

Stepwise construction of mono-, di- and tri-nuclear 2 : 1, 1 : 2, 2 : 3 ligand : mixed-metal complexes using a bis-tridentate bridging ligand

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Extended molecular structures have been constructed with the bis-tridentate ligand *N,N,N',N'*-tetrakis(2-pyridylmethyl)benzene-1,4-diamine (tpbd), and the bis-tridentate, metal 'complex' ligand, [Ru(tpbd)₂](PF₆)₂ (**1**) as building blocks. The ligand tpbd and complex **1** react analogously with Cu(II) salts to yield the corresponding di- and tri-nuclear aqua complexes, [Cu₂(tpbd)(H₂O)₄](ClO₄)₄ (**2a**) and [Cu₂Ru(tpbd)₂(H₂O)₄](BF₄)₄(PF₆)₂·2H₂O (**3a**). The labile water ligands in these complexes have been replaced by other solvents or 2,2'-bipyridine (bipy). In the latter case the mixed ligand complexes [Cu₂(tpbd)(bipy)₂](PF₆)₄·H₂O (**2b**) and [Cu₂Ru(BF₄)₂(tpbd)₂(bipy)₂](PF₆)₄·2H₂O (**3b**) respectively are obtained. These reactions represent prototype substitutions for the controlled stepwise evolution of even larger molecular entities. Recrystallisation of **3a** in 2% NaBF₄ methanol/water solution, resulted in crystals of [Cu₂Ru(tpbd)₂(H₂O)₄](BF₄)₄(PF₆)₂·8H₂O (**3a'**). Recrystallisation of **3b** in 2% NaBF₄ CH₃CN/water solution gave [Cu₂Ru(BF₄)₂(tpbd)₂(bipy)₂](BF₄)₂(PF₆)₂·H₂O (**3b'**). The X-ray structures of the mononuclear and trinuclear ruthenium-containing complexes (**1**, **3a'**, **3b'**) show *cis-fac* six-coordinate geometries around the Ru atoms. As a consequence the phenylene groups of the tpbd ligands are approximately perpendicular to each other. In the trinuclear Ru–Cu₂ complexes the copper atoms are located *anti* to each other about the [(tpbd)Ru(tpbd)]²⁺ building block. The flexibility of tpbd is demonstrated by the geometries of the copper coordinated ends of tpbd, which are coordinated meridionally in **3a'**, but facially in **3b'**. Solution spectroscopy, and the detection of appropriate ions by mass spectrometry, show that the dicopper and trinuclear copper–ruthenium complexes are present in solution. UV-Visible spectroscopy, EPR and cyclic voltammetry indicate that there is insignificant electronic communication between the metal centers in the di- and tri-nuclear complexes since salient metal-based features are additive.

Introduction

Molecular multimetallic compounds have the potential for unusual and useful photochemical, electronic and magnetic properties derived from allosteric or supramolecular cooperativity. An example of research in this area is the dendritic structures containing several different metal ions and ligands that are being developed as antennae units for use in artificial photosynthesis.^{1,2} Highly specific structural control on the molecular level of such systems is of great importance and a predicted application for such well-defined components with nanometer scale dimensions is in molecular-based computing and microelectronics.

Two fundamentally different methods can be applied in the preparation of multinuclear hetero-metallic coordination complexes; self-assembly synthesis and controlled stepwise synthesis. The first method may require less synthetic work but offers usually little structural control while the latter method requires more complicated synthetic work and extensive purification, however by careful planning construction of very large macromolecular/supramolecular structures are feasible.

As a part of our work with tetra-*N*-functionalised phenylenediamines, we have previously reported several different transition metal complexes of the redox-active bridging ligand *N,N,N',N'*-tetrakis(2-pyridylmethyl)benzene-1,4-diamine (tpbd) and the related but simpler tridentate analogue *N,N*-bis(2-pyridylmethyl)aniline (phdpa),³ see Chart 1. Complexes of tpbd include mononuclear 1 : 1 ligand : metal complexes with Zn²⁺ and Fe²⁺, 1 : 2 complexes with Cu²⁺ and Pd²⁺ and a proposed polynuclear complex with Ni²⁺.⁴⁻⁶ Furthermore, we have spectroscopically characterised a mononuclear 2 : 1 complex with Ru²⁺.⁴ This Ru-complex is a potential building block for larger molecular systems through metal coordination

