.15
T/K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	Cc	P21/c
a/Å	9.2780(1)	10.8765(2)
b/Å	12.7500(2)	12.1197(2)
c/Å	19.5881(3)	22.5406(4)
$\alpha/^\circ$	90	90
$\beta/^\circ$	103.354(1)	98.3560(10)
$\gamma/^\circ$	90	90
$V/Å^3$	2254.49(5)	2939.76(9)
Z	4	4
D_c/kgm^{-3}	1.708	1.501
F(000)	1164	1388
Crystal size/mm	0.46×0.32×0.22	0.28×0.22×0.20
θ range/$^\circ$	2.76-30.00	2.82-30.00
h/k/l	-9,13/0,15/-27,26	-15,15/0,17/0,31
No of reflections collected	8674	21772
No. of unique reflections	4837	8490
Absorption correction	empirical	empirical
$T_{max.}$ And $T_{min.}$	0.800,0.642	0.909,0.681
Data/restraints/parameters	4837/2/335	8486/0/453
GOF	1.071	1.044

Final R indices[I>2σ(I)]	R1=0.0331,wR2= 0.0814	R1=0.0535,wR2= 0.0939
R indices (all data)	R1=0.0414,wR2= 0.0869	R1=0.1209,wR2= 0.1178
Largest diff. Peak and hole/e.Å^{-3}	0.322,-0.505	0.378,-0.449

Table 2. Selected bond lengths (Å) and angles (°) for compound **1** with estimated standard deviations (e.s.d.s.) in parentheses.

Cu(1)-N(5)	1.945(5)	F(3)-B(1)	1.341(10)
Cu(1)-N(2)	1.961(5)	F(4)-B(1)	1.360(9)
Cu(1)-N(4)	1.967(5)	F(5)-B(2)	1.417(10)
Cu(1)-N(1)	1.975(5)	F(6)-B(2)	1.369(10)
F(1)-B(1)	1.416(8)	F(7)-B(2)	1.311(10)
F(2)-B(1)	1.394(8)	F(8)-B(2)	1.386(9)
N(5)-Cu(1)-N(2)	99.1(2)	F(3)-B(1)-F(1)	105.2(6)
N(5)-Cu(1)-N(4)	95.4(2)	F(4)-B(1)-F(1)	105.8(6)
N(2)-Cu(1)-N(4)	142.77(7)	F(2)-B(1)-F(1)	114.0(6)
N(5)-Cu(1)-N(1)	138.18(7)	F(7)-B(2)-F(6)	106.2(7)
N(2)-Cu(1)-N(1)	93.3(2)	F(7)-B(2)-F(8)	115.7(7)
N(4)-Cu(1)-N(1)	98.4(2)	F(6)-B(2)-F(8)	108.1(7)
F(3)-B(1)-F(4)	117.9(7)	F(7)-B(2)-F(5)	112.4(7)
F(3)-B(1)-F(2)	103.2(6)	F(6)-B(2)-F(5)	112.6(7)
F(4)-B(1)-F(2)	111.0(7)	F(8)-B(2)-F(5)	101.9(6)

Table 3. Hydrogen bonds for compound **1** (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA) C(2)-
H(2A)...F(8)#1	0.92	2.43	3.261(9)	148
C(19)-H(19A)...F(4)#2	0.92	2.47	3.272(10)	144
C(20)-H(20A)...F(5)#2	0.92	2.51	3.316(8)	145
C(12)-H(12A)...F(3)#3	0.92	2.54	3.225(9)	131

N(3)-H(3A)...F(2)#4	0.86	2.05	2.912(8)	176
N(6)-H(6A)...F(6)#5	0.86	2.02	2.874(7)	174

Symmetry Codes: #1 x,y,z; #2 1+x,y,z; #3 x-1/2,y-1/2,z;
#4 1/2+x,1/2-y,1/2+z; #5 1/2+x,1/2-y,z-1/2

Table 4. Selected bond lengths (Å) and angles (°) for compound **2** with estimated standard deviations (e.s.d.s.) in parentheses.

