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Inorganica Chimica Acta 348 (2003) 143–149

Inorganica Chimica Acta

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Copper(II) nitrite complexes of tripodal ligands derived from 1,1,1-tris(2-pyridyl)methylamine

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Received 6 September 2002; accepted 18 November 2002

Abstract

Copper nitrite complexes of stoichiometric formulae $[Cu(NO_2)_nL]$ ($n = 1$ or 2), where L is a Schiff base or amide derivative of 1,1,1-tris(2-pyridyl)methylamine, have been prepared and characterized. The crystal structures of the mononuclear Schiff base complex $[Cu(NO_2)_2(tpmbz)]$ $[tpmbz = (C_5H_4N)_3CN{=}CHC_6H_5]$, the nitrite-bridged dinuclear Schiff base complex $[\{Cu(NO_2)(tpmsal)\}_2]\cdot Et_2O$ $[tpmsalH = (C_5H_4N)_3CN{=}CHC_6H_4OH\text{-}2]$ and the polymeric amide complex $[\{Cu(NO_2)(tpms)\}_n]\cdot nH_2O$ $[tpmsH = (C_5H_4N)_3CNHC(O)CH_2CH_2CO_2H]$ are reported.

Keywords: Copper; Crystal structures; Nitrite; Schiff bases; Tripodal ligands

1. Introduction

Catalysis by molecular transition metal complexes requires supporting ligands which are sufficiently robust to mediate a variety of chemical processes without degradation, yet also versatile and capable of modification. We have recently developed a new class of tripodal ligand based on 1,1,1-tris-(2-pyridyl)methylamine (tpm) which fulfils these requirements [1]. In particular, we have examined the coordination chemistry of tpm and its derivatives with copper, inspired by the importance of copper enzymes in which the active site Cu is ligated by three histidines, especially nitrite reductase [2]. Our earlier studies showed that these ligands produce a considerable variety of copper complexes, in which the metal is coordinated by two or three of the pyridine rings, and sometimes in the case of tpm itself by the amino group also. In this paper we report the extension of this work to the preparation and characterization of copper nitrite complexes of ligands derived from tpm in which the primary amino group has been derivatised to Schiff base and amide functions.

2. Results and discussion

The ligands used in this study are illustrated in Scheme 1. Reaction of $Cu(NO_2)_2$, prepared in situ from $CuSO_4$ or $Cu(OAc)_2$ and $NaNO_2$, with these amide or Schiff base derivatives gave the corresponding copper nitrite complexes. The formulae, analytical and solution conductivity data for the complexes are given in Table 1. Two nitrito ligands were retained for the complexes of the non-ionizable ligands tpml, tpma and tpmbz (**1**, **2** and **3** respectively), whereas for the ligands containing acidic functional groups LH, namely tpmsalH and tpmsH, complexes **4** and **5**, of stoichiometric formulae $[Cu(NO_2)(L)]$, were obtained. All of the complexes are non-electrolytes in acetonitrile solution, showing that the nitrito ligands are in all cases coordinated to the metal. As well as determining the number of nitrito ligands in each complex, the organic ligand has a marked influence on the solubilities of the individual complexes; for example, the tpml complex **1** is soluble in dichloromethane and acetonitrile but not in

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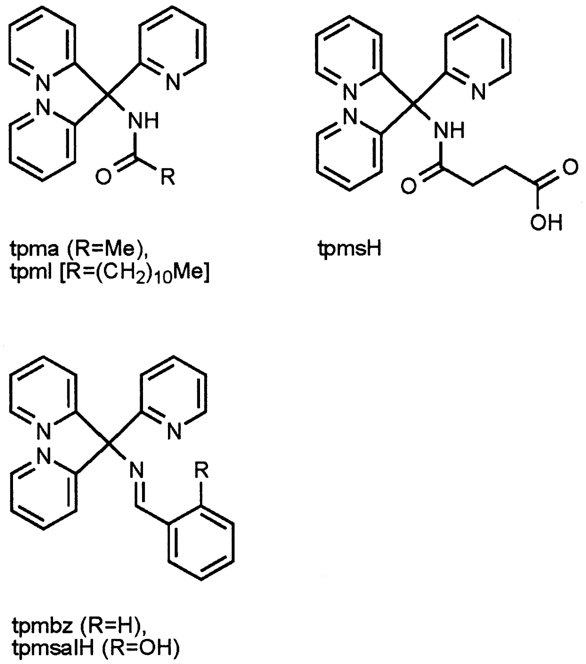
doi:10.1016/S0020-1693(02)01487-1



