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Bis(diimine)nitritocopper(II) cations: crystal and molecular structures of $[Cu(phen)_2(ONO)]BF_4 \cdot H_2O$ and $[Cu(bipy)_2(ONO)]HSO_4$ {phen = 1,10 phenanthroline, bipy = 2,2′-bipyridine}

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Abstract—The crystal and molecular structures of the bis(diimine)nitritocopper(II) complexes $[Cu(phen)_2(ONO)](BF_4) \cdot H_2O$ (**1**; phen = 1,10-phenanthroline) and $[Cu(bipy)_2(ONO)](HSO_4)$ (**2**; bipy = 2,2′-bipyridine) have been determined. The latter is isostructural with $[Cu(bipy)_2(ONO)](BF_4)$ (**4**). The coordination geometry of the Jahn–Teller distorted $[Cu(diimine)_2(ONO)]^+$ cation in **2** is best described as square pyramidal (monodentate *O*-bonded nitrite). That in **1**, which is similar to that in $[Cu(phen)_2(ONO)](BF_4)$ (**3**), is distorted towards the *cis*-distorted octahedral (bidentate chelating *O*-bonded nitrite) coordination geometry adopted by $[Cu(bipy)_2(ONO)](NO_3)$ (**5**). As the nitrite coordination mode changes from monodentate towards bidentate chelating, distinct trends in structural parameters are discernible. Identical trends are found in the analogous acetates and formates. They suggest that modification of coordination mode principally involves rotation of the nitrite (acetate, formate) moiety about its nitrogen (carboxylate carbon) atom. © 1997 Elsevier Science Ltd

Keywords: copper(II); nitrate; 1,10-phenanthroline; 2,2′-bipyridine.

Copper(II)-nitrite complexes are currently of interest as analogues [1] of copper containing nitrite reductases, such as that from *Achromobacter Cycloclastes*, the active centre of which comprises a pair of copper atoms separated by a histidine–cysteine link ($Cu \cdots Cu \simeq 12.5$ Å) [2]. In our quest to synthesize dinuclear copper(II)-nitrite complexes [3], we have targetted complexes of the type $[(\mu\text{-L})\{Cu(L')(ONO)\}_2]^{2+}$ {L = bridging diimine (pyrazine, 4,4′-bipyridine, 1,2-*trans*-bis(4′-pyridyl)ethene or 3,6-bis(imidazolyl)pyridazine) and L′ = chelating diimine [2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)]} by treatment of "copper(II) nitrite tetrafluoroborate" with bridging and chelating *N*-donor ligands (molar ratio 2 : 1 : 2) in aqueous ethanol. Success has eluded us thus far, either polymeric complexes based on bridging diimines, $\{[(\mu\text{-L})\{Cu(L')\}]^{2+}\}_n$ or $\{[(\mu\text{-L})\{Cu(H_2O)_2\}]^{2+}\}_n$, or mononuclear complexes containing two chelating diimines $[Cu(L')_2(ONO)]^+$, having been obtained. In this paper, we report the preparation and structural characterization of two novel complexes of the latter type, $[Cu(phen)_2(ONO)](BF_4) \cdot H_2O$ (**1**; phen = 1,10-phenanthroline) and $[Cu(bipy)_2(ONO)](HSO_4)$ (**2**; bipy = 2,2′-bipyridine). Comparison of the structures of the bis(diimine)(nitrito)copper(II) cations with previously reported structural data for those in $[Cu(phen)_2(ONO)](BF_4)$(**3**), [4] $[Cu(bipy)_2(ONO)](BF_4)$ (**4**) [5] and $[Cu(bipy)_2(ONO)](NO_3)$ (**5**) [6,7] has revealed interesting trends and variations which are discussed in this paper.

