Synthesis and Characterization of a New Copper(II) Phthalocyaninate Substituted with Four 15-Membered Tetraazamacrocycles and Its Water-soluble Pentanuclear Complexes

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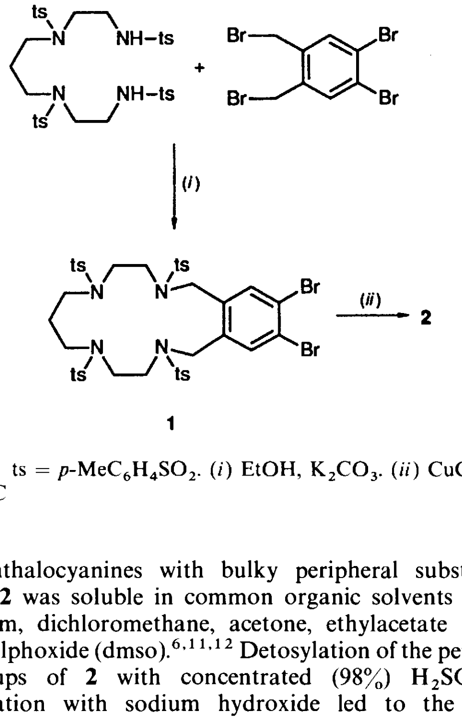
The synthesis of a new copper(II) phthalocyaninate substituted with four 15-membered tetraazamacrocycles from 15,16-dibromo-2,5,9,12-tetra(toluene-*p*-sulphonyl)-2,3,4,5,6,7,8,9,10,11,12,13-dodecahydro-1*H*-2,5,9,12-benzotetraazacyclopentadecine is described. Quaternization of the aza groups leads to water-soluble products. The tetraaza macrocyclic substituents bind transition-metal ions (Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) to give pentanuclear complexes whose electronic spectra indicate the presence of monomeric units in solution. The thermal stabilities of the compounds were determined by thermogravimetric analysis.

The importance of phthalocyanines in many fields including chemical sensors, electrochromism, batteries, photodynamic therapy, semiconductive materials and liquid crystals is increasing rapidly as a result of newly synthesized compounds.[1–3] In this context substitution on the aromatic rings of phthalocyanine by various groups leads to new products containing additional functionalities. Among these are supramolecular systems which consist of two identical molecular entities coexisting together without the assistance of covalent binding.[3,4] The notable feature of these systems is that they exhibit spectral properties different from those of the individual molecular units. In our earlier studies on tetrakis(15-crown-5) substituted phthalocyanine and its metal derivatives (15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane) we observed phenomena similar to organized condensed phases.[5,6] In these compounds, planar phthalocyanine cores stack to form columns capable of forming ion-channels for alkali-metal cations through the crown ether voids.[7] With monoaza crown ether substituents, water-soluble products have been obtained by quaternization of the aza group.[8,9] Consequently, it is of interest to investigate the effect of macroaza groups on the phthalocyanine core both from the point of view of condensed-phase properties and the solubility. Preliminary findings on a derivative of phthalocyanine with four 14-membered-tetraazamacrocyclic substituents have been reported recently by our group.[10] In the present paper, a new copper phthalocyaninate with four 15-membered tetraazamacrocyclic substituents and its pentanuclear complexes are reported.

