Journal of Fluorine Chemistry 131 (2010) 456–460

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Segregated aromatic π–π stacking interactions involving fluorinated and non-fluorinated benzene rings: $Cu(py)_2(pfb)_2$ and $Cu(py)_2(pfb)_2(H_2O)$ (py = pyridine and pfb = pentafluorobenzoate)

Raj Pal Sharma [a,*], Anju Saini [a], Sukhjinder Singh [a], Paloth Venugopalan [a], William T.A. Harrison [b,*]

[a] *Department of Chemistry, Panjab University, Chandigarh 160014, India*
[b] *Department of Chemistry of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland, United Kingdom*

ARTICLE INFO

Article history:
Received 25 September 2009
Received in revised form 21 December 2009
Accepted 22 December 2009
Available online 4 January 2010

Keywords:
Copper(II)
Pentafluorobenzoate
π–π Stacking interactions

ABSTRACT

The syntheses, physical characterization and crystal structures of two new molecular copper(II) complexes of composition $[Cu(C_5H_5N)_2(C_7F_5O_2)_2]$ (**1**) and $[Cu(C_5H_5N)_2(C_7F_5O_2)_2(H_2O)]$ (**2**) (C_5H_5N = py = pyridine and $C_7F_5O_2^-$ = pfb = pentafluorobenzoate) are reported. Single-crystal X-ray structure determinations revealed that in **1**, the Cu^{2+} ion, which lies on a crystallographic inversion centre, is coordinated to two py molecules and two oxygen atoms from two monodentate pfb anions, resulting in a *trans*-CuN_2O_2 square planar geometry. In **2**, the Cu^{2+} ion is also coordinated to two py and two pfb species in addition to a water molecule in the apical site of a distorted CuN_2O_3 square pyramid. In the crystal packing, both **1** and **2** show segregated aromatic π–π stacking interactions in which (py + py) and (pfb + pfb) ring-pairings are seen, but no (py + pfb) pairings occur. Crystal data: **1**: $C_{24}H_{10}CuF_{10}N_2O_4$, $M_r = 643.88$, space group $P\bar{1}$, $a = 8.0777$ (3) Å, $b = 8.0937$ (3) Å, $c = 10.5045$ (5) Å, $\alpha = 90.916$ (3)°, $\beta = 93.189$ (2)°, $\gamma = 118.245$ (3)°, $V = 603.36$ (4) Å^3, $Z = 1$. **2**: $C_{24}H_{12}CuF_{10}N_2O_5$, $M_r = 661.90$, space group $P\bar{1}$, $a = 7.5913$ (5) Å, $b = 15.6517$ (6) Å, $c = 21.1820$ (14) Å, $\alpha = 95.697$ (4)°, $\beta = 94.506$ (2)°, $\gamma = 91.492$ (4)°, $V = 2495.2$ (3) Å^3, $Z = 4$.

1. Introduction

It is now recognised that weak intermolecular interactions involving fluorine atoms are significant in diverse fields such as drug design [1], protein structure [2] and crystal engineering [3,4] and various types of interactions/bonds including C–H...F, F...F, C–F...π and C–F...C [5] links have been described in detail. However, the remarkable results reported by Soloshonok [6] on the self-disproportionation of enantiomers containing trifluoromethyl groups (which stimulated this special issue of *J. Fluorine Chem.*) suggest that *repulsive* interactions between $–CF_3$ groups may be equally significant in determining the structures and properties of highly fluorinated compounds.

The pentaflurobenzoate (pfb) anion is of interest in coordination chemistry due to its different coordination modes (see supplementary materials) to metal ions and its lack of hydrogen atoms, which might facilitate its role as an acceptor of C–H...F interactions. Reported crystal structures of metal complexes containing pfb show various coordination modes for the ligand including monomeric O-monodentate [7] and O,O-bidentate [8], and dimeric/polymeric O,O-bridging [9,10]. However, as yet, no clear trends in terms of the role of its F atoms in determining crystal packing have emerged.

This paper reports the syntheses, characterization and single-crystal X-ray structure determinations of the complexes $[Cu(py)_2(pfb)_2]$ (**1**) and $[Cu(py)_2(pfb)_2(H_2O)]$ (**2**), in which aromatic π–π stacking plays an important role in establishing the structures.