RESULTS AND DISCUSSION

Treatment of a 1 : 2 molar mixture of $Cu(BF_4)_2 \cdot xH_2O$ and phen in aqueous acetone (1 : 1) with a two-fold excess of $NaNO_2$ yielded **1**. Its formation was unforeseen as the corresponding reaction

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in aqueous ethanol [4,8] gives the anhydrous product. The reason for the different chemistry is unknown. The formation of **2** was also unexpected. It was obtained as a by-product of the addition of an ethanolic solution of a 2 : 1 molar mixture of 2,2-bipyridine and 4,4′-bipyridine to an aqueous solution of "copper nitrite" produced by treatment of an aqueous solution of $CuSO_4 \cdot 5H_2O$ with a stoichiometric quantity of $Ba(NO_2)_2$. We conclude that excess $Ba(NO_2)_2$ is required for quantitative precipitation of $BaSO_4$.

Crystal structures of $[Cu(phen)_2(ONO)](BF_4) \cdot H_2O$ (**1**) *and of* $[Cu(bipy)_2(ONO)](HSO_4)$ (**2**)

The two complexes comprise $[Cu(diimine)_2(ONO)]^+$ cations, the appropriate anion (BF_4^- or HSO_4^-) and in the case of **1**, non-coordinated H_2O molecules. The asymmetric unit of **1** is shown in Fig. 1; that of **2** is isostructural with that of $[Cu(bipy)_2(ONO)](BF_4)$ (**4**) [5] and is not depicted here. In **1**, the water molecule links the cation [coordinated nitrito oxygen; O(1)] and anion [tetrafluoroborate fluorine; F(14)] through a hydrogen bonding network (Fig. 1), full details of which are given in Table 1. In **2**, there are no specific O—H···O interactions between anion and cation (minimum O···O distance = 3.91 Å).

The participation of the nitrite anion of **1**, but not of **2**, in hydrogen bonding is thought to be responsible for the different frequencies of the $\nu_{as}(NO_2)$ absorption band for the two complexes: 1270 cm^{-1} for **1** and 1365 cm^{-1} for **2** {*cf.* 1368, 1370, 1365 cm^{-1} for $[Cu(bipy)_2(ONO)]X$, X = ClO_4, NO_3, NO_2, respectively [8]}. The positions of $\nu_s(NO_2)$ (typically 1150 cm^{-1} [8]) and $\delta(NO_2)$ (typically 840 cm^{-1} [8]) cannot be ascertained with certainty as they coincide with the intense, broad, T_2 absorption of the tetrahedral anions (1062 cm^{-1} for BF_4^- in **1** and 1099 cm^{-1} for HSO_4^- in **2**) and a complex series of sharp absorptions attributable to bipy, respectively.

Molecular structures of the $[Cu(bipy)_2(ONO)]^+$ *cations*

The cations in **1** and **2** are very similar to those in the corresponding phen, $[Cu(phen)_2(ONO)](BF_4)$ (**3**) [4] and bipy, $[Cu(bipy)_2(ONO)](BF_4)$ (**4**) [5] and $[Cu(bipy)_2(ONO)](NO_3)$ (**5**) [6,7] complexes. Hathaway has concluded, from a detailed analysis of the structural chemistry of **3**–**5** and of the analogous acetates and formates, that the copper(II) coordination sphere varies in geometry, as a function of co-anion [4–7] and temperature [7], from square pyramidal (monodentate *O*-bonded nitrite) to *cis*-distorted octa-