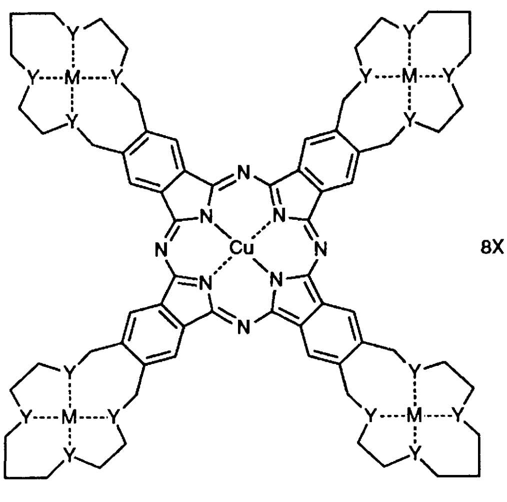
Results and Discussion

Since phthalocyanines substituted at the aromatic rings are almost always prepared from reactants which already contain these groups, the dibromo derivative of a new 15-membered tetraazamacrocycle, 15,16-dibromo-2,5,9,12-tetra(toluene-*p*-sulphonyl)-2,3,4,5,6,7,8,9,10,11,12,13-dodecahydro-1*H*-2,5,9,12-benzotetraazacyclopentadecine **1** was prepared. The cyclotetramerization reaction of **1** was carried out in tetramethylurea (tmu) in the presence of CuCN to obtain the monocopper(II) phthalocyaninate complex **2** (Scheme 1). As is the case with many phthalocyanines with bulky peripheral substituents, complex **2** was soluble in common organic solvents such as chloroform, dichloromethane, acetone, ethylacetate and dimethyl sulphoxide (dmso).[6,11,12] Detosylation of the peripheral aza groups of **2** with concentrated (98%) H_2SO_4 and neutralization with sodium hydroxide led to the copper phthalocyaninate **3** containing free amino groups. In contrast to **2**, complex **3** was insoluble in halogenated hydrocarbons but was soluble in methanol, ethanol and dmso and also slightly so in water. In order to obtain a more water-soluble phthalocyanine, complex **3** was quaternized with dimethyl sulphate in methanol and the product **4** was soluble in water over a wide pH range.[8,9] The pentanuclear complexes **5**–**8** were all prepared by treatment of a solution of **3** in absolute methanol with chloride or perchlorate salts of transition-metal ions (Co^{II}, Ni^{II}, Cu^{II} or Zn^{II}). In these pentanuclear complexes, each tetraaza macrocycle encapsulates one metal ion (Table 1) and their highly ionic character was indicated clearly by their solubility in water.



Scheme 1 ts = p-$MeC_6H_4SO_2$. (*i*) EtOH, K_2CO_3. (*ii*) CuCN, tmu, 195–200 °C

NMR measurements were precluded owing to the paramagnetic nature of the copper(II) phthalocyaninate core in all



Complex	Y	M	X
2	N(ts)		
3	NH		
3a	NH_2^+, $\frac{1}{2}SO_4^{2-}$		
4	NMe_2^+, $MeOSO_3^-$		
4a	NMe_2^+, ClO_4^-		
5	NH	Co^{II}	Cl
5a	NH	Co^{II}	ClO_4
6	NH	Ni^{II}	Cl
6a	NH	Ni^{II}	ClO_4
7	NH	Cu^{II}	Cl
7a	NH	Cu^{II}	ClO_4
8	NH	Zn^{II}	Cl

Table 1 Analytical data for the phthalocyanines*

Compound	C	H	N
1	49.80	4.65	5.40
	(49.90)	(4.60)	(5.50)
2	57.10	5.20	8.90
	(57.20)	(5.10)	(8.90)
3	62.10	7.35	25.60
	(62.20)	(7.35)	(25.60)
3a	38.80	5.40	16.00
	(38.95)	(5.40)	(16.00)
4	39.05	6.30	9.70
	(39.20)	(6.35)	(9.45)
4a	35.55	5.20	9.85
	(35.65)	(5.25)	(10.00)
5·$8H_2O$	41.10	5.70	16.90
	(41.30)	(5.70)	(17.00)
5a	34.80	4.20	14.25
	(34.85)	(4.15)	(14.35)
6	44.50	5.30	18.35
	(44.60)	(5.30)	(18.35)
6a	34.75	4.10	14.40
	(34.85)	(4.15)	(14.35)
7·$8H_2O$	40.80	5.60	16.75
	(40.95)	(5.65)	(16.85)
7a	34.50	4.10	14.15
	(34.55)	(4.10)	(14.25)
8·$8H_2O$	40.55	5.60	16.70
	(40.75)	(5.65)	(16.80)

* Required values are given in parentheses.