Scheme 1.

methanol or water, a pattern more usually associated with copper(I) complexes. The Schiff base complex **3** appears to be quite stable in solution, in contrast to the sulfato complex [Cu(SO_4)(tpmbz)], which we were unable to isolate in pure form; this species decomposes readily via hydrolysis of the Schiff base to give [Cu(SO_4)(tpm)(H_2O)] plus benzaldehyde [1b].

The X-ray crystal structures of complexes **3**, **4** and **5** have been obtained, and principal molecular dimensions are collated in Table 2. Complex **3** has the simplest structure, consisting of discrete molecules of [Cu(NO_2)$_2$(tpmbz)], Fig. 1. Both nitrito ligands are coordinated through a single O atom, though there is disorder in both. Thus, the nitrito ligand denoted by atoms 51–54 in Fig. 1 binds at either of two coordination sites, as O(51)–N(52)–O(53) or as O(54)–N(53)–O(52). The second nitrito ligand adopts several orientations, coordinated through either O(61a) or O(61b). In all cases, the Cu is five-coordinate with a square-pyramidal geometry; the apical atoms are N(11) or N(31) of the tpmbz ligand. This is coordinated to the metal via its three pyridine rings in a *fac* pattern, similar to the majority of complexes of tpm and its derivatives [1]. The imino nitrogen in complex **3** is not involved in coordination. However, the inclusion of a phenolic sidechain in the Schiff base, as in tpmsalH, results in the coordination of both the imine nitrogen and the deprotonated phenol oxygen to give complex **4**. The X-ray crystal structure of this complex, Fig. 2, shows it to be a dimer, in which the square-pyramidal coordination sphere around the copper is achieved by means of bridging nitrite groups. The tpmsal$^-$ ligand is still three-coordinate (in *mer* form, occupying three of the square base sites), with two of the pyridine rings distant from the metal. Thus, although molecular models suggest that tpmsal$^-$ could adopt a somewhat strained tetradentate coordination mode, in practice this is less favourable than completion of the coordination sphere by nitrite bridging.

Use of all three pyridine nitrogens as well as the carboxylate sidechain of the carboxylic acid derivative tpmsH is achieved in complex **5** (Fig. 3); this complex forms an infinite polymer in the solid state, in which individual tpms$^-$ ligands span two copper atoms, providing a tris-pyridyl donor set to the first and a carboxylato group to the second. Complex **5** is insoluble in organic solvents, including DMF, but does dissolve in hot water. Moreover, freshly-prepared solutions of the complex in alcohol/water mixtures are stable for several days. The X-ray crystal structure of **5** shows that the nitrite is coordinated via a single oxygen atom. The $NHCOCH_2CH_2CO_2^-$ arm in complex **5** shows an interesting difference from that in [Cu(tpms)$_2$], whose crystal structure we described previously [1b]; whereas the latter is close to the ideal all-*trans* planar arrangement, in complex **5** there is disorder in this group but in the major component (86% occupancy), the three C-C bonds of the arm have *gauche* torsion angles, of 72.5(5),

Table 1
Colours, conductivities and microanalytical data[a] for the complexes

Complex	Colour	Λ_M [b]($S\ cm^2\ mol^{-1}$)	Analysis (%)		
			C	H	N
1 [Cu(NO_2)$_2$(tpml)]	green	11	55.6 (56.0)	6.0 (6.0)	13.6 (14.0)
2 [Cu(NO_2)$_2$(tpma)]·0.5H_2O	green	6	46.0 (46.1)	3.5 (3.7)	17.8 (17.9)
3 [Cu(NO_2)$_2$(tpmbz)]	green	5	54.5 (54.6)	3.6 (3.6)	16.7 (16.6)
4 [{Cu(NO_2)(tpmsal)}$_2$]·3H_2O	green	6	55.0 (55.0)	3.7 (4.0)	13.5 (14.0)
5 [Cu(NO_2)(tpms)]·1.5H_2O	turquoise	53 [c]	48.5 (48.2)	4.0 (4.0)	14.0 (14.1)

[a] Calculated values in parentheses. Note that differences in solvent of crystallization compared to Table 3 arises from the different conditions used in the X-ray crystallization experiments.