Cu(1)-N(2)#1	2.004(2)	Cu(2)-N(4)	2.027(2)
Cu(1)-N(2)	2.004(2)	Cu(1)-O(1W)	
2.495(2)Cu(1)-N(1)#1	2.025(2)	Cu(2)-O(2W)	
2.465(2)Cu(1)-N(1)	2.025(2)	S(1)-O(1)	
1.458(2) Cu(2)-N(5)	2.022(2)	S(1)-O(4)	
1.461(2) Cu(2)-N(5)#2	2.022(2)	S(1)-O(3)	
1.466(2) Cu(2)-N(4)#2	2.027(2)	S(1)-O(2)	
1.473(2)			
N(2)#1-Cu(1)-N(2)	180.0		
N(5)-Cu(2)-N(4)	85.39(8)		
N(2)#1-Cu(1)-N(1)#1	85.93(8)		
N(5)#2-Cu(2)-N4)	94.61(8)	N(2)-Cu(1)-N(1)#1	94.07(8)
N(4)#2-Cu(2)-N(4)	180.0		
N(2)#1-Cu(1)-N(1)	94.07(8)		
O(1)-S(1)-O(4)	108.7(2)	N(2)-Cu(1)-N(1)	85.93(8)
O(1)-S(1)-O(3)	111.2(2)	N(1)#1-Cu(1)-N(1)	180.0
O(4)-S(1)-O(3)	110.2(2)	N(5)-Cu(2)-N(5)#2	180.0

O(1)-S(1)-O(2)	108.2(2)	N(5)-Cu(2)-N(4)#2	94.61(8)
O(4)-S(1)-O(2)	109.17(14)	N(5)#2-Cu(2)-N(4)#2	85.39(8)
O(3)-S(1)-O(2)	109.35(14)		

Table 5. Hydrogen bonds for compound **2** (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(1N6)...O(2)#1	0.75(3)	2.12(3)	2.854(3)	170(3)
O(7W)-H(1W7)...O(8W)#1	0.79(4)	2.24(4)	2.974(4)	156(4)
O(8W)-H(1W8)...O(4)#1	0.78(4)	2.03(4)	2.800(4)	167(4)
O(9W)-H(1W9)...O(4)#1	0.87(4)	1.97(4)	2.843(3)	176(4)
O(3W)-H(2W3)...O(5W)#1	0.76(4)	2.10(4)	2.843(5)	168(4)
O(4W)-H(2W4)...O(2)#1	0.71(4)	2.17(5)	2.858(4)	161(5)
O(5W)-H(2W5)...O(7W)#1	0.76(4)	2.17(4)	2.837(5)	170(5)
O(6W)-H(2W6)...O(1)#1	0.72(4)	2.47(4)	3.105(3)	149(4)
O(6W)-H(2W6)...O(4)#1	0.72(4)	2.57(4)	3.230(4)	154(4)
O(7W)-H(2W7)...O(3)#1	0.82(4)	1.95(4)	2.767(4)	174(4)
O(3W)-H(1W3)...O(1)#2	0.71(4)	2.41(4)	3.085(5)	160(4)
O(5W)-H(1W5)...O(4W)#2	0.77(4)	1.97(4)	2.714(4)	164(4)
O(2W)-H(2W2)...O(8W)#3	0.75(4)	2.11(4)	2.851(4)	170(4)
O(2W)-H(1W2)...O(6W)#3	0.86(4)	2.03(4)	2.854(4)	162(4)
N(3)-H(1N3)...O(1)#4	0.78(3)	2.01(3)	2.790(3)	173(3)
O(4W)-H(1W4)...O(3W)#4	0.78(4)	2.11(4)	2.878(4)	170(4)
O(6W)-H(1W6)...O(5W)#4	0.77(4)	2.09(4)	2.855(4)	170(4)
O(8W)-H(2W8)...O(3)#4	0.70(4)	2.14(4)	2.836(3)	172(4)
O(9W)-H(2W9)...O(7W)#4	0.72(4)	2.35(4)	3.043(4)	160(5)
O(1W)-H(2W1)...O(9W)#5	0.79(4)	2.08(4)	2.854(4)	165(4)
O(1W)-H(1W1)...O(3W)#6	0.82(4)	2.13(4)	2.937(4)	168(4)

Symmetry Codes: #1 x,y,z; #2 x-1,y,z; #3 1-x,1/2+y,1/2-z;
#4 1-x,-1/2+y,1/2-z; #5 1-x,-y,-z; #6 x,1/2-y,-1/2+z

Figure Captions

Fig. 1. ORTEP view of $[Cu(C_{10}H_9N_3)_2][BF_4]_2$, **1**.