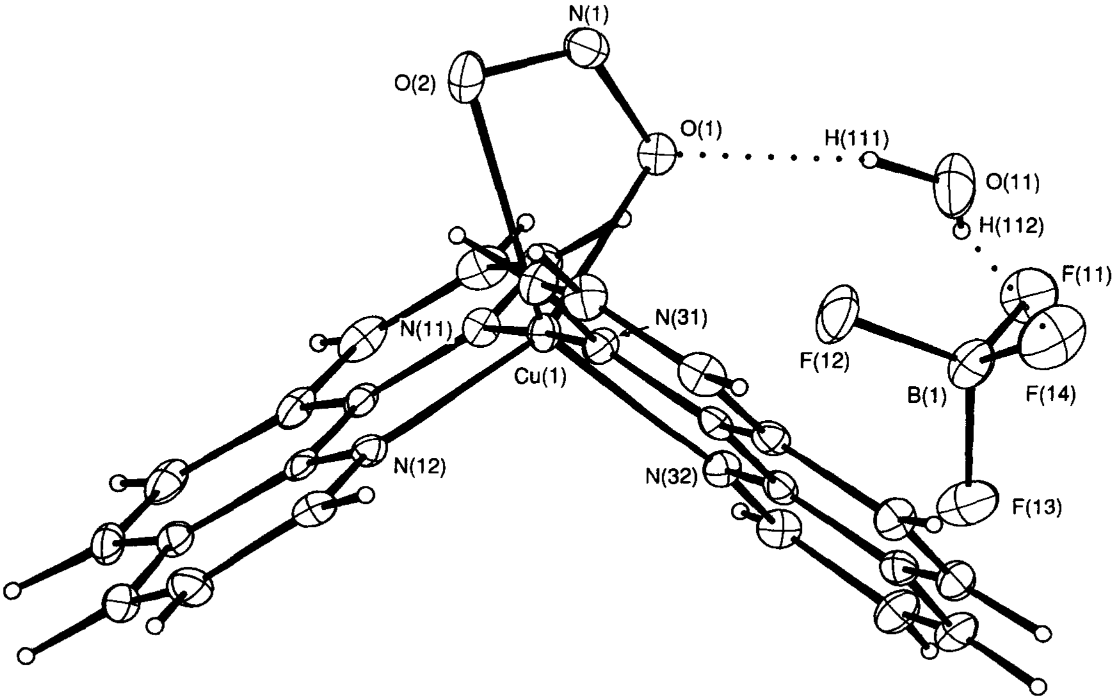
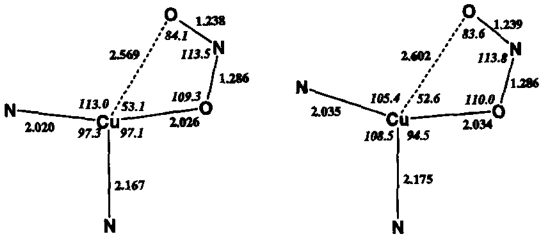


Fig. 1. Molecular structure of the asymmetric unit of $[Cu(phen)_2(ONO)[BF_4] \cdot H_2O$.

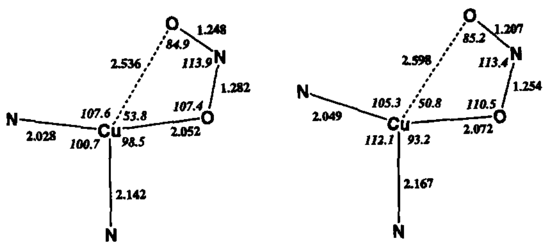
Table 1. Hydrogen-bonding interactions (distances Å and angles °) in $[Cu(phen)_2(ONO)]BF_4 \cdot H_2O$ (**1**)

Contact (O—H···X)	Symmetry of X	O···X (Å)	O—H (Å)	H···X (Å)	OHC (°)	HXX′ (°)
O(11)—H(111)···O(1)	*x,y,z*	2.902(4)	0.85(5)	2.08(5)	163(4)	127(1)
O(11)—H(112)···F(14)	*x,y,z*	2.903(4)	0.83(4)	2.11(4)	161(4)	119(2)