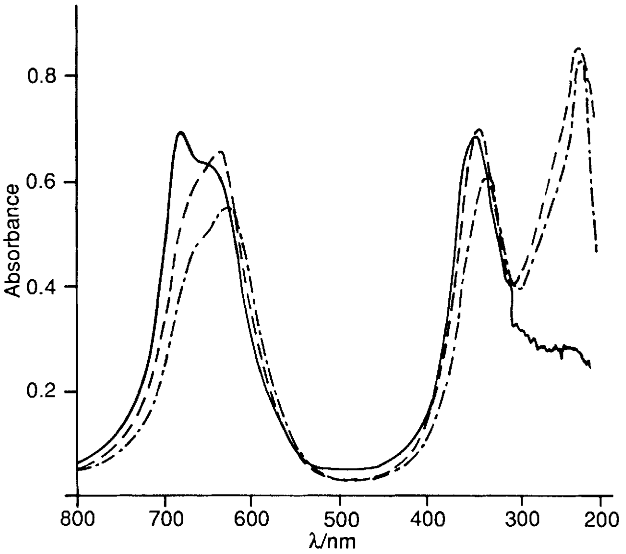


Fig. 1 Electronic spectra of **4** in water at pH values 4 (——), 7 (– – –) and 10 (– • – • –)

Table 2 Electronic spectral data for the phthalocyanine complexes in water

Compound	λ_{max}/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})
2[a]	243 (14.28), 347 (7.58), 617 (3.00),[b] 685 (13.49)
3[a]	249 (4.78), 342 (5.27), 616 (3.33), 678 (8.67)
3	220 (6.47), 332 (5.27), 639 (5.46), 669 (4.31)[b]
3a	219 (7.54), 335 (2.95), 632 (2.09), 692 (1.68)[b]
4	211 (10.68), 328 (8.31), 628 (7.88), 659 (7.34)[b]
4a	211 (10.08), 329 (8.07), 628 (7.68), 660 (7.35)
5	220 (10.03), 330 (5.16), 629 (3.81),[b] 669 (7.84)
5a	218 (10.74), 330 (6.02), 630 (5.42),[b] 660 (5.69)
6	215 (7.63), 333 (7.30), 602 (3.68),[b] 637 (4.13),[b] 668 (18.89)
6a	216 (8.16), 339 (6.46), 637 (5.46), 676 (8.62)
7	211 (6.97), 248 (6.16),[b] 330 (5.70), 627 (5.34), 667 (6.28)
7a	214 (7.35), 236 (6.64), 328 (6.26), 625 (5.60), 667 (8.20)
8	212 (7.12), 330 (6.19), 629 (5.07), 670 (10.39)

[a] In chloroform. [b] Shoulder.

of the newly synthesized compounds. However, comparison of the IR data gives sufficient support for the proposed structures. The difference between the spectra of tosylated and free amino groups is clear from the pesence of SO_2 vibrations in **2** at 1160 and 1340 cm^{-1} and the free NH stretching vibrations for **3** at 3250 cm^{-1}.[13] Quaternized derivatives can be characterized by the disappearance of free NH vibrations. Also, the characteristic absorptions of methylsulphate (1260–1220 cm^{-1}) and perchlorate (1150–1040 and 640 cm^{-1}) can differentiate between **4** and **4a**. The IR absorption patterns of the pentanuclear compounds from chloride salts, **5**–**8**, were very similar with virtually no change in the stretching (3250 cm^{-1}) and bending (1620 cm^{-1}) vibrations of the amino groups upon complexation. In the case of the perchlorate salts, intense absorptions due to this anion at 1150–1040 and 640 cm^{-1} are observed. The UV/VIS absorption spectra of the phthalocyanine complexes exhibit characteristic Q and B bands. The *N*-tosyl phthalocyanine complex **2** is soluble in halogenated hydrocarbons and its spectrum is very similar to those of crown ether-substituted phthalocyanines (Table 2).[5,6] The slight solubility of the free amino phthalocyanine complex **3** enabled us to measure its spectrum in water, which is typical of an aggregated phthalocyanine with a shoulder at the lower energy side of the Q band (669 nm) and an intense absorption at 639 nm.[14] As for monoaza crown ether-substituted phthalocyanines, quaternization makes the phthalocyanine soluble over a wide pH range (Fig. 1). The UV/VIS spectrum of **4** in water over a range of pH values maintained with phosphate buffer indicates that at higher pH values aggregation is more efficient. Since it is known that the intensity of d–d transitions in the complexes of saturated cyclic amines is very low when compared with the Q absorptions of phthalocyanines, no appreciable difference is expected upon