[b] In MeCN unless stated otherwise. Accepted range [6] for a 1:1 electrolyte in MeCN is 120–160 S cm^2 mol^{-1}.

[c] Complex poorly soluble in neat MeCN; measurement done in MeCN+20% H_2O.

Table 2
Selected molecular dimensions in complexes **3**, **4** and **5** (bond lengths (Å) and bond angles (°); e.s.d.'s are in parentheses)

Complex **3**		Complex **4**		Complex **5**	
Bond lengths					
Cu–N(11)	2.138(3)	Cu–O(1)	1.871(7)	Cu–N(11)	2.022(3)
Cu–N(21)	2.034(3)	Cu–N(3)	1.925(8)	Cu–N(21)	2.007(3)
Cu–N(31)	2.080(3)	Cu–N(332)	1.970(9)	Cu–N(31)	2.220(3)
Cu–O(51)	2.022(4)	Cu–O(41)	2.002(8)	Cu–O(441$^{\mathrm{II}}$)	2.738(4)
Cu–O(54)	1.83(2)	Cu–O(41$^{\mathrm{I}}$)	2.524(9)	Cu–O(442$^{\mathrm{II}}$)	1.958(4)
Cu–O(61a)	2.033(11)	Cu–O(51)	1.984(3)	Cu–O(44a$^{\mathrm{II}}$)	2.08(3)
Cu–O(61b)	1.953(8)			Cu–O(44b$^{\mathrm{II}}$)	2.47(3)
Bond angles					
N(21)–Cu–N(11)	85.04(12)	O(1)–Cu–N(3)	94.1(4)	N(21)–Cu–N(11)	85.72(11)
N(31)–Cu–N(11)	87.68(11)	O(1)–Cu–N(332)	174.7(4)	N(11)–Cu–N(31)	88.77(10)
O(51)–Cu–N(11)	100.62(14)	O(1)–Cu–O(41)	88.0(3)	O(442$^{\mathrm{II}}$)–Cu–N(11)	169.23(13)
O(54)–Cu–N(11)	165.0(4)	O(1)–Cu–O(41$^{\mathrm{I}}$)	91.4(3)	O(51)–Cu–N(11)	86.59(11)
O(61a)–Cu–N(11)	90.1(4)	N(3)–Cu–N(332)	83.6(4)	N(21)–Cu–N(31)	84.36(11)
O(61b)–Cu–N(11)	112.9(3)	N(3)–Cu–O(41)	177.8(4)	O(442$^{\mathrm{II}}$)–Cu–N(21)	95.37(13)
N(21)–Cu–N(31)	86.57(11)	N(3)–Cu–O(41$^{\mathrm{I}}$)	105.2(3)	O(51)–Cu–N(21)	171.94(11)
O(51)–Cu–N(21)	92.81(14)	N(332)–Cu–O(41)	94.3(3)	O(442$^{\mathrm{II}}$)–Cu–N(31)	101.99(12)
O(54)–Cu–N(21)	97.1(4)	N(332)–Cu–O(41$^{\mathrm{I}}$)	93.7(3)	O(51)–Cu–N(31)	97.90(11)
O(61a)–Cu–N(21)	169.8(4)	O(41)–Cu–O(41$^{\mathrm{I}}$)	75.3(4)	O(442$^{\mathrm{II}}$)–Cu–O(51)	91.74(12)
O(61b)–Cu–N(21)	161.2(3)			N(11)–Cu–O(44a$^{\mathrm{II}}$)	113.7(7)
O(51)–Cu–N(31)	171.59(14)			N(21)–Cu–O(44a$^{\mathrm{II}}$)	92.9(7)
O(54)–Cu–N(31)	107.2(4)			O(44a$^{\mathrm{II}}$)–Cu–N(31)	157.1(7)
O(61a)–Cu–N(31)	102.1(4)			O(51)–Cu–O(44a$^{\mathrm{II}}$)	88.0(7)
O(61b)–Cu–N(31)	88.7(2)				
O(51)–Cu–O(61a)	79.3(3)				
O(61b)–Cu–O(51)	89.2(2)				
O(54)–Cu–O(61a)	85.4(5)				
O(54)–Cu–O(61b)	67.0(5)				
Proposed hydrogen bonding in complex ***5***					
D–H···A	D–H	H···A	D···A	D–H···A	
N(1)–H(1)···O(53$^{\mathrm{III}}$)	0.68(4)	2.43(4)	3.018(4)	146(4)	
O(6)–H(6a)···O(442$^{\mathrm{IV}}$)	0.93(5)	2.08(5)	2.986(6)	163(4)	
O(6)–H(6a)···O(44b$^{\mathrm{IV}}$)	0.93(5)	1.70(6)	2.57(3)	154(5)	
O(6)–H(6b)···O(41$^{\mathrm{V}}$)	1.10(9)	1.93(9)	3.022(5)	171(7)	