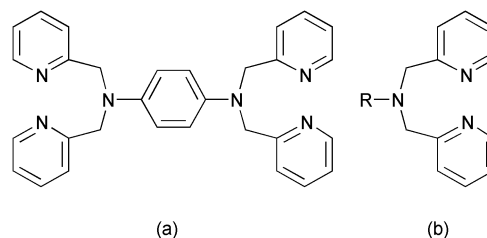
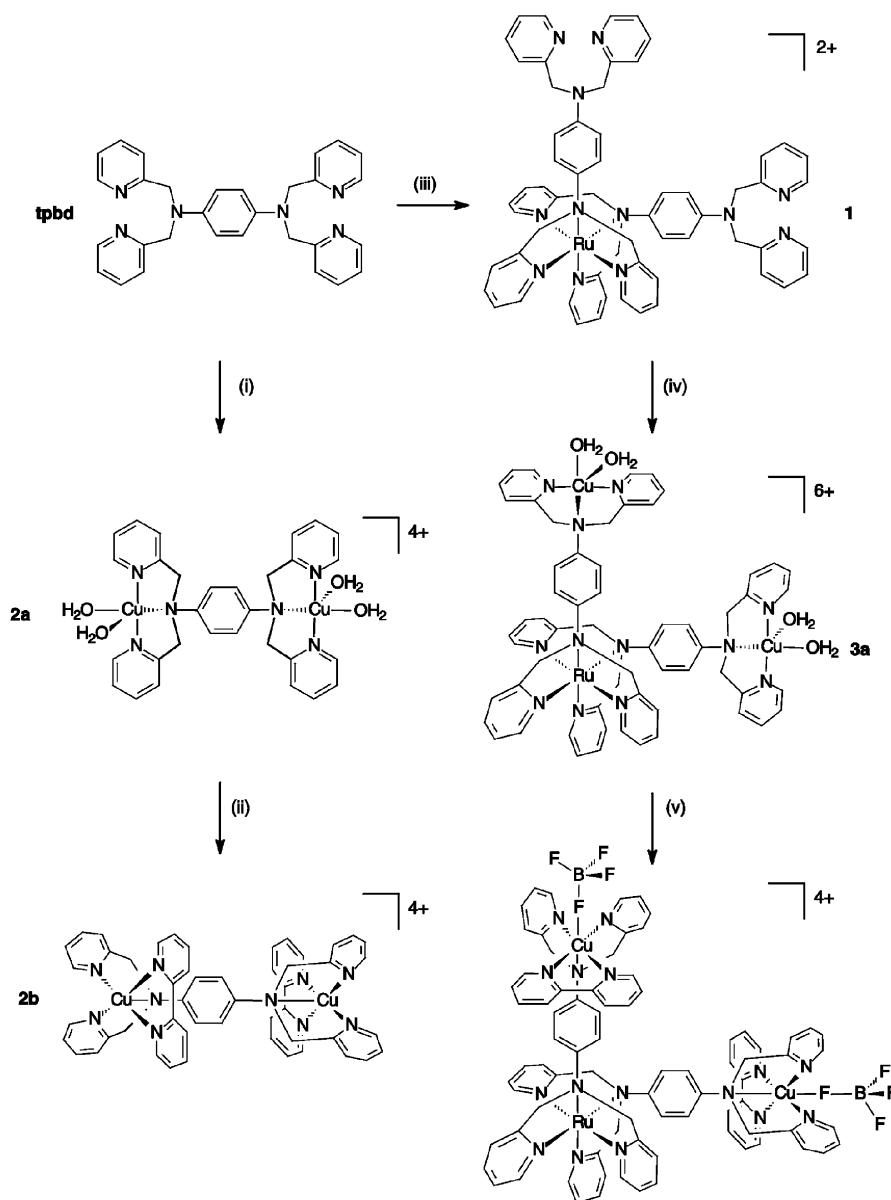


Chart 1 The structures of (a) tpbd and (b) dpa, R = H; etdpa, R = CH₂CH₃; phdpa, R = C₆H₅.

by the free tridentate ends. In the present work we have crystallographically characterized the Ru-complex and some of its copper-containing derivatives.

Results and discussion

The 1 : 2 and 2 : 3 tpbd : metal complexes [Cu₂(tpbd)(H₂O)₄](ClO₄)₄ (**2a**) and [Cu₂Ru(tpbd)₂(H₂O)₄](BF₄)₄(PF₆)₂·2H₂O (**3a**) were prepared analogously by reaction of tpbd or [Ru(tpbd)₂](PF₆)₂ (**1**) with copper(II) salts. The stepwise preparations are summarized in Scheme 1. The cation in **2a** has previously been structurally characterized in the less soluble dithionate complex [Cu₂(tpbd)(H₂O)₄](S₂O₆)₂.⁵ The water ligands in **2a** and **3a** can be replaced by other solvent ligands, e.g. dmf, pyridine, and by 2,2'-bipyridine (bipy). A di-copper complex formulated as [Cu₂(tpbd)(bipy)₂](PF₆)₄·H₂O (**2b**) and the trinuclear [Cu₂Ru(BF₄)₂(tpbd)₂(bipy)₂](PF₆)₄·2H₂O (**3b**) were isolated from reactions of **2a** and **2b** with bipy. The substitution of the terminal solvent ligands by bipy were accompanied by a color change from turquoise in **2a** and dark green in **3a** to pale green in **2b** and **3b**. The addition of excess sodium tetrafluoroborate was necessary during recrystallisation of **3a**



Scheme 1 Full synthesis of **2b** and **3b**. (i) 2 equiv. $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in water; (ii) 2 equiv. bipy; (iii) $\text{Ru}(\text{C}_6\text{H}_5\text{CN})_4\text{Cl}_2$ in ethanol, 48 h, chromatography; (iv) excess $\text{Cu}(\text{BF}_4)_2$ in water/ CH_3CN ; (v) 2 equiv. bipy in water/ CH_3CN , NaBF_4 .