2. Results and discussion

2.1. Synthesis

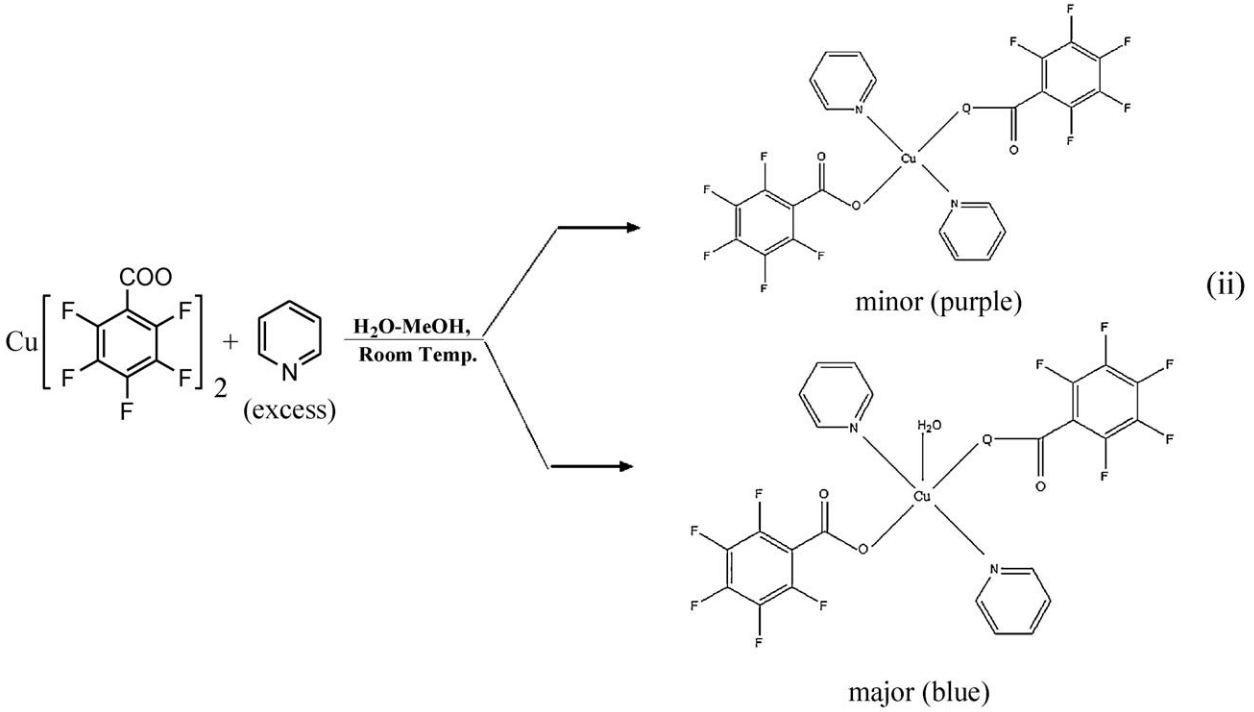
The intermediate $Cu(pfb)_2$ salt (water content unknown) in the form of a light blue precipitate was obtained when $CuSO_4{\cdot}5H_2O$ was reacted with sodium pentafluorobenzoate in a 1:2 molar ratio in water at room temperature. The $Cu(pfb)_2$ was then dissolved/suspended in water–methanol solution. To this solution, pyridine was added (at room temperature) drop-wise with constant stirring until the solution turned deep blue, which was then allowed to evaporate at room temperature, giving a mixture of purple (minor component) and blue (major component) single crystals. Elemental analyses of hand-separated purple and blue crystals were consistent with the structural formulae $[Cu(py)_2(pfb)_2]$ and

---

* Corresponding authors. Tel.: +91 172 2534433; fax: +91 172 2545074.
E-mail addresses: rpsharmapu@yahoo.co.in (R.P. Sharma), w.harrison@abdn.ac.uk (William T.A. Harrison).

0022-1139/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2009.12.020

$$CuSO_4 + 2\,Na(pfb) \xrightarrow{H_2O} Cu(pfb)_2 + Na_2SO_4 \qquad (i)$$



Scheme 1. Pictorial representation of the chemical reaction.