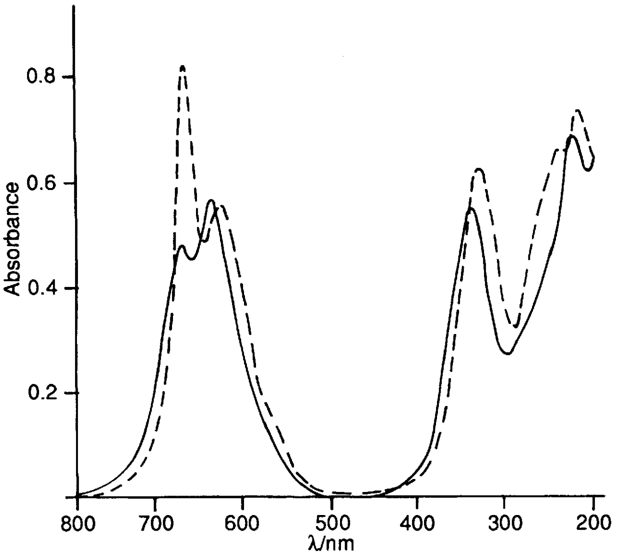


Fig. 2 Electronic spectra of **3** (——) and **7a** (– – –) in water

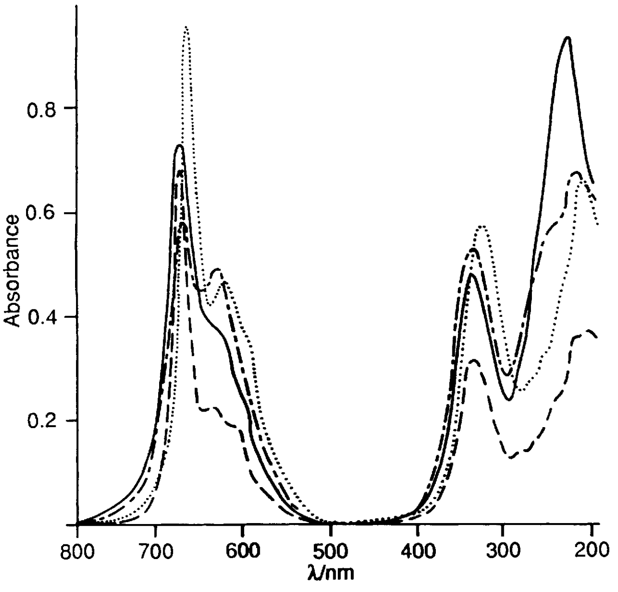


Fig. 3 Electronic spectra of pentanuclear chloride salts in water; **5** (——), **6** (– – –), **7** (–•–•–) and **8** (••••)

