

Copper(II) complexes of pentadentate 17-membered macrocyclic diamido-diamines with N, O or S as additional donors

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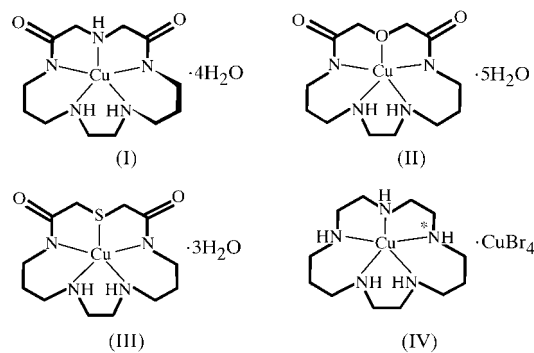
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The crystal structures of (2,6-dioxo-1,4,7,11,14-pentaazacycloheptadecanato)copper(II) tetrahydrate, [Cu(C₁₂H₂₃N₅O₂)]·4H₂O, (I), (3,16-dioxo-1-oxa-4,8,11,15-tetraazacycloheptadecanato)copper(II) pentahydrate, [Cu(C₁₂H₂₂N₄O₃)]·5H₂O, (II), and (3,16-dioxo-1-thia-4,8,11,15-tetraazacycloheptadecanato)copper(II) trihydrate, [Cu(C₁₂H₂₂N₄O₂S)]·3H₂O, (III), are reported. The coordination geometry in each case is approximately square pyramidal with two amine groups and two deprotonated amide groups in the basal plane. The apical position is occupied by an amine group, an ether O atom or a thio S atom. Trigonal distortion increases in the sequence S < O < N as apical donor. The relation between the distortion in the basal plane of the complexes and the maxima in their electronic spectra is discussed.

Comment

The coordination chemistries in aqueous solutions of 2,6-dioxo-1,4,7,11,14-pentaazacycloheptadecane (*L*¹), of 1-oxa-3,16-dioxo-4,8,11,15-tetraazacycloheptadecane (*L*²) and of 1-thia-3,16-dioxo-4,8,11,15-tetraazacycloheptadecane (*L*³) with Cu²⁺ ions have been published recently (Steenland *et al.*, 1997, 1999). The main complexes formed with the three ligands were found to be CuLH₂ complexes, *viz.* (I) with *L*¹, (II) with *L*² and (III) with *L*³; LH₂ in the three complexes indicates the twice deprotonated ligand. The electronic spectra of these CuLH₂ complexes exhibited two well defined maxima of about the same intensity, resulting in twin peaks, at 14 490 cm⁻¹ ($\epsilon = 133 M^{-1} \text{ cm}^{-1}$) and 18 520 cm⁻¹ ($\epsilon = 125 M^{-1} \text{ cm}^{-1}$) for (I), at 16 050 cm⁻¹ ($\epsilon = 157 M^{-1} \text{ cm}^{-1}$) and 19 420 cm⁻¹ ($\epsilon = 115 M^{-1} \text{ cm}^{-1}$) for (II), and at 15 400 cm⁻¹ ($\epsilon = 154 M^{-1} \text{ cm}^{-1}$) and 19 610 cm⁻¹ ($\epsilon = 150 M^{-1} \text{ cm}^{-1}$) for (III).