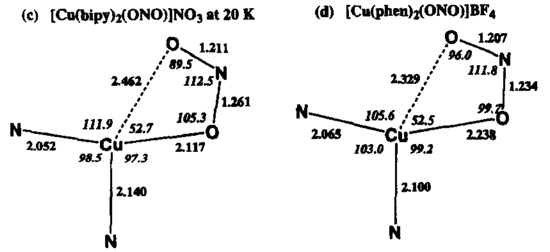
hedral (bidentate chelating *O*-bonded nitrite). If the nitrite anion is considered to be a monoatomic ligand, the latter may also be described as trigonal bipyramidal. Projections of the copper(II) coordination spheres onto the plane containing the nitrite anion are shown schematically for the five complexes (**1** and **2** at 150 K, **3** and **4** at 298 K and **5** at 20 and 298 K) in Fig. 2, together with pertinent interatomic distances and angles. The two coordination sites perpendicular to the projection are occupied by diimine nitrogens with Cu—N distances varying within the limited range 1.98–2.02 Å. Whereas the $[Cu(bipy)_2(ONO)]^+$ cations in **2** [Fig. 2(a)] and **5** [298 K; Fig. 2(f)] are close to square pyramidal and *cis*-distorted octahedral, respectively, those in **4** [Fig. 2(e)] and **5** [20 K; Fig. 2(c)] have intermediate geometries, similar to those of the $[Cu(phen)_2(ONO)]^+$ cations in **1** [Fig. 2(b)] and **3** [Fig. 2(d)]. The different geometries of the cations in the isostructural species, **2** and **4**, are noteworthy, that of **2** being much closer to square pyramidal than that of **4**. Although the diffraction experiments were carried out at different temperatures [150 K (**2**) and 298 K (**4**)], the differences in structural parameters (Fig. 2) are considered to be real as the structural data for **5** at 165 and 298 K are within the standard deviations; it is only at much lower temperatures (100 and 20 K) that significant differences arise [7].



(a) $[Cu(bipy)_2(ONO)]HSO_4$ (b) $[Cu(phen)_2(ONO)]BF_4.H_2O$



(c) $[Cu(bipy)_2(ONO)]NO_3$ at 20 K (d) $[Cu(phen)_2(ONO)]BF_4$



(e) $[Cu(bipy)_2(ONO)]BF_4$ (f) $[Cu(bipy)_2(ONO)]NO_3$ at 298 K

Fig. 2. Comparison of $[Cu(diimine)_2(ONO)]^+$ coordination geometries.

Nitrite binding in the $[Cu(bipy)_2(ONO)]^+$ *cations*

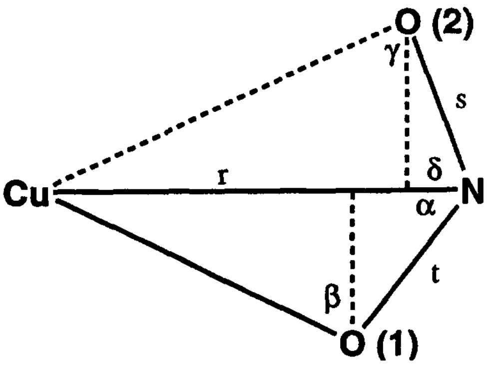
The different coordination geometries originate in the nitrite binding which varies from monodentate [**2**; Fig. 2(a)] to bidentate chelating [**5** at 298 K; Fig. 2(f)]. Structural parameters for the coordinated nitrite anions are summarized in Table 2. Particularly interesting is the limited variation in the Cu···N distance (2.732–2.772 Å; average 2.742 Å; Table 1), which suggests that the variation in coordination mode is determined simply by the pivoting of the anion about its central nitrogen atom. This is clear from Fig. 3 in which the structural parameters are shown as a function of the pivot angle, Cu—N—O(1). Distinct trends (linear relationships) are discernible in Cu···O(1), Cu···O(2), Cu—O(1)—N and Cu—O(2)—N; similar but less obvious trends occur in N···O(1) and N···O(2); Cu···N, O(1)—Cu—O(2) and O(1)—N—O(2) are effectively independent of Cu—N—O(1). Monodentate *O*-bonded nitrite binds strongly with a short Cu···O(1) distance and Cu—O(1)—N close to the sp^2 angle of 120°. As this binding weakens, Cu···O(1) increases markedly, Cu—O(1)—N decreases markedly and both N—O bonds shorten (strengthen) slightly. This is surprising as (i) N···O(1) and N···O(2) should be the same for the symmetrically coordinated bidentate chelating *O*-bonded nitrite and (ii) an increasing Cu···O(2) interaction would be expected to result in a lengthening, albeit extremely limited, of the N···O(2) bond.