Symmetry operations: in complex **4**, I: $1-x$, $-y$, $-z$; in complex **5**, II: x, $1/2-y$, $z+1/2$; III: $1/2-x$, $1/2+y$, z; IV: $1/2-x$, $1-y$, $1/2+z$; V: $-x$, $1-y$, $1-z$.

62.4(5) and 84.2(5)/−96.7(5)° for the NCCC, CCCC and the two CCCO angles, respectively. This most likely results from the packing requirements of the polymer; the sidechain is effectively coiled up to minimise the overall length of the ligand. The minor component [with alternative sites for C(43), O(441) and O(442)] is coiled differently, with corresponding torsion angles of 122.8(12), −38(2) and 149(2)/−11(3)°. Due to this disorder in the tpms tail group in complex **5**, the carboxylate group coordinates the next copper atom in the polymeric chain in two distinct ways: the major component has the arrangement shown in Fig. 3, but in the remainder, the short Cu–O bond Cu–O(44a$^{\mathrm{II}}$) is *trans* to N(31) and the second carboxylate oxygen atom O(44b$^{\mathrm{II}}$) is 2.47(3) Å from the copper and *trans* to N(11). There is a rather weak hydrogen bond from the amide N–H to O(53) of an adjacent nitrite group, and there are stronger bonds from the solvent water (whose hydrogen atoms were located and refined) to the amide oxygen atom O(41) and a carboxylate oxygen [in either major O(442) or minor O(44b) orientation] in neighbouring molecules; a rather wavy hydrogen-bonded sheet is thus formed normal to the *b* axis. The polymer chain zigzags between the sheets along the *c* axis to create a rigid three-dimensional structure.

The UV–Vis spectra of all five complexes show a weak copper(II) d–d band at 600–650 nm (see Section 4). In addition, all of these nitrito complexes show a band at 360–380 nm; however the assignment of this band to nitrite must be treated with caution since the spectra of some related non-nitrito complexes also show a shoulder at 336–382 nm, probably associated with charge transfer [1]. The nitrite ligands generally give medium intensity bands in the IR spectra of these complexes, which could only be assigned with certainty by isotopic substitution. The spectrum of the Schiff base

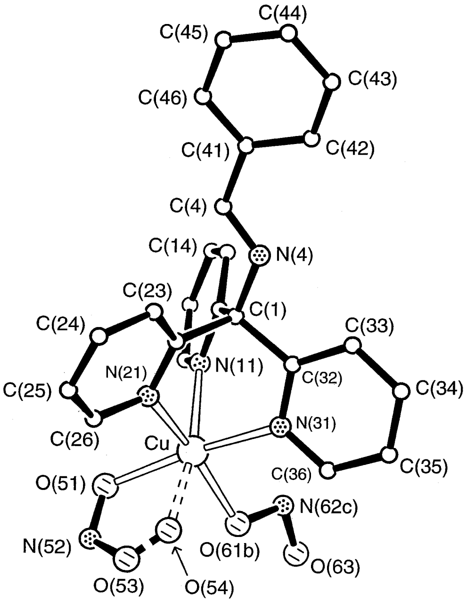


Fig. 1. One molecule of [Cu$(NO_2)_2$(tpmbz)] (**3**) showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity (as in all the figures). There is disorder in both nitrito ligands: one ligand is bound principally through O(51) but, in ca. 19% of sites, alternatively through O(54); the ligand of O(61), N(62), O(63) is found in several conformations.