The band at the highest energy may be attributed for each complex to an electron transition from the d_{xy} , d_{xz} , d_{yz} group of orbitals to $d_{x^2-y^2}$, and the band at lower energy to an electron transition from d_{z^2} to $d_{x^2-y^2}$ (Hathaway & Billing, 1970; Lever, 1984). The observation that the peak at the highest energy, which reflects the in-plane ligand field strength, had the lowest value (18 520 cm⁻¹) for the strongest CuLH₂ complex, *viz.* (I), and the largest value (19 610 cm⁻¹) for the weakest CuLH₂ complex, *viz.* (III), was puzzling and not readily understood from the thermodynamic stabilities of the complexes. Moreover, the ν_{d-d} bands of the copper(II) complex of the fully saturated 1,4,7,11,14-pentazacycloheptadecane, (IV), were found at even lower wavenumbers, *viz.* 17 180 cm⁻¹ ($\epsilon = 180 M^{-1} \text{ cm}^{-1}$) and a shoulder at 11 900 cm⁻¹ ($\epsilon = 65 M^{-1} \text{ cm}^{-1}$) (Hay *et al.*, 1984). A five-coordinate square-pyramidal structure was proposed for this latter CuL complex, which was later confirmed by X-ray crystallography (Boeyens *et al.*, 1990) to be a conformer in which the nitrogen (indicated in the *Scheme* above by an asterisk) in the apical position is linked to its two neighbouring N atoms in the basal plane by an ethylene and a propylene chain, respectively. The four N atoms in the basal plane form consecutive 5–6–5-membered linked chelate rings with the copper ion.

To get a better understanding of these observations, the CuLH₂ complexes of the three title ligands were prepared and obtained in the solid state. The structures of the three complexes consist of discrete neutral CuLH₂ entities solvated by a number of water molecules [see Figs. 1, 2 and 3 for (I), (II) and (III), respectively]. The coordination geometry in each of the three complexes is square pyramidal overall, with two amine groups and two deprotonated amide groups making up the basal plane. The axial position is occupied by a fifth amine group in (I), an ether O atom in (II) and a thio S atom in (III). Each of the CuLH₂ entities forms hydrogen bonds with the water molecules through the amide O atoms and through the secondary amine groups (see Tables 2, 4 and 6 for details). In (I), the amine N–H group is also involved. Water O atoms act as both donors and acceptors with other water molecules. All hydrogen bonds combine to form an extensive three-dimensional framework. It is remarkable that only in compound (II) is there a direct hydrogen-bond contact between complex units, *via* an N71–H71···O21 hydrogen bond.

The three CuLH₂ complexes occur in the same conformation, with consecutive 6–5–6-linked chelate rings in the basal plane. The angular structural parameter τ , an index for

trigonality in these five-coordinate structures (Addison *et al.*, 1984), is 0.30 in (I), 0.16 in (II) and 0.03 in (III). The distortion from a regular square-pyramidal geometry is thus largest with a nitrogen donor and smallest with a sulfur in the axial position. The two six-membered chelate rings in the three complexes have chair conformations, distorted towards a boat and with a high puckering amplitude. Q values (Cremer & Pople, 1975) are, on average, 0.654 (5) in (I), 0.701 (5) in (II) and 0.676 (11) in (III). The conformations of the five-membered chelate rings (Duax *et al.*, 1976) are envelope with a local pseudo-mirror along C82 and the mid-point of Cu—N71 for (I) and (II), and a half-chair with a local pseudotwofold axis along Cu and the mid-point of C8A—C8B for (III). The weighted average Cu—N bond distance in the basal plane is 2.01 (2) Å in (I), 2.01 (2) Å in (II) and 2.00 (3) Å in (III). These bond lengths are appreciably shorter than in CuL complex (IV) [2.07 (6) Å; Hay *et al.*, 1984]. This is certainly due to the presence of the two negatively charged amide N atoms in the basal plane and offers an obvious explanation for the much stronger in-plane ligand field in these CuLH₂ complexes compared with the in-plane ligand field in complex (IV). Also, the difference in the sequence of the linked chelate rings is a consequence of the presence in the basal plane of the two deprotonated N atoms, which are stronger σ -donors than amine N atoms (Miyoshi *et al.*, 1983). The observed sequence of the in-plane ligand-field strength for the three CuLH₂ complexes, *viz.* (III) > (II) > (I), can now be understood from the distortion of the basal plane formed by the four independent N atoms (N31, N32, N71 and N72) in compounds (I) and (II). In (III), there is no distortion at all due to mirror symmetry in the basal plane formed by atoms N3 and N7. In fact, the largest displacement from the mean plane through atoms N31, N32, N71 and N72 is observed for N72, *viz.* 0.099 (4) Å in (II) and 0.298 (3) Å in (I), the largest value. The displacement of the Cu atom from the mean plane does not follow the same trend for the three complexes, but again the largest displacement is observed in (I) [0.203 (1) Å] compared with 0.134 (1) Å in (II) and 0.182 (1) Å in (III).