Similar trends in structural parameters with binding

Table 2. Selected interatomic distances (Å) and angles (°) in $[Cu(diimine)_2(ONO)]X$

Diimine Anion	2,2′-bipy HSO_4^-	1,10-phen BF_4^-	2,2′-bipy NO_3^- (20 K)	1,10-phen BF_4^-	2,2′-bipy BF_4^-	2,2′-bipy NO_3^- (298 K)
Cu—O(1)	2.026	2.034	2.052	2.072	2.117	2.238
Cu—O(2)	2.569	2.602	2.536	2.597	2.462	2.329
Cu—N(1)	2.735	2.754	2.725	2.772	2.734	2.732
N(1)—O(1)	1.286	1.286	1.282	1.254	1.261	1.234
N(1)—O(2)	1.238	1.239	1.248	1.207	1.211	1.207
O(1)—Cu—O(2)	53.1	52.7	53.8	50.7	52.7	52.5
O(1)—N(1)—O(2)	113.5	113.8	113.9	113.4	112.5	111.9
Cu—O(1)—N(1)	109.3	110.1	107.4	110.5	105.3	99.7
Cu—O(2)—N(1)	84.1	83.6	84.9	85.2	89.4	95.9

type are also found in the analogous acetates [4,9,10] and formates [11]. The dependence of the structural parameters on the pivot angle (α; Scheme 1), assuming the pivot atom to be a constant distance from the copper (Cu···N = 2.742; Cu···C = 2.664 Å) was determined trigonometrically for the nitrites and acetates. For these calculations, N···O(1) and C···O(1) were allowed to decrease slightly with decreasing pivot angle, but N···O(2) and C···O(2) were held constant (Scheme 1).



Scheme 1.

$$Cu\cdots O(1) = t.\sin\alpha/\{\sin[\tan^{-1}(t.\sin\alpha)/(r\text{-}t.\cos\alpha)]\}$$
$$Cu\cdots O(2) = s.\sin\delta/\{\sin[\tan^{-1}(s.\sin\delta)/(r\text{-}s.\cos\delta)]\}$$
$$Cu\text{-}O(1)\text{-}N = (90\text{-}\alpha)+\beta = (90\text{-}\alpha)+\{90\text{-}[\tan^{-1}(t.\sin\alpha/(r\text{-}t.\cos\alpha)]\}$$
$$Cu\text{-}O(1)\text{-}N = (90\text{-}\delta)+\gamma = (90\text{-}\delta)+\{90\text{-}[\tan^{-1}(s.\sin\delta/(r\text{-}s.\cos\delta)]\}$$

For nitrates: $r = 2.742$ Å; $s = 1.235$ Å; $1.235 \leq t \leq 1.285$; $\delta = 113.0\text{-}\alpha$

For acetates: $r = 2.664$ Å; $s = 1.232$ Å; $1.232 \leq t \leq 1.265$; $\delta = 120.2\text{-}\alpha$

Selected experimental and trigonometrically calculated structural parameters for the nitrites and acetates [Cu···O(1), Cu···O(2), Cu—O(1)—X, Cu—O(2)—X (X = N or C)] are compared in Fig. 4; the former are shown as points, the latter as continuous lines. The excellent correlation for both systems supports the contention that the coordination mode simply differs by the pivoting of the anion about its central atom.