[Cu(py)$_2$(pfb)$_2$(H$_2$O)], respectively. The pictorial representation of above synthesis is given in Scheme 1.

2.2. Molar conductance

Conductance measurements were carried out at 25 °C in acetone and a plot of Λ_m (molar conductance) *versus* $\sqrt{C}$ (square root of concentration) was constructed. When *C* was extrapolated to zero, it gave a negligible value for Λ_o, indicating the presence of non-ionic/neutral species in solution, as confirmed by the crystal-structure studies of **1** and **2**.

2.3. Spectroscopic characterization

IR data for **1** and **2** (KBr pellets) were recorded in the region 4000–400 cm^{-1} and gave almost identical spectra (see supplementary materials), in which all the observed bands could be tentatively assigned by comparison with literature values for related compounds [11,12]. The expected vibrations due to the water molecules in **2** were not seen distinctly: it is possible that water loss occurs while making the pellets under pressure, as it was observed that the blue sample turned to purple at room temperature. However, a nujol smear/mull of the un-ground blue crystals kept at 10 °C in air-tight storage tube shows a strong water absorption band at 3524 cm^{-1}.

UV/visible spectra were recorded in acetone, compound **1** peaks at 730 nm (broad, strong), 585 nm (shoulder) and 950 nm (shoulder), which are typical of those associated with d–d transitions in square planar Cu^{2+} complexes [13]. Compound **2** shows bands at 741 nm (strong, broad) and at 971 nm (weak, broad), which are in good arrangement with literature data [14] for square pyramidal complexes of copper(II).

2.4. Magnetic measurements

The room-temperature magnetic susceptibilities of **1** and **2** were measured to be 1.96 and 1.92 μ_B, respectively, which are consistent with copper in its +2 oxidation state in both cases. The increase in magnetic moment compared to the calculated d^9 spin-only moment of 1.73 μ_B may be ascribed to spin–orbit coupling [15].

2.5. Crystal structures

In **1**, the complete [Cu(py)$_2$(pfb)$_2$] molecule is generated by crystallographic inversion symmetry, with the copper ion lying on the inversion centre (Fig. 1). This results in a *trans*-CuN$_2$O$_2$ square planar geometry for the metal ion (Table 1), the metal being bonded to two pyridine molecules and two O-monodentate pfb ligands. The Cu–N and Cu–O bond lengths in **1** are typical [14] for complexes containing Cu^{2+}. In **1**, crystal symmetry dictates that the dihedral angles between the pairs of symmetry related molecules are zero, whereas the dihedral angle between the py and pfb ring planes in the asymmetric unit is 46.40 (11)°.

In the crystal of **1** (Fig. 2), the molecules form pseudo-layers propagating in the *bc*-plane. It is striking that in a perpendicular sense to the layers, py rings are only overlapped with py rings and pfb rings are only overlapped with pfb rings, and there are no “mixed” (py–pfb) aromatic π–π stacking interactions. However, it should be noted that the centroid–centroid separations of the aromatic rings are relatively long: the py–py distances are 3.984 (3) and 4.127 (3) Å and the pfb–pfb separations are 4.029 (4) and 4.052 (4) Å. A weak C–H...F interaction [H...F = 2.44 Å, C–H...F = 149°] may further consolidate the packing in **1**.