and **3b** in order to isolate crystals suitable for crystallography. Recrystallisation of **3a** resulted in inclusion of additional lattice solvent, as seen in the crystal structure of **3a'**. Crystals isolated from recrystallisation of **3b** were identified as the mixed tetrafluoroborate/hexafluorophosphate double salt $[\text{Cu}_2\text{Ru}(\text{BF}_4)_2(\text{tpbd})_2(\text{bipy})_2](\text{BF}_4)_2(\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ (**3b'**). A summary of crystal parameters and refinement details are given in Table 1. Selected bond distances and angles for **1**, **3a'** and **3b'** are listed in Table 2. The structures of the trinuclear complexes **3a'** and **3b'** are of poor quality due to disorder and thereby poor diffracting power. The crystal structure of the cation in **1** is shown in Fig. 1. The ruthenium atom in **1** is six-coordinated in a roughly octahedral geometry with the bis-tridentate sites of the two tpbd ligands oriented in a *cis-fac* arrangement, which is the most common coordination geometry of octahedral complexes of bis(2-pyridylmethyl)amine derived ligands.^{3,7-9} The Ru–N1 distances of 2.191(4) Å are longer than the Ru–N11 and Ru–N21 distances of 2.066(4) Å and 2.088(4) Å. The complex cation has an exact 2-fold axis.

A view of the helical cation in **3a'** is shown in Fig. 2. The *cis-fac* coordination geometry observed in **1** is retained in **3a'**. The Ru–N1 and Ru–N11 distances are similar to those found in the structure of **1** within the standard deviations. The $\text{N}_{\text{amine}}-$

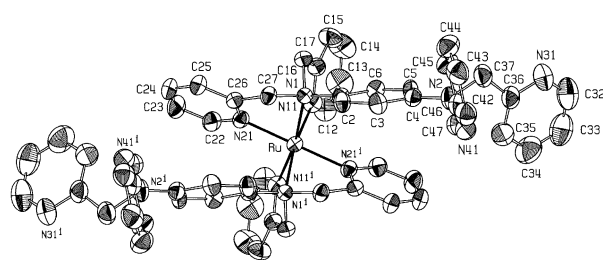


Fig. 1 ORTEP-III²² drawing of the X-ray structure of the $[(\text{tpbd})\text{Ru}(\text{tpbd})]^{2+}$ cation of **1**. Ellipsoids shown at 50% probability.

N_{amine} vectors of the two tpbd ligands are oriented perpendicular relative to each other. The copper atoms are coordinated in a square pyramidal geometry with the 3 nitrogen atoms and one water molecule in the basal plane and the second water molecule in the apical position, similar to that observed in the crystal structure of $[\text{Cu}_2(\text{tpbd})(\text{H}_2\text{O})_4](\text{S}_2\text{O}_6)_2$.⁵ A hexafluorophosphate anion is weakly coordinated to each copper atom with the fluorine atom positioned at a distance of 2.767(20) Å from the Cu atom. A similar weak coordination of a tetrafluoroborate with a Cu–F distance of 2.61–2.85 Å has been observed

Table 1 Crystal data and structure refinements

	1	3a'	3b'
Molecular formulation	[Ru(tpbd) ₂](PF ₆) ₂	[Cu ₂ Ru(tpbd) ₂ (H ₂ O) ₄](BF ₄) ₄ (PF ₆) ₂ ·8H ₂ O	[Cu ₂ Ru(BF ₄) ₂ (tpbd) ₂ (bipy) ₂](BF ₄) ₂ (PF ₆) ₂ ·H ₂ O
Empirical formula	C ₆₀ H ₅₆ N ₁₂ F ₁₂ P ₂ Ru	C ₆₀ H ₈₀ N ₁₂ B ₄ Cu ₂ F ₂₈ O ₁₂ P ₂ Ru	C ₈₀ H ₇₄ N ₁₆ B ₄ Cu ₂ F ₂₈ OP ₂ Ru
Formula weight	1336.18	2026.81	2140.88
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Fddd</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> /Å	25.578(1)	30.059(6)	14.122(2)
<i>b</i> /Å	27.030(1)	17.996(4)	21.427(3)
<i>c</i> /Å	35.028(2)	20.338(4)	30.472(5)
<i>a</i> °	90	90	90
<i>β</i> °	90	132.337(4)	93.110(4)
<i>γ</i> °	90	90	90
<i>V</i> /Å ³	24217(2)	8132(3)	9207(2)
<i>Z</i>	16	4	4
<i>D</i> _{calc} /g cm ⁻³	1.466	1.655	1.544
<i>T</i> /K	120	120	120
<i>μ</i> (Mo-Kα)/mm ⁻¹	0.399	0.87	0.765
Reflections collected	67793	55898	57193
independent (<i>R</i> _{int})	6779 (0.049)	9297 (0.132)	13183 (0.079)
observed [<i>I</i> >3σ <i>I</i>]	4565	5037	7282
<i>R</i> indices ^a [<i>I</i> >3σ <i>I</i>] <i>R</i> 1	0.054	0.211	0.140
<i>wR</i> 1	0.058	0.282	0.142
Δρ _{max} , Δρ _{min} /e Å ⁻³	0.98(4), -0.62(4)	1.5(2), -1.9(2)	1.7(1), -2.4(1)