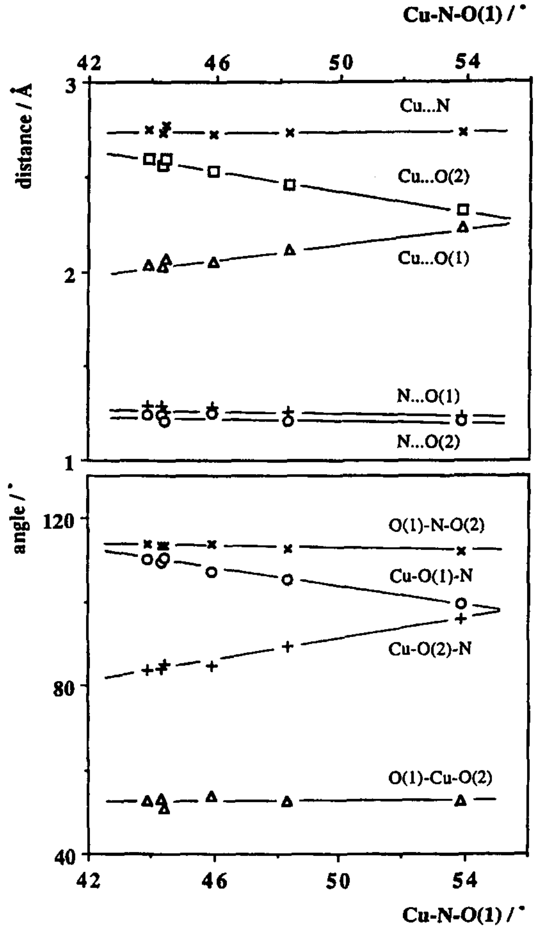


Fig. 3. Variation of $[Cu(diimine)_2(ONO)]^+$ interatomic distances and angles as a function of nitrite pivot [Cu—N—O(1)] angle.

The observed change from square pyramidal to *cis*-distorted octahedral coordination geometry and

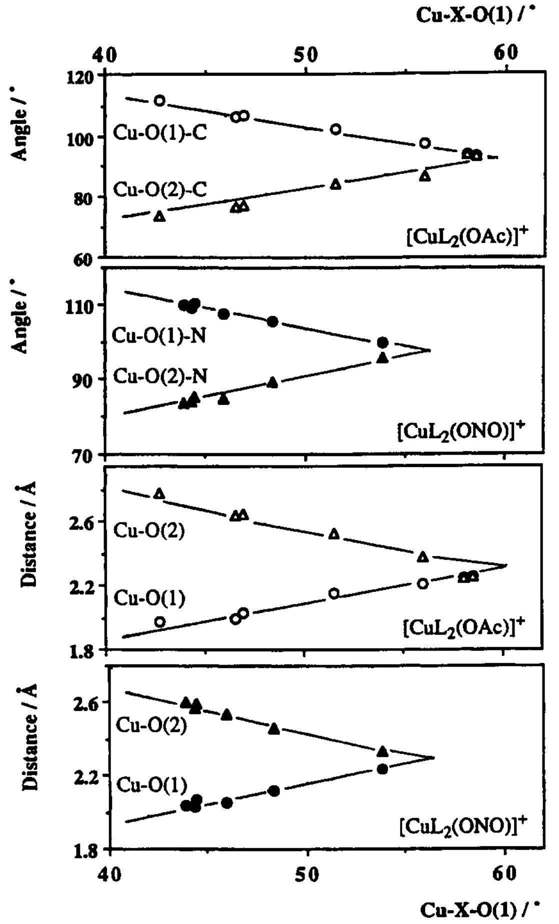


Fig. 4. Variation of selected $[Cu(diimine)_2(ONO)]^+$ and $[Cu(diimine)_2(OAc)]^+$ interatomic distances and angles as a function of nitrite or acetate pivot [Cu—X—O(1) (X = N or C)] angle.

associated change from monodentate to bidentate chelating nitrite (acetate) coordination mode, with increasing temperature for **5**, suggests that increasing thermal energy results in the more symmetrical system [with pseudo C_2 axis along the Cu—X(1) (X = N or C) vector]. Indeed, Hathaway [7] has suggested that the more symmetrical structures are actually interconverting asymmetric structures giving average, not static, C_2 structures. The invariance in Cu—N (Table 2) is significant in this context, the extent of thermal motion of the anion about the pivot atom being determined by temperature. The sensitivity of the coordination mode to temperature suggests that the energy difference between the two conformers (extreme geometries) is very small (77 cm^{-1} for **5** [7]). The fact that different anions (HSO_4^- and BF_4^-) in the isostructural species $[Cu(phen)_2(ONO)]X$ (**2** and **4**) give different cation geometries suggests that this particular structure is sufficiently open and flexible to permit rotation of the nitrite anion around the pivotal nitrogen and modified hydrogen-bonding interactions {e.g. lattice water in $[Cu(phen)_2(ONO)](BF_4) \cdot xH_2O$; **1** and **3**}.