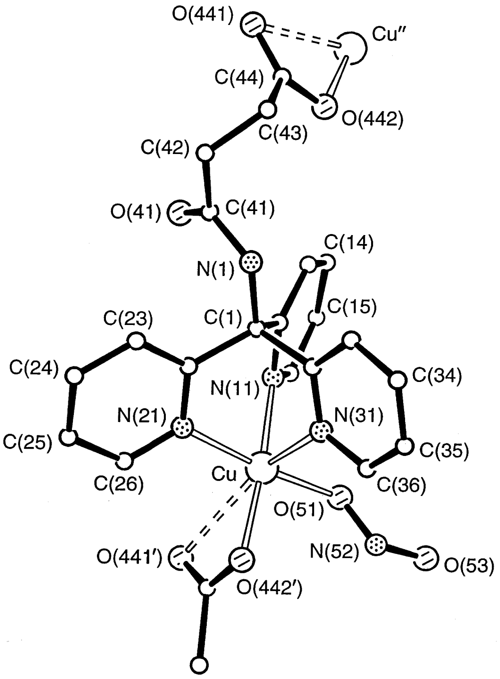


Fig. 3. One complex molecule in [{Cu(NO_2)(tpms)}$_n$]·n(H_2O) (**5**) in a polymer chain. There is disorder in the carboxylate tail; the principal arrangement is shown here.

complex **3** was clearest and gave bands assigned to the ^{14}N nitrito group at 1377 [ν(N=O)] and 1146 [ν(NO)] cm^{-1}, shifted to 1348 and 1123 cm^{-1}, respectively, for the ^{15}N isotopomer. These are consistent with nitrito (Cu–O) rather than the nitro (Cu–N) coordination of the NO_2^- ligands [3]. The absence of a δ(ONO) mode at approximately 840–890 cm^{-1} suggests that the nitrito ligands are monodentate, consistent with the X-ray crystal structure (Fig. 1). The tpma complex **2** gave a similar ν(N=O) band at 1383 and 1367 cm^{-1} for the ^{14}N and ^{15}N isotopomers, respectively, but the lower frequency band could not be assigned with certainty, even with isotopic labelling, due to the presence of a number of other bands in this region. The other nitrite com-

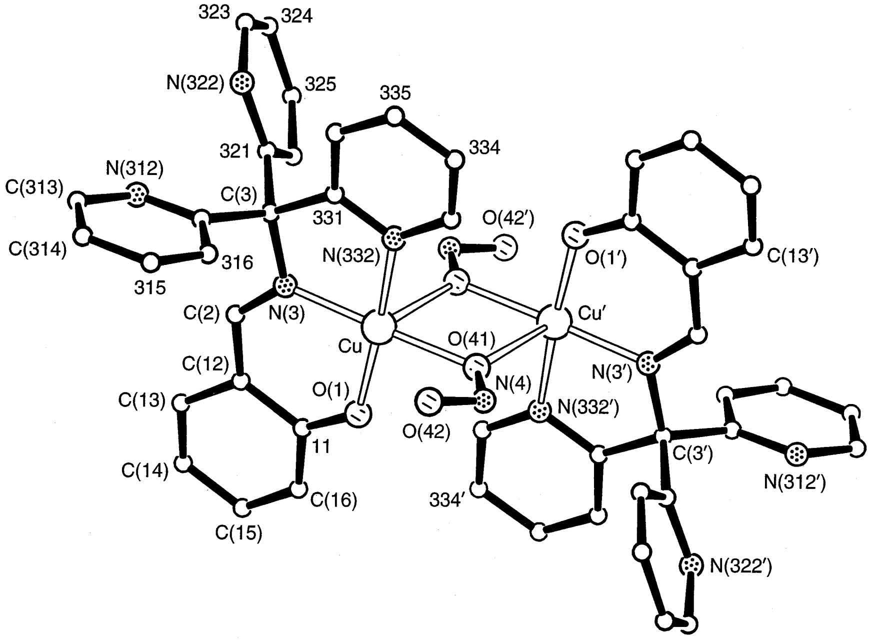


Fig. 2. The Cu-complex molecule in [{Cu(NO_2)(tpmsal)}$_2$]·Et_2O (**4**) in which the dimer lies about a centre of symmetry. Atoms labelled ‘n’ represent the carbon atoms C(n).