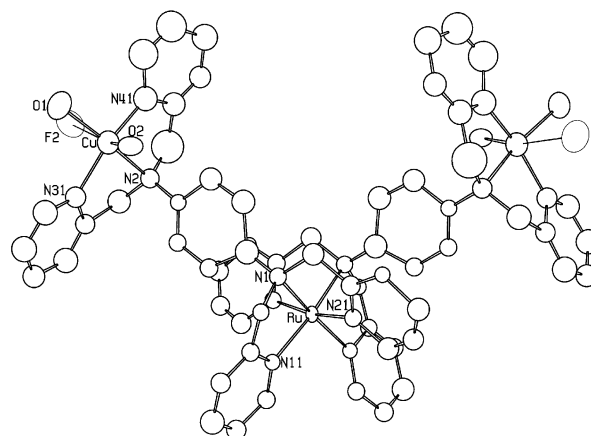
$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. wR1 = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}. w = 1 / \{(\sigma(F_o^2))^2 + B + (1 + A)F_o^2\} - |F_o|^2.$$

Table 2 Selected bond distances (Å) and angles (°) for **1**, **3a'** and **3b'**

	1	3a'	3b'
Ru–N1	2.191(4)	2.176(23)	2.183(9)
Ru–N11	2.066(4)	2.064(21)	2.067(10)
Ru–N21	2.088(4)	2.068(22)	2.111(9)
Cu–N2	–	2.148(26)	2.377(10)
Cu–N31	–	2.005(26)	2.043(10)
Cu–N41	–	1.818(34)	1.996(10)
Cu–N51/O1	–	1.970(23)	2.031(10)
Cu–N61/O2	–	2.271(21)	2.005(10)
Cu–F	–	2.767(20)	2.385(7)
N1–Ru–N11	80.0(2)	81.5(8)	79.9(3)
N1–Ru–N21	77.2(1)	77.9(8)	77.8(3)
N1–Ru–N1i	101.6(2)	101.4(12)	102.1(5)
N1–Ru–N11i	170.5(1)	169.2(8)	169.8(3)
N1–Ru–N21i	96.7(1)	96.5(9)	96.6(3)
N11–Ru–N21	92.8(2)	94.2(8)	93.7(4)
N11–Ru–N11i	100.0(2)	97.6(12)	99.9(6)
N11–Ru–N21i	93.3(2)	91.5(8)	92.0(4)
N21–Ru–N21i	170.6(2)	171.4(14)	171.2(5)
N2–Cu–N31	–	82.7(10)	77.0(4)
N2–Cu–N41	–	81.2(13)	81.0(4)
N2–Cu–N51/O1	–	161.9(10)	100.0(4)
N2–Cu–N61/O2	–	109.4(0)	96.2(4)
N2–Cu–F	–	83.3(9)	170.8(3)
N31–Cu–N41	–	163.2(13)	91.6(4)
N31–Cu–N51/O1	–	94.3(10)	175.2(4)
N31–Cu–N61/O2	–	98.5(9)	95.1(4)
N31–Cu–F	–	85.6(9)	94.2(4)
N41–Cu–N51/O1	–	99.6(13)	91.6(4)
N41–Cu–N61/O2	–	91.4(12)	172.0(4)
N41–Cu–F	–	87.8(12)	97.0(4)
N51/O1–Cu–N61/O2	–	88.7(9)	81.4(4)
N51/O1–Cu–F	–	78.7(9)	88.9(4)
N61/O2–Cu–F	–	167.0(8)	87.0(4)

Symmetry codes: **1**: i) $1\frac{3}{4} - x, y, \frac{3}{4} - z$. **3a'** and **3b'**: i) $-x, y, \frac{1}{2} - z$.

in the mixed penta- and hexa-coordinate structure of [Cu(dpa)₂](BF₄)₂.¹⁰ The anions tetrafluoroborate and hexafluorophosphate are disordered and the crystal contains some water and possibly methanol solvent. In the planar arrangement of the bis-tridentate site of tpbd around the copper atoms, there is some flexibility; the methylene bridges can flip resulting in small displacements of the ring atoms. Anisotropic displacement parameters could not describe this, and a constrained refine-

**Fig. 2** X-Ray structure of the [Cu₂Ru(tpbd)₂(H₂O)₄]⁶⁺ cation of **3a'**. The weakly coordinated PF₆⁻-derived fluoride atom is indicated.

ment where the pyridine rings and the benzene rings were each allowed two orientations was attempted. No improvement was obtained and a conventional least squares refinement with all tpbd atoms isotropic was preferred.

Fig. 3 shows the structure of the cation in **3b'**. The overall structure of the cation is helical like that of **3a'** with the two Cu-sites facing in opposite directions ('anti' orientation) at each end. The [(tpbd)Ru(tpbd)]²⁺ core is similar to that of

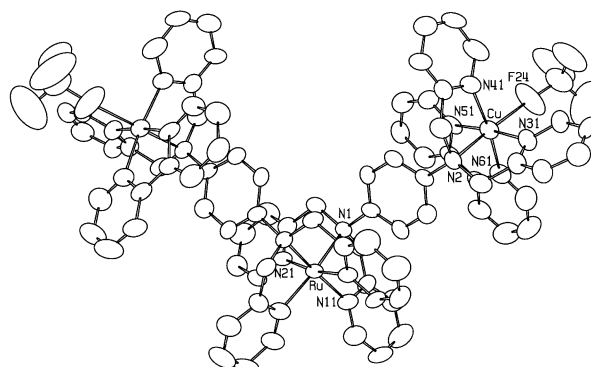
**Fig. 3** X-Ray structure of the [Cu₂Ru(BF₄)₂(tpbd)₂(bipy)₂]⁴⁺ cation of **3b'**.