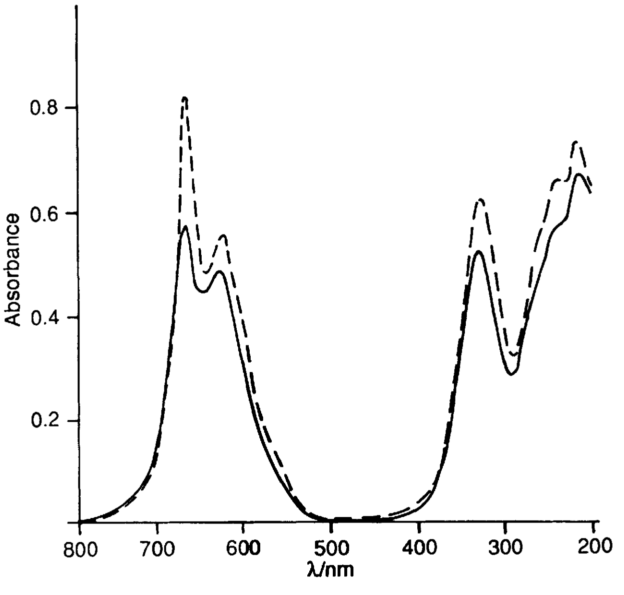


Fig. 4 Electronic spectra of **7** (——) and **7a** (– – –) in water

Table 3 Thermal properties of the phthalocyanine complexes

Compound	Dehydration temp./°C	Initial decomposition temp./°C	Main decomposition temp./°C
2	—	300	350
3	—	250	325
3a	—	250	300
4	—	230	300
4a	—	225	275
5	130	350	405
6	—	335	430
7	140	290	420
8	145	355	400

complexation of macroaza groups,[15] and any variation is the result of aggregation phenomena (Fig. 2). The spectra of the pentanuclear phthalocyanine complexes in water are shown in Fig. 3 and indicate the pesence of discrete species. Increasing the polarity of the solvent has been shown to generally result in the aggregation of phthalocyanines.[5,16–18] The reason why the pentanuclear phthalocyanine complexes **5–8** do not display aggregation behaviour in water is possibly a result of the 1:1 complexation of the tetraaza macrocycles with M^{2+} transition-metal centres, which increases the overall charge of the phthalocyanine complexes. The effect of different counter anions on the solution properties of the pentanuclear compounds have been investigated for the Cu_5 derivatives **7** (X = Cl) and **7a** (X = ClO_4). The UV/VIS spectra of these two phthalocyanine complexes show the same pattern with only slight change in molar absorption coefficients (Fig. 4). Consequently, similar participation of these anions in complex formation can be predicted. When the thermal properties of the new phthalocyanine complexes **5**, **7** and **8** were investigated by thermogravimetric analysis (TGA), they showed a weight loss corresponding to eight water molecules at *ca.* 140 °C (Table 3). Initial decomposition occurs at *ca.* 290–355 °C and then extensive decomposition occurs at *ca.* 400–430 °C. These temperatures are higher than those found for crown ether-substituted phthalocyanine complexes.[6] Even the catalytic effect of transition-metal ions co-ordinated into the tetraaza-macrocycles does not cause a significant lowering in the decomposition temperatures of the phthalocyanine complexes. The properties of the synthesized molecules are consistent with the formation of supramolecular entities possessing a central phthalocyanine core surrounded by four cyclic voids which are capable of complexing transition-metal cations. The significantly enhanced solubility in water upon the co-ordination of transition-metal ions to the peripheral donor group is comparable to that observed on adding anionic (sulphonate) or cationic (ammonium) substituents on the aromatic ring, and should be mentioned as a significant result of this work.

Experimental

Routine IR spectra were recorded on a Perkin-Elmer 983 Spectrophotometer as KBr pellets. Electronic spectra were recorded on a Varian DMS 90 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of TUBITAK Gebze Research Center. 1,4,8,11-Tetraazaundecane was prepared according to the reported procedures[19] and its tetra(tosyl) derivative isolated by usual methods.[20] Thermogravimetric analyses were run on a Du Pont differential thermo-instrument type 990 at 10 °C min^{-1} in a nitrogen flow (100 cm^3 min^{-1}).