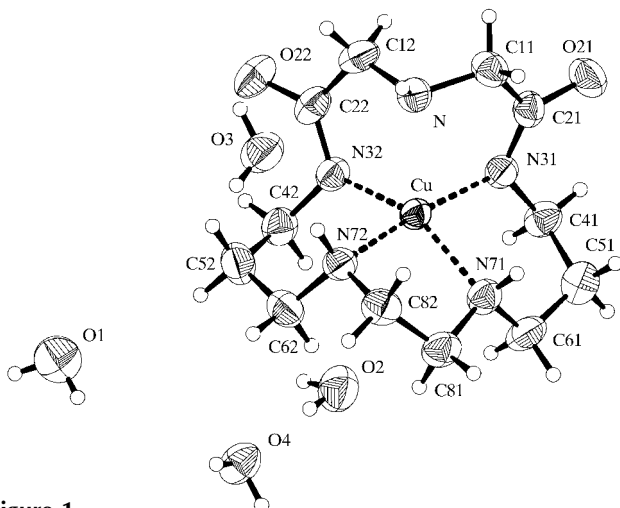


Figure 1

A view of the molecule of (I) with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

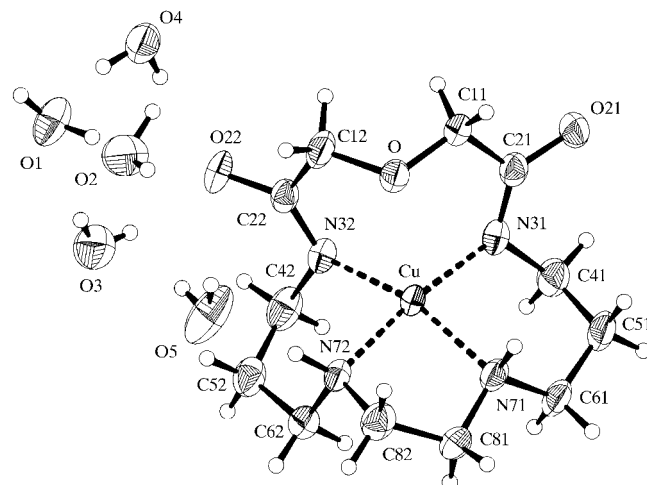


Figure 2

A view of the molecule of (II) with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

In the axial position, the nitrogen donor, which is the strongest of the three donors, produces the strongest deviation in the basal plane, resulting in the weakest in-plane ligand field. The sulfur donor with the longest Cu—S axial bond distance causes less distortion in the basal plane, resulting in the strongest in-plane ligand field. The position of the peak with the lowest energy ($d_{z^2} \rightarrow d_{x^2-y^2}$ transition) is then determined by two aspects: first, the stronger the intrinsic axial donor strength (N > S > O), the lower the energy for this transition to occur; secondly, the stronger the in-plane ligand field (N < O < S), the higher the energy for this transition. These two aspects combine and result in the lowest position of the second peak for (I) with the N atom in the axial position. Deviation of the axial donor from a position more or less perpendicular above the mid-point in the basal plane may explain the much higher molar absorptivity of this transition and the appearance of the twin peak feature in the electronic spectra of these CuLH₂ complexes.

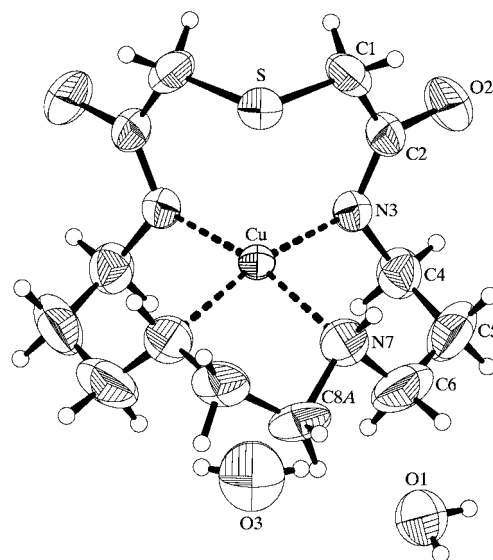


Figure 3

A view of the molecule of (III) with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Experimental