plexes show similar spectroscopic features, suggesting that in all these complexes nitrite is coordinated through a single oxygen. The same was observed for the related complex [Cu(NO$_2$)(tepa)]PF$_6$ (tepa = tris[2-(2-pyridyl)ethyl]amine) [4], whilst for [Cu(NO$_2$)(tpa)]PF$_6$ (tpa = tris[2-(2-pyridyl)methyl]amine) both nitrito and nitro forms were observed in solution and characterized by X-ray crystallography in the solid state [5].

3. Conclusions

Five new complexes of general formula [Cu(NO$_2$)$_n$L], where L is a Schiff base or amide derivative of 1,1,1-tris(2-pyridyl)methylamine (tpm) and $n = 1$ or 2, have been prepared and characterized, three of them by X-ray crystallography. The number of nitrito ligands and the donor set employed by the organic ligand are determined by the nature of the group used to derivatise the tpm. The present system also suggests that judicious substitutions at the six-positions of the pyridine rings might allow control of the mode of nitrite binding through internal hydrogen bonding or electrostatic effects and this is being investigated further. Complex **5** has a number of attributes which are of interest in the context of nitrite reductase; the copper coordination sphere of three pyridine nitrogens and two O-bound ligands approaches the biologically characterised type 2 copper site, involving three histidine nitrogens and a single O-bound nitrite. The linkage of copper centres in the polymeric structure of **5** is particularly interesting as it can be viewed as a first step towards building redox-linked, differentiated copper centres, as found in the enzyme [1].

4. Experimental

4.1. Synthesis

Commercially available reagents and solvents were purchased from standard suppliers. Acetonitrile was distilled from CaH$_2$ under N$_2$ before use. Infrared (400–5000 cm^{-1}, Nujol mulls) and UV–Vis (200–800 nm) spectra were recorded using Shimadzu FTIR-8300 and UV-2101 PC spectrophotometers respectively. Solution conductivities were obtained using a Portland Electronic conductivity meter. Microanalyses were determined by Mr. A. Saunders (University of East Anglia).

4.2. Preparation of [Cu(NO$_2$)$_2$(tpml)] (1)

A solution of CuSO$_4$·5H$_2$O (0.11 g, 0.45 mmol) plus NaNO$_2$ (0.1 g, 1.5 mmol) in water (5 cm^3) was added to a stirred solution of tpml (0.2 g, 0.45 mmol) in EtOH (20 cm^3). The mixture was stirred for 20 min, then filtered; the solid was washed with EtOH and dried in vacuo, then recrystallized from acetone as [Cu(NO$_2$)$_2$(tpml)] **1** (0.12 g, 44%). IR (KBr disc): 3385m (NH), 2926s, 2855m, 1695s (amide I), 1597m (py ring), 1508m, 1468s, 1437s, 1379m (NO$_2$), 1269w, 1163m (NO$_2$), 1136w, 1053m, 789m, 756m, 660m and 579w cm^{-1}. UV (MeCN): 626 (ε 121), 376 (ε 1750) and 265 nm (ε 15600).

4.3. Preparation of [Cu(NO$_2$)$_2$(tpma)] (2)

Following the same procedure as for **1** but using tpma rather than tpml gave [Cu(NO$_2$)$_2$(tpma)]·0.5H$_2$O **2** (37% yield). IR (KBr disc): 3377m (NH), 1697s (amide I), 1597 (py ring), 1466s, 1437s, 1383m (NO$_2$), 1269m, 1165w, 1140w, 1085m, 1061m, 1015w, 775m, 756m, 669m and 556m cm^{-1}. UV (MeCN): 637 (ε 59), 377 (ε 1680) and 264 nm (ε 15900).