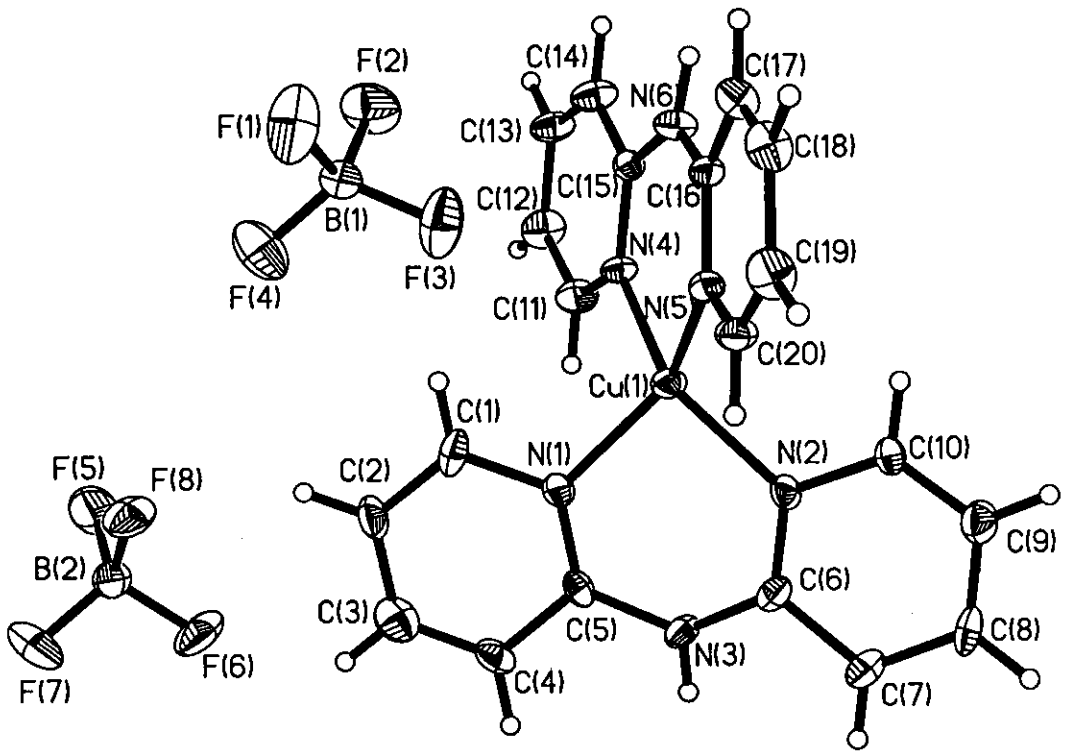
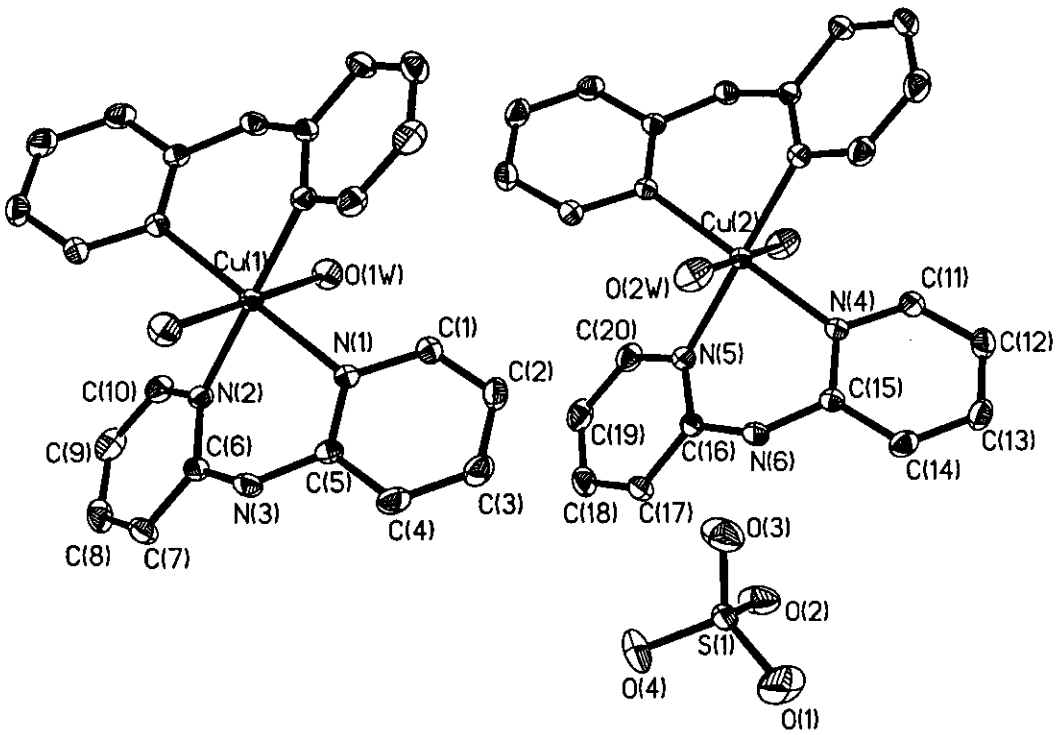