Table 3 UV-Visible and EPR spectral data

Complex	UV-Visible (CH ₃ CN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	EPR	
		MeOH/dmf (3 : 1)	MeOH/H ₂ O (9 : 1)
1	320sh (13650), 361sh (11250), 389 (12100)	–	–
[Cu ₂ (tpbd)(H ₂ O) ₄](S ₂ O ₆) ₂	^a	$g_{\perp} = 2.058, g_{\parallel} = 2.248, A_{\parallel} = 176 \text{ G}$	
[Cu(phdpa)(dmf) ₂](ClO ₄) ₂ ¹⁴	^b	$g_{\perp} = 2.049, g_{\parallel} = 2.251, A_{\parallel} = 176 \text{ G}$	
2a	318sh (2700), 416 (2200), 624 (730)	$g_{\perp} = 2.049, g_{\parallel} = 2.248, A_{\parallel} = 175 \text{ G}$	$g_{\perp} \approx 2.068, g_{\parallel}^1 = 2.311, g_{\parallel}^2 = 2.258,$ $A_{\parallel}^1 = 141 \text{ G}, A_{\parallel}^2 = 138 \text{ G}$
2b	477sh (230), 566 (78), 612 (78), 850 (61)	$g_{\perp} = 2.048, g_{\parallel} = 2.254, A_{\parallel} = 174 \text{ G}$	$g_{\perp} = 2.051, g_{\parallel} = 2.253, A_{\parallel} = 178 \text{ G}$
3a	328sh (11750), 351sh (12750), 384 (13400), 615 (870)	$g_{\perp} = 2.052, g_{\parallel} = 2.251, A_{\parallel} = 178 \text{ G}$	$g_{\perp} = 2.068, g_{\parallel} = 2.283, A_{\parallel} = 144 \text{ G}^c$
3b	304 (32700), 311sh (31700), 359 (12580), 384 (12850), 601 (120), 879 (41)	$g_{\perp} = 2.047, g_{\parallel} = 2.251, A_{\parallel} = 178 \text{ G}$	$g_{\perp} = 2.046, g_{\parallel} = 2.255, A_{\parallel} = 176 \text{ G}$

^a UV-Visible spectra were not obtained due to low solubility of the complex. ^b Not measured. ^c A weak second signal was evident but *g*-values could not be resolved.

3a', however in contrast the periphery tpbd nitrogen atoms coordinate to Cu(II) in a facial arrangement. The difference of *mer* versus *fac* geometries in **3a'** and **3b'**, respectively demonstrates the flexible nature of tpbd. The Ru(II) site is essentially unaffected by the substitution of the terminal copper-bound water ligands by bipy. The four pyridine rings in each of the Cu(II) sites form the equatorial plane of a distorted octahedron with the tertiary nitrogen of tpbd and one fluorine atom of a tetrafluoroborate located in the axial positions at 2.377(10) Å and 2.385(7) Å, respectively, from the copper atom. This distance is 0.386 Å less than the Cu–F distance in **3a'** suggesting a significantly stronger bond. Accordingly, the other bond distances in the Cu octahedron are increased in **3b'** compared to **3a'**. Three structures have been reported with similar short Cu–F distances, but only one is octahedral; in that case two BF₄[–] ions are *trans* to one another with Cu–F distances of 2.383 Å.¹¹ A Jahn–Teller distorted axial elongation is not unusual in hexa-coordinate Cu(II) complexes; in the crystal structure of the *trans-fac* [CuL₂](ClO₄)₂·2H₂O [L = (bis(2-benzimidazolmethyl)amine)]¹² an even larger Cu–N(amine) distance of 2.597(6) Å is found. A BF₄[–] ligand, as revealed in the crystal structure of **3b'**, is generally considered a weak ligand. Consequently, it is likely to dissociate in solution with a penta-coordinated square pyramidal or trigonal bipyramidal geometry as a result. The anions in **3b'** are even more disordered than those in **3a'**; data were collected from 3 crystals which differed in the ratios of the anions and amount of lattice solvent. In one crystal the hexafluorophosphate was to a large extent replaced by tetrafluoroborate, at the same time extra solvent was included so that the cell dimensions were altered by 1–2%. The results so far show no indication that hexafluorophosphate anions can substitute the specific coordinated tetrafluoroborate anions.

UV-Visible and EPR spectroscopy results for **1**, **2a**, **3a**, **2b** and **3b** are summarised in Table 3. UV-Visible spectra of all complexes were measured in acetonitrile solution immediately after dissolution of the complexes. The spectrum of **1** shows three bands at 320, 361 and 389 nm, which are assigned to ligand based π – π^* transitions. The spectrum is similar to that of the closely analogous chromophore [Ru(etdpa)₂](PF₆)₂,¹³ etdpa is shown in Chart 1. The Ru-based features of **1** are essentially unaltered in the spectra of **3a** and **3b**. Furthermore, the di-copper aqua complex **2a** and the analogous ruthenium containing complex **3a** show similar Cu based d–d transitions at 624 nm and 615 nm, respectively. See Fig. 4 for a comparison. This indicates that the coordination geometries and electronic structures of the mono- and di-nuclear complexes **1**, **2a** and **2b** are largely preserved in the hetero-metallic systems in acetonitrile solutions. The visible absorption spectrum of **2b** in