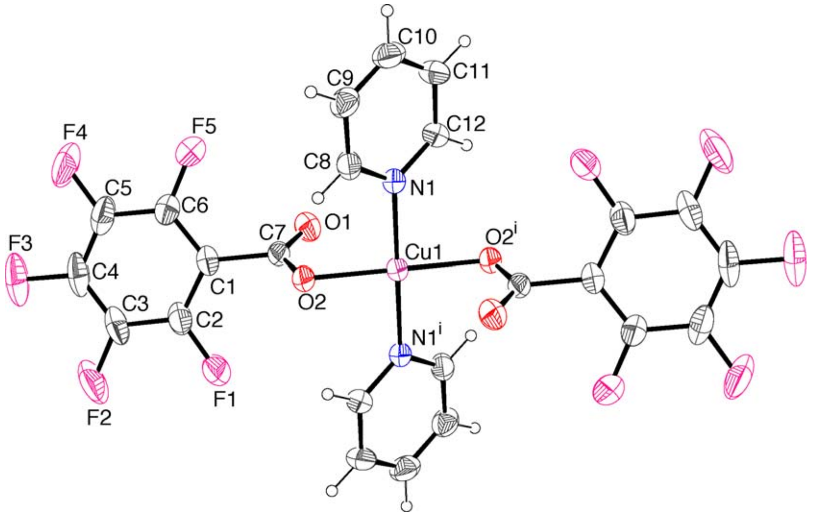


Fig. 1. The molecular structure of 1 showing 50% displacement ellipsoids for the non-hydrogen atoms. Symmetry code: (i) $1-x$, $1-y$, $1-z$.

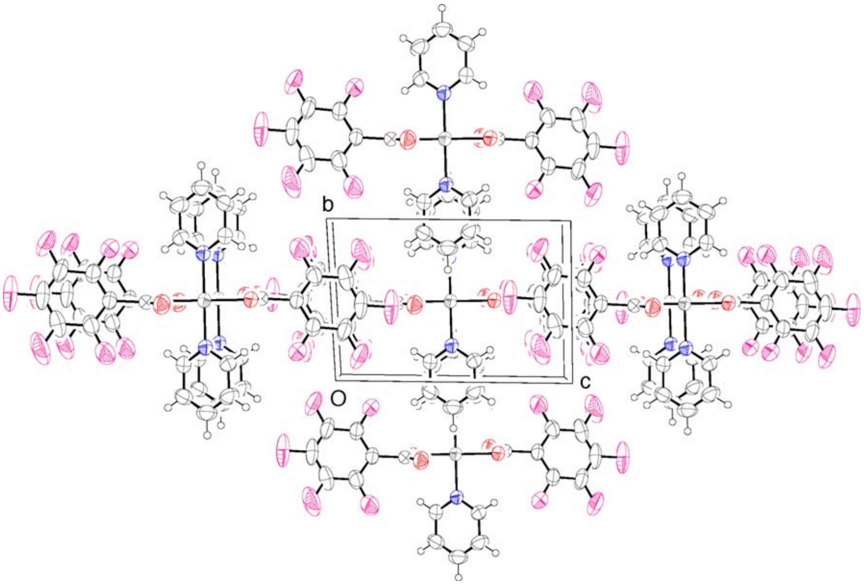


Fig. 2. The crystal packing for 1 viewed down [1 0 0].

In **2**, there are two complete [Cu(py)$_2$(pfb)$_2$(H$_2$O)] molecules in the asymmetric unit. Both copper ions adopt CuN$_2$O$_3$ square-based pyramidal coordination geometries (Table 2) with two py molecules and two pfb ligands in the basal plane, such that the N atoms are in a *trans* conformation, and the water molecule in the apical site (Fig. 3). In both molecules, the Cu–O(water) bond is significantly longer than the other bonds from the metal, which is a normal feature of this geometry [16].

In the crystal of **2** (Fig. 4), *bc*-plane pseudo-layers and exactly the same pattern of segregated π–π stacking (*i.e.* py–py and pfb–pfb contacts but no mixed py–pfb contacts) occur, as was seen in **1**. In **2**, the centroid–centroid separations associated with the py rings are 3.817 (3), 3.875 (3), 4.053 (3) and 4.170 (3) Å (mean = 3.979 Å). For the pfb–pfb aromatic stacking, the equivalent distances are 3.765 (3), 3.882 (3), 3.885 (3) and 4.120 (3) Å (mean = 3.913 Å). It is interesting that the aromatic stacking interactions involving the bulkier *penta*-fluorobenzene rings in **2** show a slightly shorter mean separation than those involving the pyridine rings. The

Table 1
Selected bond lengths [Å] and angles [°] for **1**.

Cu1–O2	1.969 (2)	Cu1–N1	2.000 (3)
Cu1–O2^i	1.969 (2)	Cu1–N1^i	2.000 (3)
O2^i–Cu1–O2	180.0	O2^i–Cu1–N1^i	90.51 (10)
O2–Cu1–N1^i	89.49 (10)	O2^i–Cu1–N1	89.49 (10)
O2–Cu1–N1	90.51 (10)	N1^i–Cu1–N1	180.0

Symmetry code: (i) $1-x$, $1-y$, $1-z$.