4.4. Preparation of [Cu(NO$_2$)$_2$(tpmbz)] (3)

Use of the same procedure as for **1** but using tpmbz rather than tpml gave [Cu(NO$_2$)$_2$(tpmbz)] **3** (25% yield). IR (KBr disc): 3080w, 1641s (C=N), 1601m (Ph ring), 1582m (py ring), 1460s, 1441s, 1377m (NO$_2$), 1146s (NO$_2$), 1059m, 1024m, 853w, 773m, 758m, 692m, 658m, 573w, 557w and 523w cm^{-1}. UV (MeCN): 648 (ε 70), 382 (ε 2040) and 263 nm (ε 42900).

4.5. Preparation of [{Cu(NO$_2$)(tpmsal)}$_2$] (4)

Cu(OAc)$_2$·H$_2$O (0.15 g, 0.75 mmol) was dissolved in warm EtOH (8 cm^3) and the solution was added to a suspension of tpmsalH (0.275 g, 0.75 mmol) in hot EtOH (10 cm^3) with stirring. The resulting dark green solution was allowed to cool to room temperature. A solution of NaNO$_2$ (0.145 g, 1.5 mmol) in H$_2$O (2.5 cm^3) was added, whereupon a solid began to precipitate almost immediately. The mixture was allowed to stand for 30 min at room temperature, then the solid was filtered off and washed with Et$_2$O (5 cm^3) and air-dried as [{Cu(NO$_2$)(tpmsal)}$_2$] **4** (0.283 g, 80%). IR (Nujol mull): 1606s (C=N), 1583m, 1569m, 1532m, 1378s (NO$_2$), 1149m (NO$_2$), 1105m, 1041m, 759s, 662m and 556m cm^{-1}. UV (MeCN): 605 (ε 328), 382 (ε 18400) and 269 nm (ε 73000).

4.6. Preparation of [{Cu(NO$_2$)(tpms)}$_n$] (5)

tpmsH (0.20 g, 0.55 mmol) was dissolved in a mixture of EtOH (15 cm^3) plus water (5 cm^3). A solution of [Cu$_2$(OAc)$_4$(H$_2$O)$_2$] (0.11 g, 0.28 mmol) in water (5 cm^3) was added and the solution was stirred for 10 min. Aqueous NaNO$_2$ (0.084 g, 1.21 mmol) was added, and the green solution was stirred for 5 h. The resulting precipitate was filtered off, washed with EtOH, and dried in vacuo as $[\{Cu(NO_2)(tpms)\}_n]\cdot nH_2O$ **4** (0.23 g, 87%). IR (KBr disc): 3526m, 3452m, 3304m, 1690s (amide I), 1612s (CO_2), 1535m, 1466m, 1441m, 1396m, 1383m (NO_2), 1275m, 1196w, 1121s, 1024w, 876w, 787m, 779m, 756m, 662m, 586w and 436w cm^{-1}. UV ($MeCN+20\%H_2O$): 644 (ε 35), 361sh (ε 250) and 266 nm (ε 16400).

4.7. Crystal structure analyses

The crystal structure analysis of $[Cu(NO_2)_2(tpmbz)]$ **3**, is described here; the procedures for the other complexes were similar. Crystallographic and refinement data for the three complexes are collected in Table 3.

Crystals of **3** were dark green needles. One, ca. 0.46 × 0.11 × 0.10 mm^3, was mounted on a glass fibre. After preliminary photographic examination, this was transferred to an Enraf–Nonius CAD4 diffractometer (with monochromated Mo Kα radiation), at room temperature, for determination of accurate cell parameters (from the settings of 24 reflections, $\theta = 10–11°$, each centred in four orientations) and measurement of diffraction intensities. During processing, corrections were applied for Lorentz-polarisation effects, slight crystal deterioration, absorption (by semi-empirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). The structure was determined by the direct methods routines in the SHELXS program [7] and refined by full-matrix least-squares methods, on F^2 values, in SHELXL [8]. The Cu atom and all the non-hydrogen atoms in the tpmbz ligand were refined with anisotropic thermal parameters; the U_{iso} values of the hydrogen atoms, included in idealised positions, were also refined freely. There is disorder in both the nitro

Table 3
Crystal and structure refinement data for complexes, **3**, **4** and **5**