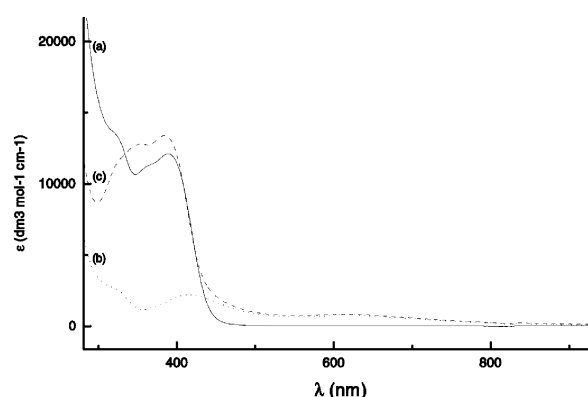


Fig. 4 UV-Visible spectra of (a) **1**, (b) **2a** and (c) **3a** in acetonitrile solution. Concentrations approx. 100 μM .

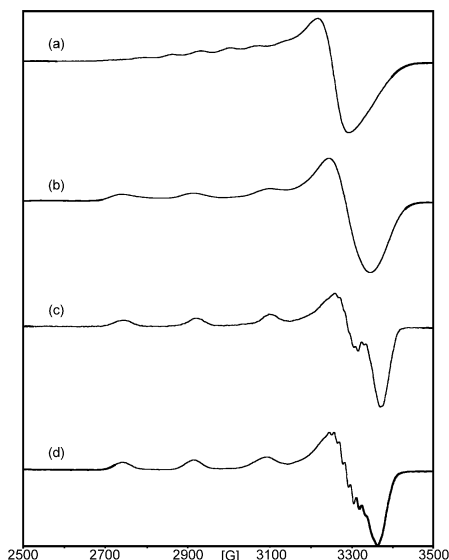
acetonitrile solution shows two bands in the Cu-based d–d region, suggesting the presence of two different structures in acetonitrile solutions of **2b**. Substitution of solvent ligands may account for this observation. EPR spectroscopy and cyclic voltammetry results (see below) similarly suggest lability and furnish no additional information.

The EPR spectra obtained for the series have been compared to those for the structurally analogous monomeric complexes [Cu(phdpa)(dmf)₂](ClO₄)₂¹⁴ and [Cu(dpa)(bipy)](ClO₄)₂¹⁰ in order to assist in the separation of spectroscopic features of the copper based moieties in the dinuclear copper and trinuclear copper ruthenium complexes. EPR spectra of the di- and trinuclear complexes in frozen MeOH/dmf (3 : 1) and MeOH/water (9 : 1) glasses at *ca.* 100 K are shown in Fig. 5. All di- and tri-nuclear complexes show essentially identical axial copper(II) signals in MeOH/dmf with $g_{\perp} = 2.047$ – 2.052 , $g_{\parallel} = 2.248$ – 2.254 and $A_{\parallel} = 174$ – 178 G . The spectra show superhyperfine structures with seven lines on the g_{\perp} component, consistent with three nitrogen atoms coordinated to the Cu(II) atoms. The EPR spectrum of the closely related, crystallographically characterised square pyramidal [Cu(phdpa)(dmf)₂](ClO₄)₂ in MeOH/dmf is identical and suggests iso-structural geometries of this and the Cu(II) sites in all di- and tri-nuclear complexes. This indicates substitution of terminal water and bipy ligands with dmf ligands in methanol/dmf glass. In MeOH/water the EPR spectrum of **2a** shows two different axial copper(II) signals with $g_{\perp} \approx 2.068$, $g_{\parallel}^1 = 2.311$, $g_{\parallel}^2 = 2.258$, $A_{\parallel}^1 = 141 \text{ G}$ and $A_{\parallel}^2 = 138 \text{ G}$. No information about the donor environment is available due to lack of superhyperfine structures. The two closely related copper(II) signals are assigned to two slightly different solution Cu coordination environments, of which one or both are gener-

Table 4 Redox data. Voltammograms were obtained in acetonitrile solutions with 0.1 M Bu₄NPF₆ as electrolyte. Scan rate: 0.100 V s⁻¹

	Cu ^{II} /Cu ^I			Ru ^{III} /Ru ^{II}			tpbd		
	<i>E</i> _{pc} /V	<i>E</i> _{pa} /V	<i>E</i> _{1/2} /V	<i>E</i> _{pc} /V	<i>E</i> _{pa} /V	<i>E</i> _{1/2} /V	<i>E</i> _{pc} /V	<i>E</i> _{pa} /V	<i>E</i> _{1/2} /V
tpbd	–	–	–	–	–	–	0.28	0.34	0.31 ^a
1	–	–	–	0.82	0.90	0.86	– ^b	0.69	–
2a	–0.36	–0.25	–0.31	–	–	–	0.66	0.84	0.75
	0.11	0.14	0.02 ^c	–	–	–	–	–	–
2b	–0.35	–0.10	–0.23	–	–	–	– ^b	0.95	–
3a	–0.09	0.14	0.03	0.94	1.02	0.98	–	–	–
3b	–0.46	–0.10 ^d	–0.28	0.84	0.98	0.91	–	–	–

^a From ref. 5; tpbd shows a second, irreversible oxidation at *E*_{1/2} = 0.67 V. ^b No reduction response observed. ^c Two Cu^{II}/Cu^I redox processes are observed. ^d Weak response.