Table 2
Selected bond lengths [Å] and angles [°] for **2**.

Cu1–O4	1.967 (3)	Cu1–O2	1.978 (3)
Cu1–N1	1.996 (4)	Cu1–N2	1.998 (4)
Cu1–O5	2.350 (3)	Cu2–O7	1.966 (3)
Cu2–O9	1.972 (3)	Cu2–N4	2.005 (4)
Cu2–N3	2.015 (4)	Cu2–O10	2.296 (3)
O4–Cu1–O2	164.67 (14)	O4–Cu1–N1	90.03 (15)
O2–Cu1–N1	89.05 (15)	O4–Cu1–N2	91.94 (15)
O2–Cu1–N2	89.39 (15)	N1–Cu1–N2	177.64 (17)
O4–Cu1–O5	96.11 (13)	O2–Cu1–O5	99.15 (13)
N1–Cu1–O5	87.68 (14)	N2–Cu1–O5	90.82 (13)
O7–Cu2–O9	170.35 (13)	O7–Cu2–N4	88.98 (15)
O9–Cu2–N4	89.27 (14)	O7–Cu2–N3	90.72 (15)
O9–Cu2–N3	90.36 (15)	N4–Cu2–N3	175.99 (16)
O7–Cu2–O10	96.24 (13)	O9–Cu2–O10	93.32 (13)
N4–Cu2–O10	93.07 (14)	N3–Cu2–O10	90.94 (14)

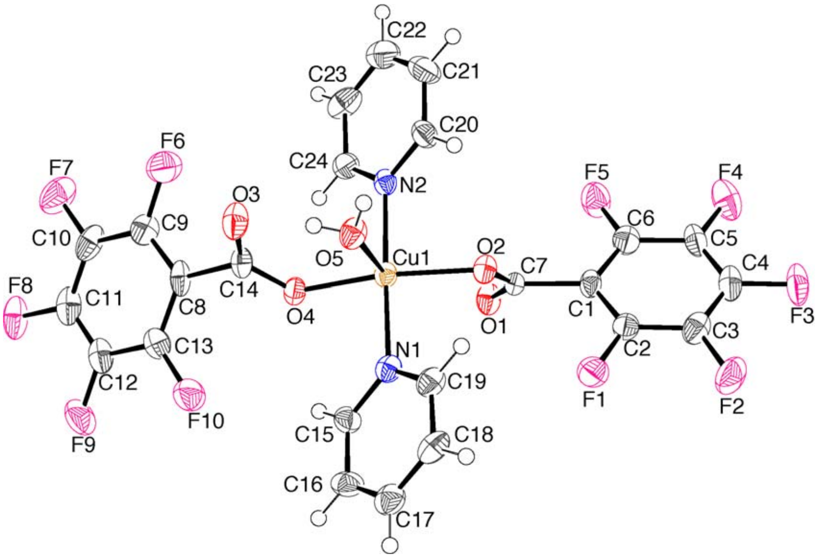


Fig. 3. The molecular structure of one of the molecules (containing atom Cu1) of 2 showing 50% displacement ellipsoids for the non-hydrogen atoms. The other molecule, containing Cu2, is almost identical.

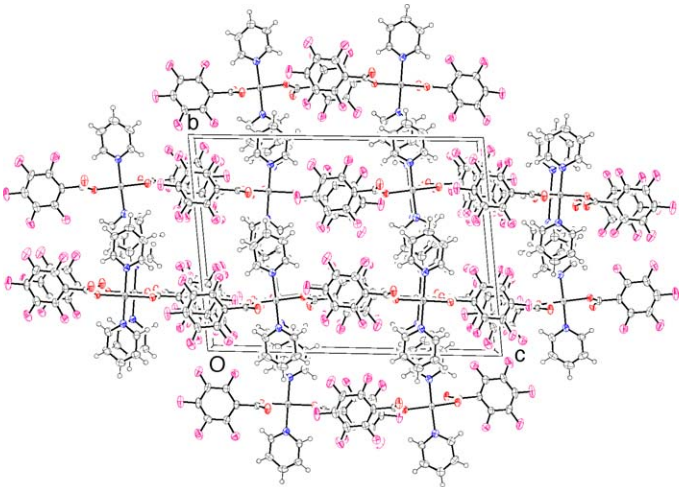


Fig. 4. The crystal packing for 2 viewed down [1 0 0].

structure of **2** is completed by O–H…O hydrogen bonds (Table 3), which link the molecules into chains propagating in the crystallographic *a* direction.