The title complexes were obtained by mixing in water at room temperature equimolar amounts of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (444.6 mg, 1.20 mmol) and the ligands L^1 (478.4 mg, 1.20 mmol), L^2 (345.9 mg, 1.20 mmol) or L^3 (455.8 mg, 1.20 mmol) in their hydrated hydrochloride form, and by adding a calculated amount of a concentrated aqueous 1.0 M KOH solution to bring the pH to 7. The solvent was then evaporated on a rotary evaporator and the solid residue taken up in ethanol. Diethyl ether was then added to the ethanol solution to precipitate most of the inorganic salts. The ethanol solution was then evaporated and the remaining solid dissolved in water. The aqueous solution was allowed to concentrate slowly. After about two weeks, crystals of the three complexes were obtained [yields: 203.6 mg (42%) for (I); 345.9 mg (68%) for (II); 300.6 mg (62%) for (III)]. Suitable crystals were selected for X-ray structure determination. Analysis found [calculated for $\text{C}_{12}\text{H}_{23}\text{CuN}_5\text{O}_2 \cdot 4\text{H}_2\text{O}$, (I), %]: C 35.3 (35.6), Cu 15.5 (15.7), N 16.9 (17.3); found [calculated for $\text{C}_{12}\text{H}_{22}\text{CuN}_4\text{O}_3 \cdot 5\text{H}_2\text{O}$, (II), %]: C 33.8 (34.0), Cu 14.8 (15.0), N 13.1 (13.2); found [calculated for $\text{C}_{12}\text{H}_{22}\text{CuN}_4\text{O}_2\text{S} \cdot 3\text{H}_2\text{O}$, (III), %]: C 35.5 (35.6), Cu 15.7 (15.7), N 13.8 (13.9). The number of solvate water molecules in each complex was determined from titrations of known amounts of the complexes in water with standardized hydrochloric acid, and is the nearest whole number value determined from the equivalence point in the titration. IR spectra (KBr pellets): ν (cm^{-1}) 3400–3200 (*br*), 1599 (*s*), 1585 (*s*), 1305 (*s*), 1100 (*s*) for (I); 3415 (*br*), 3168 (*s*), 3087 (*s*), 1599 (*s*), 1321 (*s*), 1112 (*s*) for (II); 3392 (*br*), 3226 (*br*), 1592 (*s*), 1565 (*s*), 1385 (*s*), 1041 (*s*) for (III). EPR (powders at room temperature) 34.00 GHz (*Q*-band): g_{parallel} and $g_{\text{perpendicular}}$, respectively, are 2.2170 and 2.0442 for (I), 2.2098 and 2.0469 for (II), and 2.2034 and 2.0415 for (III).

Compound (I)

Crystal data

$[\text{Cu}(\text{C}_{12}\text{H}_{23}\text{N}_5\text{O}_2)] \cdot 4\text{H}_2\text{O}$	Cu $K\alpha$ radiation
$M_r = 404.96$	Cell parameters from 41 reflections
Orthorhombic, $Pna2_1$	$\theta = 10.9\text{--}27.7^\circ$
$a = 13.3375$ (5) Å	$\mu = 1.98 \text{ mm}^{-1}$
$b = 8.9992$ (3) Å	$T = 293$ (2) K
$c = 15.5637$ (4) Å	Tablet, dark blue
$V = 1868.06$ (11) Å ³	$0.48 \times 0.40 \times 0.11 \text{ mm}$
$Z = 4$	
$D_x = 1.44 \text{ Mg m}^{-3}$	