Complex	$[Cu(NO_2)_2(tpmbz)]$ (**3**)	$[\{Cu(NO_2)(tpmsal)\}_2]\cdot Et_2O$ (**4**)	$[\{Cu(NO_2)(tpms)\}_n]\cdot nH_2O$ (**5**)
Elemental formula	$C_{23}H_{18}CuN_6O_4$	$C_{46}H_{34}Cu_2N_{10}O_6\cdot C_4H_{10}O$	$C_{20}H_{17}CuN_5O_5\cdot H_2O$
Formula weight	506.0	1024.0	488.9
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (equiv. to no. 14)	*Pbca* (no. 61)
Unit cell dimensions			
a (Å)	13.937(2)	13.326(6)	14.5745(13)
b (Å)	9.0701(9)	10.980(6)	17.292(2)
c (Å)	18.560(2)	16.656(12)	15.456(2)
α (°)	90	90	90
β (°)	109.495(9)	111.28(5)	90
γ (°)	90	90	90
V (Å^3)	2211.6(4)	2271(2)	3895.2(7)
Z	4	2	8
D_{calc} (Mg m^{-3})	1.520	1.50	1.668
$F(000)$	1036	1056	2008
Absorption coefficient (mm^{-1})	1.03	1.00	1.174
Crystal colour, shape	dark emerald green needles	dark green translucent prisms	deep blue and turquoise prisms
Crystal size (mm^3)	0.46 × 0.11 × 0.10	0.33 × 0.24 × 0.21	0.31 × 0.17 × 0.14
θ Range for data collection (°)	1.5–27.0	1.5–24.0	2.2–27.0
Index ranges for *h*, *k*, *l*	−1/17, −1/11, −23/23	−1/15, −1/12, −19/19	0/18, 0/22, 0/19
Crystal degradation (%)	1.7	4.3	0
Max. and min. transmission	0.998 and 0.978	0.256 and 0.181	0.15 and 0.13
Total no. of reflections measured (not including absences)	5387	3760	4232
R_{int} for equivalents	0.013	0.073	
Total no. of unique reflections	4817	3554 (2780 to $\theta_{max} = 22°$)	4232
No. of observed reflections ($I > 2\sigma(I)$)	2502	1520 (1411 to $\theta_{max} = 22°$)	2610
Structure determined by	direct methods	direct methods	automated Patterson methods
Data/restraints/parameters	4817/0/333	2780/0/322	4232/0/378
Goodness-of-fit on F^2, *S*	1.073	1.006	1.019
Final *R* indices (observed data)	$R_1 = 0.049$, $wR_2 = 0.111$	$R_1 = 0.086$, $wR_2 = 0.209$	$R_1 = 0.043$, $wR_2 = 0.095$
Final R indices (all data)	$R_1 = 0.102$, $wR_2 = 0.140$	$R_1 = 0.142$, $wR_2 = 0.274$	$R_1 = 0.078$, $wR_2 = 0.117$
Reflections weighted [a]	$w = [\sigma^2(F_o^2)+(0.0554P)^2]^{-1}$ [a]	$w = [\sigma^2(F_o^2)+(0.1660P)^2]^{-1}$	$w = [\sigma^2(F_o^2)+(0.0515P)^2]^{-1}$
Largest difference peak and hole (e Å^{-3})	0.43 and −0.41	0.83 and −1.29	0.54 and −0.50
Location of largest difference peak	amongst the disordered NO_2 groups	close to the Cu atom	close to Cu atom

[a] Where $P = (F_o^2+2F_c^2)/3$.

groups; some atoms in these ligands were refined with partial occupancies and isotropic thermal parameters. Scattering factors for neutral atoms were taken from Ref. [9]. Computer programs used in this analysis have been noted above or in Ref. [10], Table 4, and were run on a DEC-AlphaStation 200 4/100 in the Nitrogen Fixation Laboratory, John Innes Centre.

In the analysis of complex **4**, an unresolved region of electron density about a centre of symmetry in the crystal is believed to result from disordered solvent molecules, probably diethyl ether; seven peaks were included in the refinement as carbon part-atoms.

Acknowledgements

We thank the BBSRC for financial support for this work, and EPSRC for a ROPA award (to support P.C.S. and P.J.A.).

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