2.6. Conclusion

The reaction of $Cu(pfb)_2$ with pyridine leads to two new complexes $[Cu(py)_2(pfb)_2]$ **1** (purple) and $[Cu(py)_2(pfb)_2(H_2O)]$ **2** (blue). Physical and spectroscopic data for **1** and **2** are consistent with results for related materials. The molecular structures of **1** and **2** show that pfb adopts monodentate-O coordination to the copper(II) ion. The recently reported [14] structure of $Cu(pfb)_2(im)_2$ (im = imidazole, $C_3H_4N_2$) is very similar to that of 1, with the Cu(II) ion adopting a *trans*-CuN_2O_2 square-planar coordination arising from two pfb anions and two imidazole molecules. In their crystal structures, both **1** and **2** show aromatic π–π stacking such that py rings overlap with py rings and pfb rings with pfb rings, whereas mixed py–pfb interactions are avoided. This is novel and theoretical calculations might give insight into whether this arises from electronic effects. Conversely, C–H…F interactions appear to play a minor role in these structures.

Table 3
Hydrogen bonding parameters for **2** [Å and°].

	D–H	H…A	D…A	D–H…A
O5–H5A…O1^{i}	0.95	1.97	2.881 (5)	162
O5–H5B…O3	0.78	2.04	2.723 (5)	147
O10–H10A…O8^{ii}	0.87	2.08	2.880 (5)	154
O10–H10B…O6	0.92	1.97	2.700 (5)	135

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$.

3. Experimental

3.1. Materials

Analytical grade reagents were used throughout this work without any further purification.

3.2. Synthesis

1.175 g (4.71 mmol) of $CuSO_4·5H_2O$ was dissolved in the minimum quantity of distilled water in a beaker. In a second beaker, 0.377 g (9.43 mmol) NaOH was dissolved in 20 ml distilled water and 2 g (9.43 mmol) of pentafluorobenzoic acid was added to it. Both solutions were mixed and a light sky-blue precipitate appeared on mixing the two solutions after 5–6 days. It was filtered through a fine filter paper and dried at room temperature. The sky-blue product $[Cu(pfb)_2]$ was dissolved in water–methanol (1:4) solution, then pyridine was added to the solution drop-wise, until the colour of the solution changed to deep blue. The solution was allowed to evaporate at room temperature and purple and blue crystals of **1** and **2** appeared after a week. These crystals were hand separated and are stable in air up to 10 °C; however at 20 °C, **2** converts to **1** over a few hours and on crushing, the blue compound very rapidly changes colour to purple. Compounds **1** and **2** are freely soluble in chloroform and acetone but almost insoluble in water and methanol. **1** decomposes at 140–142 °C. Anal. Calcd. $Cu(py)_2(pfb)_2$ [purple] C 44.75%; H 1.55%, N 4.35%, O 9.94%, Cu 9.87%; found: C 44.27%; H 1.47%, N 4.29%,O 9.87%, Cu 9.54%. $Cu(py)_2(pfb)_2(H_2O)$ [blue]: Anal. Calcd. C 43.54%; H 1.81%, N 4.23%,O 12.09%,Cu 9.59%; found: C 43.31%; H 1.77%. N 4.33%,O 12.07%,Cu, 9.60.

Table 4
Crystallographic and data-collection parameters.