Data collection

Siemens P4 four-circle diffractometer	$R_{\text{int}} = 0.033$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 69.1^\circ$
Absorption correction: ψ scan (XEMP; Siemens, 1989)	$h = -1 \rightarrow 16$
$T_{\text{min}} = 0.400$, $T_{\text{max}} = 0.804$	$k = -1 \rightarrow 10$
2267 measured reflections	$l = -16 \rightarrow 1$
1856 independent reflections	3 standard reflections every 100 reflections
1824 reflections with $I > 2\sigma(I)$	intensity decay: 3%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0$
$R(F) = 0.040$	$\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$
$wR(F^2) = 0.104$	$\Delta\rho_{\text{min}} = -0.54 \text{ e \AA}^{-3}$
$S = 1.11$	Extinction correction: SHELXL97
1856 reflections	Extinction coefficient: 0.0062 (5)
218 parameters	Absolute structure: Flack (1983), 138 Friedel pairs
H-atom parameters constrained	Flack parameter = 0.03 (4)
$w = 1/[\sigma^2(F_o^2) + (0.0764P)^2 + 0.2709P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (Å, °) for (I).

Cu—N31	1.980 (3)	Cu—N71	2.055 (4)
Cu—N32	1.995 (3)	Cu—N	2.281 (4)
Cu—N72	2.032 (3)		
N31—Cu—N32	100.6 (1)	N72—Cu—N71	84.3 (1)
N31—Cu—N72	171.2 (1)	N31—Cu—N	78.6 (1)
N32—Cu—N72	88.2 (1)	N32—Cu—N	80.0 (1)
N31—Cu—N71	87.8 (1)	N72—Cu—N	103.1 (1)
N32—Cu—N71	153.0 (1)	N71—Cu—N	126.9 (1)

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N—H \cdots O1 ⁱ	0.90	2.16	2.997 (6)	155
O1—H1A \cdots O3 ⁱⁱ	0.85	2.01	2.825 (5)	157
O1—H1B \cdots O21 ⁱⁱⁱ	0.85	2.07	2.910 (5)	173
O2—H2A \cdots O21 ⁱⁱ	0.85	2.12	2.955 (5)	172
O2—H2B \cdots O4	0.85	2.03	2.835 (5)	158
O3—H3A \cdots O2 ^{iv}	0.85	1.99	2.825 (6)	166
O3—H3B \cdots O22 ⁱⁱⁱ	0.85	1.89	2.732 (6)	174
O4—H4A \cdots O21 ⁱⁱⁱ	0.85	1.93	2.770 (4)	170
O4—H4B \cdots O22 ^v	0.85	1.82	2.665 (4)	176
N71—H71 \cdots O4 ⁱ	0.86	2.17	3.023 (5)	169
N72—H72 \cdots O3	0.87	2.18	3.045 (5)	174

Symmetry codes: (i) $x, 1+y, z$; (ii) $x, y-1, z$; (iii) $\frac{1}{2}+x, -\frac{1}{2}-y, z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$.

Compound (II)

Crystal data

$[\text{Cu}(\text{C}_{12}\text{H}_{22}\text{N}_4\text{O}_3)] \cdot 5\text{H}_2\text{O}$	$D_x = 1.448 \text{ Mg m}^{-3}$
$M_r = 423.96$	Mo $K\alpha$ radiation
Monoclinic, Cc	Cell parameters from 25 reflections
$a = 12.098$ (9) Å	$\theta = 20\text{--}25^\circ$
$b = 20.337$ (14) Å	$\mu = 1.17 \text{ mm}^{-1}$
$c = 8.134$ (5) Å	$T = 293$ (2) K
$\beta = 103.68$ (5)°	Prism, blue
$V = 1944$ (2) Å ³	$0.43 \times 0.29 \times 0.29 \text{ mm}$
$Z = 4$	

Data collection

Stoe Stadi-4 four-circle diffractometer	$R_{\text{int}} = 0.033$
ω scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: ψ scan (EMPIR; Stoe & Cie, 1989)	$h = -15 \rightarrow 15$
$T_{\text{min}} = 0.670$, $T_{\text{max}} = 0.710$	$k = -26 \rightarrow 2$
3348 measured reflections	$l = -2 \rightarrow 10$
3020 independent reflections	3 standard reflections frequency: 60 min
2510 reflections with $I > 2\sigma(I)$	intensity decay: 3%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0$
$R(F) = 0.043$	$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
$wR(F^2) = 0.101$	$\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$
$S = 1.04$	Absolute structure: Flack (1983), 773 Friedel pairs
3020 reflections	Flack parameter = -0.005 (18)
226 parameters	
H atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 3
Selected geometric parameters (Å, °) for (II).