Fig. 2. ORTEP view of a chromophore of $[Cu(C_{10}H_9N_3)_2(H_2O)_2][SO_4].7H_2O$, **2**.



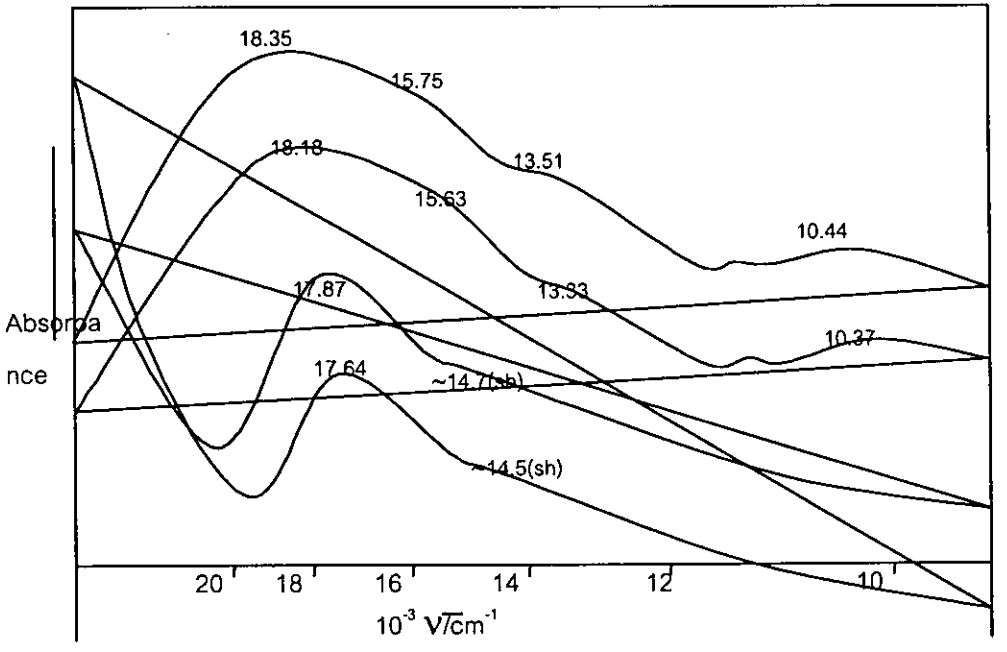


Figure 3. The electronic reflectance spectra of $[Cu(bipyam)_2][BF_4]_2$ 1 (——), $[Cu(bipyam)_2(H_2O)_2]$-$[SO_4].7H_2O$ 2 (——), $[Cu(bipyam)_2][ClO_4]_2$ 3 (——)and $[Cu(bipyam)_2(NO_3)_2]$ 4 (——)