**Fig. 5** EPR spectra of (a) **2a** in MeOH/water (9 : 1), (b) **2b** in MeOH/water (9 : 1), (c) **3a** in MeOH/dmf (3 : 1) and (d) **3b** in MeOH/dmf (3 : 1) at 104 K.

ated by substitution of one or more of the labile water ligands with methanol. The analogous EPR spectrum of **3a** in MeOH/water shows one dominating signal with $g_{\perp} = 2.068$, $g_{\parallel} = 2.283$ and $A_{\parallel} = 144$ G, which is different to the signals observed for **2a**. Apart from this signal a much weaker signal is present as shoulders to the main signal, but the g -values could not be derived. The EPR spectra of **2b** and **3b** in MeOH/water and MeOH/dmf glasses are all very similar with $g_{\perp} = 2.046$ – 2.051 , $g_{\parallel} = 2.251$ – 2.255 and $A_{\parallel} = 174$ – 178 G and resemble the spectra of **2a** and **3a** obtained in MeOH/dmf. However, g -values are comparable for Cu(II) complexes with oxygen donor atoms versus aromatic nitrogen donor atoms.¹⁵ The EPR spectrum of [Cu(dpa)(bipy)](ClO₄)₂ shows similar g -values in MeOH at 77 K ($g_{\perp} = 2.07$, $g_{\parallel} = 2.222$), but a contrasting A_{\parallel} value of 202 G in MeOH at 77 K. The similarity of the solution EPR spectrum of **3b** to the spectra of **2a**, **3a**, [Cu(phdpa)(dmf)]₂(ClO₄)₂ and [Cu(dpa)(bipy)](ClO₄)₂ in which the copper ions are five-coordinated suggest that decoordination of the tetrafluoroborate occurs upon dissolution in MeOH/dmf and MeOH/water.

Redox activity based on the copper ions, ruthenium ion and tpbd ligand is feasible for the trinuclear complexes, potentially bipy-based redox chemistry is also possible. Several oxidation levels can be envisaged, ranging from [Cu^I(tpbd)Ru^{II}(tpbd)-Cu^I]⁴⁺ to [Cu^{II}(tpbd^{•+})Ru^{III}(tpbd^{•+})Cu^{II}]⁹⁺ with four levels between these two formal oxidation state extremes. The trinuclear entities might be expected to decompose under further reduction or oxidation beyond these extremes. Thus we have electrochemically characterised the series in acetonitrile solution using cyclic voltammetry. The electrochemical responses in Table 4 are assigned as Cu-, Ru- or tpbd-based on internal

comparisons within the series. Our previous experience shows that the normally facile tpbd oxidation to a stable radical cation, tpbd^{•+}, is inhibited by coordination, no doubt due to the coulombic repulsion which would result. However our interest in this system is the ability of tpbd to transfer electrons between metal centres. Potentially redox isomers may exist for all the intermediate oxidation levels, e.g., [Cu^{II}(tpbd)Ru^{II}(tpbd)Cu^{III}]⁶⁺ ↔ [Cu^I(tpbd^{•+})Ru^{II}(tpbd)Cu^{II}]⁶⁺; [Cu^{II}(tpbd)-Ru^{III}(tpbd)Cu^{II}]⁷⁺ ↔ [Cu^{II}(tpbd^{•+})Ru^{II}(tpbd)Cu^{II}]⁷⁺, etc. The electrochemical properties of tpbd have been described previously. The metal complexes **1**, **2a** and **2b** exhibit ligand-based and metal-based oxidation processes. No tpbd-based redox process was seen for **1** and **2b**, however metal–ligand charge transfer may account for this observation. The Ru-based redox potential observed for **1** is slightly higher than that observed at 0.79 V for the related, structurally characterised [Ru(etdpa)]₂(PF₆)₂ in acetonitrile.¹³ The Cu redox processes resemble the structurally related complex, [Cu(dpa)(bipy)]-(ClO₄)₂,¹⁰ for which a redox potential of –0.40 V was observed in MeOH.

A stable radical cation is accessible for tpbd, thus an initial speculation was the potential of this bis-tridentate ligand, when bridging between metal ions, to mediate electronic communication. Our results so far have not shown evidence for this. The likely explanation is that oxidation of tpbd is inhibited when it is coordinated to an electropositive metal ion.

In summary, the stepwise syntheses described here show the potential of the strategy. The complexes **1**, **2a** and **3a** might serve as building blocks for the subsequent synthesis of larger molecular structures. The *anti* orientation of the Cu atoms in the trinuclear complexes show that this unit could function topologically as a ‘cornerstone’ building block. Thus in an extended structure with tpbd e.g. in a 1D polymer, the chains would have a helical topology. Such heteronuclear coordination polymers are feasible by use of a bridging ligand based on the bipy-ligand such as 1,2-bis(4-(4′methyl)-2,2′-bipyridyl)ethene.¹⁶ By choice of appropriate bis(monodentate) bridging ligands for substitution of the water ligands in **2a** and **3a** each Cu-site could be connected to two or three other Cu-sites, and thereby the potential for larger self-assembly network structures is opened. Attempts to isolate one such complex with 4,4′-bipyridine have been made, but not yielded tractable products. Several other ligands should be tested for this purpose.