Cu—N31	1.963 (4)	Cu—N71	2.056 (4)
Cu—N32	1.987 (4)	Cu—O	2.428 (4)
Cu—N72	2.017 (4)		
N31—Cu—N32	100.2 (2)	N72—Cu—N71	84.0 (2)
N31—Cu—N72	173.2 (2)	N31—Cu—O	76.2 (2)
N32—Cu—N72	85.8 (2)	N32—Cu—O	75.4 (2)
N31—Cu—N71	89.4 (2)	N72—Cu—O	108.6 (2)
N32—Cu—N71	163.9 (2)	N71—Cu—O	119.7 (2)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...O21 ^v	0.85	1.9	2.744 (6)	174
O1—H1B...O4 ^{vi}	0.85	2.06	2.865 (7)	159
O2—H2A...O22	0.85	1.91	2.762 (7)	180
O3—H3A...O22	0.85	2.06	2.863 (7)	158
O3—H3B...O1	0.85	2.13	2.862 (7)	144
O4—H4A...O22	0.85	1.99	2.839 (6)	176
O4—H4B...O2 ^{vi}	0.85	1.99	2.803 (7)	161
O5—H5A...O3	0.85	2.02	2.852 (8)	165
O5—H5B...O2 ^{vii}	0.85	1.96	2.723 (8)	149
N71—H71...O21 ^{vi}	0.90	1.96	2.858 (6)	173
N72—H72...O5	0.91	1.92	2.834 (7)	176

Symmetry codes: (v) 1 + *x*, −*y*, $\frac{1}{2}$ + *z*; (vi) *x*, −*y*, $\frac{1}{2}$ + *z*; (vii) *x*, *y*, 1 + *z*.

Compound (III)

Crystal data

[Cu(C₁₂H₂₂N₄O₂S)]·3H₂O
M_r = 403.98
 Monoclinic, *P*₂₁/*m*
a = 7.4905 (6) Å
b = 16.1160 (9) Å
c = 7.6404 (4) Å
 β = 107.553 (5)°
V = 879.38 (10) Å³
Z = 2

D_x = 1.526 Mg m^{−3}
 Cu *K*α radiation
 Cell parameters from 38 reflections
 θ = 22.0–56.0°
 μ = 3.13 mm^{−1}
T = 293 (2) K
 Prism, dark blue
 0.32 × 0.26 × 0.14 mm

Data collection

Siemens *P*4 four-circle diffractometer
 ω/2θ scans
 Absorption correction: ψ scan (*XEMP*; Siemens, 1989)
T_{min} = 0.43, *T_{max}* = 0.645
 2013 measured reflections
 1536 independent reflections
 1415 reflections with *I* > 2σ(*I*)

R_{int} = 0.050
 θ_{max} = 68.9°
h = −1 → 9
k = −19 → 1
l = −7 → 7
 3 standard reflections every 100 reflections
 intensity decay: 3%

Refinement

Refinement on *F*²
R(*F*) = 0.047
wR(*F*²) = 0.133
S = 1.07
 1536 reflections
 119 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0756*P*)² + 0.7615*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0
 Δρ_{max} = 0.41 e Å^{−3}
 Δρ_{min} = −0.61 e Å^{−3}
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0022 (8)

Table 5
Selected geometric parameters (Å, °) for (III).