Compound	1	2
Empirical formula	$C_{24}H_{10}CuF_{10}N_2O_4$	$C_{24}H_{12}CuF_{10}N_2O_5$
Formula weight	643.88	661.90
Habit, colour	Slab, purple	Block, blue
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	8.0777 (3)	7.5913 (5)
b (Å)	8.0937 (3)	15.6517 (6)
c (Å)	10.5045 (5)	21.1820 (14)
α (°)	90.916 (3)	95.697 (4)
β (°)	93.189 (3)	94.506 (2)
γ (°)	118.245 (3)	91.492 (4)
V (Å^3)	603.36 (4)	2495.2 (3)
Z	1	4
T (K)	120	120
ρ_{calc} (g cm^{-3})	1.772	1.762
$R(F)$ [$I > 2\sigma(I)$]	0.053	0.063
$wR(F^2)$ [all data]	0.140	0.167
Min., max. $\Delta\rho$ (e Å^{-3})	−0.42, +0.32	−0.57, +0.53

3.3. Instrumentation

Carbon, hydrogen, nitrogen and oxygen were measured microanalytically by Flash CHNS-O elemental analyzer (Model 1112) (Thermo Electron Corporation, USA) and copper was determined by standard methods [17]. FT-IR spectra were recorded as KBr pellets on a Perkin-Elmer RXFT-IR system. Magnetic susceptibility data were collected on a Gouy's balance and electronic spectra were recorded in acetone using a Hitachi 330 spectrophotometer.

3.4. X-ray crystallography

Single crystals of **1** and **2** suitable for X-ray diffraction studies were grown directly from aqueous solution by slow evaporation of the reaction mixture. X-ray diffraction data were collected using a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 120 K. Crystal data and refinement parameters are summarized in Table 4. The structures were solved by direct methods and refined by full-matrix least squares against $|F^2|$. The water H atoms in **2** were located in a difference map and refined as riding atoms in their as-found relative positions. All the other H atoms in **1** and **2** were geometrically placed.

4. Supplementary data

Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (deposition numbers CCDC 746831 and 746832). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgement

Ms Anju Saini is grateful to UGC, New Delhi for providing a "Teacher Fellowship" under the Faculty Improvement Program.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2009.12.020.

References

[1] S.G. DiMagno, H. Sun, Curr. Top. Med. Chem. 6 (2006) 1473–1482.
[2] P. Zhou, J. Zou, F. Tian, Z. Shang, J. Chem. Inf. Model 49 (2009) 2344–2355.
[3] M.D. Prasanna, T.N. Guru Row, CrystEngCommun. 2 (2000) 134–140.
[4] A. Forni, P. Metrangolo, T. Pilati, G. Resnati, Cryst. Growth Des. 4 (2004) 291–295.
[5] F. Hof, D.M. Scofield, W.B. Schweizer, F. Diedrich, Angew. Chem. Int. Ed. 43 (2004) 5056–5059.
[6] V.A. Soloshonok, Angew. Chem. Int. Ed. 45 (2006) 766–769.
[7] M.D. Santana, G. Garcia, G. Lopez, A. Lozano, C. Vicente, L. Garcia, J. Perez, Polyhedron 26 (2007) 1029–1036.
[8] G.B. Deacon, P.I. Mackinnon, J.C. Taylor, Polyhedron 4 (1985) 103–113.
[9] D.A. Brown, M.G.H. Wallbridge, W.-S. Li, M. McPartlin, Polyhedron 13 (1994) 2265–2270.
[10] Y. Sevryugina, O. Hietsoi, M.A. Petrukhina, Chem. Commun. (2007) 3853–3855.
[11] S.-G. Roh, J.B. Oh, M.-K. Nah, N.S. Baek, Y. Lee, Bull. Korean Chem. Soc. 25 (2004) 1503–1508.
[12] G.B. Deacon, R.J. Philips, Coord. Chem. Rev. 33 (1980) 227–250.
[13] M. Suzuki, Y. Nishida, Inorg. Chim. Acta 44 (1980) L9–L11.
[14] C.-H. Ge, X.-Y. Zhang, F. Yu, Y.-N. Gou, X.-D. Zhang, Q.-T. Liu, J. Chem. Crystallorg. 38 (2008) 501–505.
[15] K. Shindo, A. Morita, H. Kamimura, J. Phys. Soc. Jpn. 20 (1965) 2054–2059.
[16] B.B. Liu, T. Weng, H.Z. Xie, Acta Cryst. E65 (2009) m376–m377.
[17] M.A. Malati, Experimental Inorganic Chemistry, 1st ed., Harwood Publishing, Chichester, 1999.