Synthesis.—*15,16-Dibromo-2,5,9,12-tetra(toluene-*p*-sulphonyl)2,3,4,5,6,7,8,9,10,11,12,13-dodecahydro-*1H*-2,5,9,12-benzotetraazacyclopentadecine* **1**. The compound 1,4,8,11-tetrakis (toluene-*p*-sulphonyl)-1,4,8,11-tetraazaundecane (28.50 g, 37 mmol) was dissolved in absolute ethanol (700 cm^3) containing finely-ground anhydrous K_2CO_3 (12.39 g, 88 mmol) and refluxed for 1 h. A solution of 1,2-dibromo-4,5-bis(bromomethyl)-benzene (19.20 g, 45.52 mmol) in absolute ethanol (320 cm^3) was added dropwise over a period of 8 h. After refluxing the reaction mixture for a further 24 h, the solvent was removed by distillation and the yellow residue dissolved in CH_2Cl_2 (100 cm^3) and filtered to separate any inorganic residue. The filtrate was evaporated to dryness and the yellowish white residue was chromatographed (silica gel, CH_2Cl_2). Yield: 15 g (40%). This compound was soluble in chloroform, dichloromethane, ethanol, dmso and dimethylformamide (dmf). M.p. 253–255 °C (decomp.); ν_{max}/cm^{-1} 550, 660, 690, 740, 810, 930, 1020–1040, 1090, 1160, 1340, 1450, 1490, 1600 and 2940–3150; NMR ($CDCl_3$): ^1H, δ 1.30 (2 H, t), 2.43 (6 H, s), 2.46 (6 H, s), 2.92 (8 H, m), 3.19 (4 H, t), 4.27 (4 H, s), 7.30–7.78 (18 H, m). ^{13}C, δ 21.57, 27.73, 48.17, 48.66, 49.28, 124.94, 127.27, 127.48, 129.90, 130.14, 134.13, 134.28, 134.50, 134.88, 143.83 and 144.35.

Complex **2**. A mixture of **1** (2 g, 1.93 mmol), CuCN (0.5 g, 5.58 mmol) and dry tmu (1.7 cm^3) was heated and stirred at 195–200 °C in a sealed glass tube for 5 h under argon. After cooling to room temperature the dark green mixture was diluted with ethanol (10 cm^3) and the crude product was precipitated. This was filtered off and washed with hot ethanol to remove unreacted organic material. The precipitate was then refluxed four times with a solution of NaCN in water–ethanol (1:2) to remove excess CuCN and filtered off. The greenish blue powder was then washed further with H_2O, refluxed with EtOH and filtered off, washed with diethyl ether and dried. Yield: 0.645 g (35%). This compound was soluble in chloroform, dichloromethane, dmf and dmso; ν_{max}/cm^{-1} 550, 660, 690–730, 820, 940, 1020–1040, 1090, 1160, 1340, 1450, 1490, 1600, 1620 and 2940–3150.

Complex **3** (*detosylation of* **2** *with* H_2SO_4). Compound **2** (3.75 g, 0.99 mmol) was treated with concentrated (98%) H_2SO_4 (40 cm^3) at 130–135 °C for 6 h. After cooling it was poured into cold ethanol (200 cm^3) and centrifuged. The greenish blue precipitate was mixed with EtOH to remove excess H_2SO_4, centrifugated and then dried with diethyl ether to give the protonated sulphate salt **3a**. Yield: 1.90 g (90%); ν_{max}/cm^{-1} 680, 720, 750, 890, 1050, 1120–1220, 1340, 1410, 1450, 1620, 2900–2960 and 3200.

Compound **3a** (1.9 g, 0.91 mmol) was then dissolved in H_2O (40 cm^3) and the pH of the mixture was raised to 12 by addition of an aqueous solution of NaOH (2 mol dm^{-3}). The solution was extracted with portions (3 × 50 cm^3) of chloroform. The combined extracts were dried over anhydrous Na_2SO_4 and the solvent evaporated to dryness. The dark blue crude product was dissolved in absolute ethanol (5 cm^3), the mixture filtered and the filtrate was evaporated to dryness to afford the pure product. This compound was soluble in methanol, ethanol and dmso. Yield: 0.450 g (37%); ν_{max}/cm^{-1} 710, 750, 900, 1030, 1100, 1320, 1410, 1450, 1500, 1620, 2900–2960 and 3250.

Complex **4**. A 100 cm^3 flask was charged with **3** (0.055 g, 4.2×10^{-2} mmol), Na_2CO_3 (0.144 g, 1.344 mmol), absolute methanol (20 cm^3) and excess dimethyl sulphate (0.53 g, 4.2 mmol) and stirred at reflux temperature for 36 h under argon. The mixture was then filtered and the volume of the filtrate reduced to 5 cm^3. The resulting dark blue precipitate was filtered off, washed with dry diethyl ether and dried at 100 °C. The yield of the hygroscopic product was 0.060 g (25%); ν_{max}/cm^{-1} 590, 620, 760, 1000, 1060, 1120, 1220–1260, 1400, 1470, 1640, 2680 and 2980–3020.