Experimental

Physical measurements

UV-Visible absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Elemental analyses were carried out by the microanalytical laboratory of the H. C. Ørsted Institute, Copenhagen. Electron spin resonance measurements at X-band frequency were obtained using a Bruker EMX-113 spectrometer. Cyclic voltammetry was carried out on an Eco

Chemie Autolab potentiostat under N₂ with acetonitrile solutions and tetrabutylammonium hexafluorophosphate as electrolyte. The working electrode was a platinum electrode, the auxiliary electrode was a platinum wire and the reference a Ag–AgCl electrode (calibrant, ferrocene–ferrocenium at 450 mV). Redox potentials are listed vs. Ag–AgCl.

Materials

All commercially available chemicals were used without any prior purification [Ru(tpbd)₂](PF₆)₂ (**1**)⁴ and Cu₂(tpbd)Cl₄⁵ were synthesised as previously reported. Diffraction quality crystals of **1** were grown by slow evaporation of a solution of the complex in acetonitrile/water (1 : 3) solution.

CAUTION: although no problems were encountered in the preparation of the perchlorate salt, suitable care should be taken when handling such potentially hazardous compounds.

Preparations

[Cu₂(tpbd)(H₂O)₄](ClO₄)₄ (2a**).** Cu(NO₃)₂·2.5H₂O (98.5 mg, 0.424 mmol) in water (2 ml) was added to a suspension of tpbd (100 mg, 0.212 mmol) in water (5 ml). The mixture was heated to ca. 50 °C for 1 h and NaClO₄·H₂O (200 mg, 1.42 mmol) in water (2 ml) was added and after 1 h the turquoise coloured crystalline material was isolated by filtration and washed with water. Yield 156 mg, 69%. Anal calcd. for C₃₀H₃₆Cl₄Cu₂N₆O₂₀: C, 33.69; H, 3.39; N, 7.86. Found: C, 33.96; H, 3.08; N, 7.86%.

[Cu₂(tpbd)(bipy)₂](PF₆)₄·H₂O (2b**).** Cu₂(tpbd)Cl₄ (100 mg, 0.134 mmol) was hydrolysed in 200 ml water (to give a solution of [(H₂O)₂Cu(tpbd)Cu(H₂O)₂]²⁺). After addition of 2,2'-bipyridine (41.8 mg, 0.268 mmol) the solution was stirred for 20 min and NH₄PF₆ (400 mg, 2.46 mmol) was added. The pale green microcrystalline product precipitated immediately and was isolated by filtration to yield 148 mg, 73%. Anal calcd. for C₅₀H₄₆Cu₂F₂₄N₁₀OP₄: C, 39.77; H, 3.07; N, 9.28. Found: C, 39.63; H, 2.91; N, 9.15%.

[Cu₂Ru(tpbd)₂(H₂O)₄](BF₄)₄(PF₆)₂·2H₂O (3a**).** Cu(BF₄)₂·xH₂O (47.5 mg, 0.200 mmol) in water (50 ml) was added to **1** (100 mg, 0.0745 mmol) in acetonitrile (50 ml). After addition of NaBF₄ (150 mg, 1.365 mmol) in water, the solution was allowed to stand for 6 days and the crystalline material was isolated by filtration. Yield 100 mg, 70% of dark green rods. Anal calcd. for C₆₀H₆₈B₄Cu₂F₂₈N₁₂O₆P₂Ru: C, 37.56; H, 3.57; N, 8.76. Found: C, 37.36; H, 3.59; N, 8.46%. Crystals (**3a'**) for crystallography were obtained by recrystallisation from methanol/water (1 : 1) solution containing approx. 2% NaBF₄.

[Cu₂Ru(BF₄)₂(tpbd)₂(bipy)₂](PF₆)₄·2H₂O (3b**).** This complex was prepared analogously to **3a** except that 2,2'-bipyridine (47 mg, 0.150 mmol) was added after the ruthenium complex. Various yields (45–72%) of pale green crystals. Anal calcd. for C₈₀H₇₆B₂Cu₂F₃₂N₁₆O₂P₄Ru: C, 42.23; H, 3.37; N, 9.85. Found: C, 42.11; H, 3.39; N, 9.72%. Crystals (**3b'**) for crystallography were obtained by recrystallisation from acetonitrile/water (1 : 3) solution containing approx. 2% NaBF₄.

X-Ray crystallography

Structures were determined using graphite monochromatized radiation. Data were collected at 120 K on a Siemens SMART diffractometer.¹⁷ Crystal data and experimental parameters are

presented in Table 1. The data were corrected for Lorentz-polarization effects and for absorption.¹⁷ The structures were solved by direct methods using SIR97¹⁸ and refined by least-squares techniques using programs from the KRYSTAL¹⁹ package. Atomic scattering factors were taken from elsewhere.²⁰ Attempts at refinement of disordered models using constraint refinement²¹ were done on **3a'** and **3b'** but they were abandoned if they did not lead to improvements. In the end only the BF₄⁻ ions in **3b'** were constrained.

CCDC reference numbers 200507–200509.

See <http://www.rsc.org/suppdata/dt/b2/b212624a/> for crystallographic data in CIF or other electronic format.

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