The geometries of the bipy and phen ligands in **1** and **2**, respectively, are unremarkable; the same applies for the HSO_4^- and BF_4^- anions. Full details have been included in supplementary data together with fractional atomic coordinates and thermal displacement amplitudes for all atoms.

EXPERIMENTAL

All products were characterized using elemental analyses, IR and UV–vis spectroscopy. Carbon, nitrogen and hydrogen analyses (microanalyses) were carried out in the University of Nottingham Chemistry Department by Mr T. J. Spencer. IR and UV–vis spectra were obtained on a Perkin–Elmer PE983G spectrometer as KBr pressed pellets and a Unicam UV2-100 spectrometer, respectively.

Copper(II) salts [$CuSO_4 \cdot 5H_2O$ and $Cu(BF_4)_2 \cdot xH_2O$ ($x \sim 3.4$ by copper analysis)] were obtained from Aldrich Chemical Company Ltd and recrystallized from deionized water prior to use. The *N*-donor ligands, 2,2′-bipy, phen, 4,4′-bipyridine and $NaNO_2$ were obtained from Aldrich Chemical Company Ltd and used without further purification.

Synthesis of $[Cu(phen)_2(ONO)]((BF_4) \cdot H_2O$ (**1**)

Compound **1** was prepared following the method described by Hathaway and co-workers [10] for the synthesis of $[M(phen)_2(OAc)]X \cdot 2H_2O$ (M = Cu, X = NO_3, ClO_4; M = Zn, X = BF_4). $Cu(BF_4)_2 \cdot xH_2O$ (0.33 g, 1.39 mmol) and phen (0.5 g, 2.77 mmol) were dissolved in a 1 : 1 acetone:water mixture and heated to boiling. $NaNO_2$ (0.38 g, 5.55 mmol) was added, the solution diluted by addition of the solvent mixture (450 cm^3), boiled, filtered, cooled to room temperature and left to stand for 4 days, after which green needles of **1** (0.166 g, 0.289 mmol, 20% yield) had formed. Found (Calc. for $C_{24}H_{18}BCuF_4N_5O_3$): C, 50.5 (50.1); H, 3.0 (3.1); N, 12.2 (12.2)% IR, 3425 s, br, 1587 m, 1519 s, 1429 s, 1382 w, 1270 s, 1062 br, 854 s, 723 s.

Synthesis of $[Cu(bipy)_2(ONO)](HSO_4)$ (**2**)

$CuSO_4 \cdot 5H_2O$ (1.00 g, 4.0 mmol) was dissolved in water (30 cm^3) and $Ba(NO_2)_2 \cdot H_2O$ (0.917 g, 4.0 mmol) added. A white solid precipitated immediately leaving a green solution. Water (20 cm^3) was added to the mixture, which was then boiled and filtered under reduced pressure. A boiling ethanolic solution (50 cm^3) of 4,4-bipyridine ((0.312 g, 2 mmol) and 2,2-bipyridine (0.625 g, 4 mmol) was added to the filtrate. After boiling for 20 min the resultant dark green solution yielded a green precipitate which was removed by filtration. A small quantity of dark green crystals of **2** grew from the mother liquor over a period of 5 days

(0.084 g, 0.162 mmol). Found (Calc. for $C_{20}H_{17}CuN_5O_6S$) C, 45.3 (46.3); H, 2.9 (3.3); N, 13.5 (13.5)% IR, 3076 m, 1599 s, 1566 *w*, 1494 m, 1473 s, 1444 s, 1365 m, 1314 m, 1248 m, 1099 br, s, 1027 s, 767 s, 733 m, 623 s.

X-ray crystallography

Small regularly shaped crystals of **1** and **2** were selected and mounted on fibres for preliminary study. Oscillation and Weissenberg photographs gave preliminary dimensions for monoclinic unit cells with space groups $P2_1/a$ (**1**) and $P2_1/n$ (**2**). The crystals of **1** and **2** were mounted on a two-stage fibre with RS3000 before being transferred to the diffractometer. The data were collected using a Stoe Stadi-4 four-circle diffractometer equipped with Oxford Cryosystems open flow cryostat [12]. The data were corrected for Lorentz and polarization effects; absorption corrections based on Psi-scans were applied. Crystal data, together with details of the diffraction experiment are listed in Table 3.