Complex **4a**. Complex **4** (0.040 g, 1.12×10^{-2} mmol) was dissolved in H_2O–$HClO_4$ (1:2, 6 cm^3), under argon, and precipitated with ethanol (1 cm^3). The resulting dark blue precipitate was filtered off, washed with dry ethanol until the filtrate was neutral, washed further with dry diethyl ether and then dried at 100 °C. Yield: 0.030 g (79%); ν_{max}/cm^{-1} 640, 750, 1040–1150, 1340, 1400, 1470, 1640, 2680 and 2980–3020.

Complex **5**. To a stirred solution of **3** (0.120 g, 9.14×10^{-2} mmol) in absolute methanol (30 cm^3) was added a solution of $CoCl_2 \cdot 6H_2O$ (0.261 g, 1.096 mmol) in absolute methanol (5 cm^3). The mixture was refluxed for 3 h under argon. The dark blue precipitate was filtered off and washed with absolute methanol and then with diethyl ether. Yield: 0.150 g (83%); ν_{max}/cm^{-1} 710, 750, 880, 940, 980, 1020, 1050, 1100, 1170, 1190, 1240, 1430, 1500, 1620, 2860–2960 and 3200.

Complex **5a**. To a stirred solution of **3** (0.150 g, 0.114 mmol) in ethanol (30 cm^3) was added a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.501 g, 1.370 mmol) in ethanol (5 cm^3). The mixture was refluxed for 3 h. The resulting dark blue precipitate was filtered off, washed with ethanol to remove the excess metal salt, and then with diethyl ether. Yield: 0.225 g (84%); ν_{max}/cm^{-1} 640, 710, 750, 880, 940, 980, 1040–1150, 1240, 1330, 1440, 1500, 1620, 2880–2940 and 3220.

CAUTION: Transition-metal perchlorates are known to explode. These materials should be made only in small quantities and treated with extreme caution.

Complex **6**. Prepared as described for **5**, starting from **3** (0.045 g, 0.034 mmol) and $NiCl_2$ (0.053 g, 0.408 mmol). The reaction was carried out under argon. Yield: 0.050 g (79%); ν_{max}/cm^{-1} 710, 750, 870, 940, 980, 1030, 1070, 1110, 1170, 1190, 1240, 1330, 1430, 1500, 1620, 2880–2940 and 3240.

Complex **6a**. Prepared as described for **5a**, starting from **3** (0.150 g, 0.114 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.501 g, 1.370 mmol). Yield: 0.200 g (75%); ν_{max}/cm^{-1} 640, 710, 750, 870, 940, 980, 1040–1150, 1240, 1330, 1450, 1500, 1620, 2870–2940 and 3240.

Complex **7**. Prepared as described for **5**, starting from **3** (0.150 g, 0.114 mmol) and $CuCl_2 \cdot 2H_2O$ (0.234 g, 1.370 mmol). Yield: 0.195 g (86%); ν_{max}/cm^{-1} 710, 750, 870, 960, 1030, 1070, 1100, 1170, 1190, 1240, 1330, 1430, 1500, 1620, 2870–2940 and 3200.

Complex **7a**. Prepared as described for **5a**, starting from **3** (0.150 g, 0.114 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.500 g, 1.370 mmol). Yield: 0.246 g (91%); ν_{max}/cm^{-1} 640, 710, 750, 870, 940, 980, 1040–1150, 1240, 1330, 1440, 1500, 1620, 2870–2940 and 3200.

Complex **8**. Prepared as described for **5**, starting from **3** (0.150 g, 0.114 mmol) and $ZnCl_2$ (0.187 g, 1.370 mmol). Yield: 0.180 g (79%); ν_{max}/cm^{-1} 710, 750, 870, 960, 980, 1030, 1050, 1100, 1170, 1190, 1240, 1330, 1450, 1500, 1620, 2880–2940 and 3220.

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