Cu—N3	1.967 (3)	Cu—N7	2.042 (3)
Cu—N3 ^{viii}	1.967 (3)	Cu—S	2.6594 (13)
Cu—N7 ^{viii}	2.042 (3)		
N3—Cu—N3 ^{viii}	98.29 (15)	N7 ^{viii} —Cu—N7	84.28 (19)
N3—Cu—N7 ^{viii}	167.40 (13)	N3—Cu—S	81.37 (9)
N3 ^{viii} —Cu—N7 ^{viii}	87.76 (12)	N3 ^{viii} —Cu—S	81.37 (9)
N3—Cu—N7	87.76 (12)	N7 ^{viii} —Cu—S	110.58 (11)
N3 ^{viii} —Cu—N7	167.40 (13)	N7—Cu—S	110.58 (11)

Symmetry codes: (viii) *x*, $\frac{1}{2}$ − *y*, *z*.

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1C...O2 ^{ix}	0.85	1.93	2.749 (5)	163
O1—H1D...O2 ^x	0.85	2.05	2.813 (5)	148
O3—H3...O1	0.85	2.15	2.932 (4)	152
N7—H7...O1 ^{xi}	0.91	2.14	3.040 (5)	173
N7—H71...O1 ^{xi}	0.91	2.2	3.040 (5)	155

Symmetry codes: (ix) −*x*, −*y*, 1 − *z*; (x) 1 + *x*, *y*, 1 + *z*; (xi) *x*, *y*, *z* − 1.

The coordinates of the water H atoms in the three title compounds were calculated using the program *HYDROGEN* (Nardelli, 1999) and were introduced in the refinements keeping the O—H distances and the H—O—H angles constrained. All other H atoms were treated as riding, with C—H distances of 0.97 Å and N—H distances in the range 0.85–0.90 Å. The structure of (III) has pseudosymmetry, with a mirror plane through atoms Cu, S and O3 for all atoms except C8A and C8B. The pseudosymmetry resulted in high correlation factors and poor convergence on refinement in space group *P*₂₁. Therefore, the structure was refined in the centrosymmetric space group *P*₂₁/*m* with a disorder model for C8A/C8B. The structure of (III) was refined with three solvate water molecules, in accord with the chemical analysis, although the occupancy of water atom O3 refined from the initial value of 0.5 to 0.385. The occupancy of the other O atom (O1) did not change from the initial value of 1 when it was refined, so it was fixed at 1.

For compounds (I) and (III), data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *REDUCE* in *XSCANS*. For compound (II), data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992). For all compounds, program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1585). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

- Altomare, A., Cascarano, G., Giacobozzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Bergerhoff, G. (1996). *DIAMOND*. Gerhard-Domagk-Straße 1, 53121 Bonn, Germany.
- Boeyens, J. C. A., Dobson, S. M. & Oosthuizen, E. B. (1990). *J. Crystallogr. Spectrosc. Res.* **20**, 407–413.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Duax, W. L., Weeks, C. M. & Roher, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by E. L. Eliel & N. Allinger, pp. 271–383. New York: John Wiley.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hathaway, B. J. & Billing, D. E. (1970). *Coord. Chem. Rev.* **5**, 143–207.
- Hay, R. W., Bembli, R., McLaren, F. & Moodie, W. T. (1984). *Inorg. Chim. Acta*, **85**, 23–31.
- Lever, A. B. P. (1984). Editor. *Inorganic Electronic Spectroscopy*, 2nd ed., pp. 568–569. Amsterdam: Elsevier.
- Miyoshi, K., Tanaka, H., Kimura, E., Tsuboyama, S., Murata, S., Shimizu, H. & Ishizu, K. (1983). *Inorg. Chim. Acta*, **78**, 23–30.
- Nardelli, M. (1999). *J. Appl. Cryst.* **32**, 563–571.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1989). *XEMP*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Steenland, M. W. A., Dierck, I., Herman, G. G., Devreese, B., Lippens, W., Van Beeumen, J. & Goeminne, A. M. (1997). *J. Chem. Soc. Dalton Trans.* pp. 3637–3642.
- Steenland, M. W. A., Westbroek, P., Dierck, I., Herman, G. G., Lippens, W., Temmerman, E. & Goeminne, A. M. (1999). *Polyhedron*, **18**, 3417–3424.
- Stoe & Cie (1992). *DIF4* (Version 7.09), *REDU4* (Version 7.03) and *EMPIR* (Version 1.03). Stoe & Cie, Darmstadt, Germany.