The structures were solved by direct methods (SIR92 [13]) and hydrogen atoms located from difference Fourier syntheses (CRYSTALS [14]). They were refined by full-matrix least-squares methods on F^2 using all data with anisotropic displacement parameters for non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms (CRYSTALS [14]). The final cycle of refinement, with

Table 3. Crystallographic data for $[Cu(phen)_2(ONO)](BF_4)\cdot H_2O$ (**1**) and $[Cu(bipy)_2(ONO)](HSO_4)$ (**2**)[a]

	1	2
Formula	$C_{24}H_{18}BCuF_4N_5O_3$	$C_{20}H_{17}CuN_5O_6S$
Formula weight (amu):	574.79	518.99
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$ (alt. $P2_1/c$ No. 14)	$P2_1/n$ (alt. $P2_1/c$ No. 14)
Cell constants		
a (Å)	12.615(4)	10.779(3)
b (Å)	11.718(2)	12.285(2)
c (Å)	15.821(2)	16.340(3)
β (°)	96.63	106.75(2)
Z	4	4
U (Å^3)	2323.0(7)	2071.9(6)
Reflections for unit cell	47	51
Range (°)	$29.2 \leqslant 2\theta \leqslant 31.4$	$24 \leqslant 2\theta \leqslant 33$
Crystal colour and shape	Emerald green block	Green wedge
Absorption corrections	Psi-scans [min TF = 0.778, max TF = 0.822]	Psi-scans [min TF = 0.545, max TF = 0.580]
Scan width (°)	1.0	1.4
Absorption coefficient, μ_{calc} (cm^{-1})	10.1	12.0
D_c (g cm^{-3})	1.644	1.664
D_m (g cm^{-3}) (bromoform/hexane)	1.69	1.64
$F(000)$	1164	1060
Crystal dimensions (mm^3)	$0.19 \times 0.24 \times 0.38$	$0.23 \times 0.27 \times 0.46$
Index ranges	$-15 \leqslant h \leqslant 15$	$-12 \leqslant h \leqslant 12$
	$0 \leqslant k \leqslant 13$	$0 \leqslant k \leqslant 14$
	$-18 \leqslant l \leqslant 18$	$-12 \leqslant l \leqslant 19$
$2\theta_{max}$ (°)	24.99	25.00
Reflections collected	5490	3942
Unique reflections	3822 (R_{int} = 0.0367)	3380 (R_{int} = 0.0577)
Number of parameters	415	366
Data/parameter ratio	9.21	9.23
Refinement method (full matrix least squares on)	F^2	F^2
ρ_{min}, ρ_{max}	−0.551, 0.530	−0.515, 0.595
$(\Delta/\sigma)_{max}$	0.0041	0.0571
Final R indices	$R = 0.0532$; $wR_2 = 0.0597$	$R = 0.0523$; $wR_2 = 0.0506$
Conventional final R indices[b]	$R = 0.0391$; $wR_2 = 0.0503$	$R = 0.0448$; $wR_2 = 0.0465$

[a] Stoe Stadi-4 four circle diffractometer, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), T = 150.0(2) K and ω-θ scans.

[b] $I > 2\sigma(I)$ for both **1** (3100 reflections) and **2** (3032 reflections).

three-parameter Chebychev weighting scheme [15] (77.1, 99.1, 22.9 for **1**; 35.0, 42.2, 8.12 for **2**), gave conventional *R* indices $[I > 2\sigma(I)]$ of 0.0391 (for **1**) and 0.0448 (for **2**). Full details of the structure solution are given in Table 3. Structure diagrams were generated using the CAMERON suite of programs [16].

Fractional atomic coordinates and atomic displacement parameters are given in the supplementary data together with a complete list of interatomic distances and angles.

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