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Inorganica Chimica Acta 357 (2004) 3279–3288
Inorganica Chimica Acta
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Effect of pyrazole-substitution on the structure and nuclearity of Cu(II)-pyrazolato complexes

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Received 25 February 2004; accepted 13 March 2004
Available online 8 May 2004

Abstract

Trinuclear Cu(II)-pyrazolates of the general formula $(Bu_4N)_2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}4\text{-}R\text{-}pz)_3Cl_3]$ (pz = pyrazolato anion, R = Cl, Br, I, Me), **1**–**4**, have been prepared and characterized by X-ray diffraction and/or ^1H NMR, IR, UV–Vis spectroscopy and elemental analysis. Their structure and spectroscopic properties match the ones of the parent unsubstituted complex $(Bu_4N)_2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}pz)_3Cl_3]$, indicating that 4-substitution of the pyrazole ligands with halogen or methyl groups does not induce structural variation. In contrast, dinuclear complexes $(Bu_4N)_4[Cu_2(\mu\text{-}3\text{-}Me\text{-}pz)_2Cl_4]Cl_2 \cdot 4H_2O$, $Cu_2(\mu\text{-}Cl)(\mu\text{-}3,5\text{-}Me_2\text{-}pz)(3,5\text{-}Me_2\text{-}pzH)_4Cl_2$, $Cu_2(\mu\text{-}Cl)(\mu\text{-}OH)(3\text{-}Me\text{-}5\text{-}Ph\text{-}pzH)_4Cl_2 \cdot 3\text{-}Me\text{-}5\text{-}Ph\text{-}pzH$ and $Cu_2(\mu\text{-}Cl)_2(3,5\text{-}Ph_2\text{-}pzH)_4Cl_2$, **5**–**8**, have been prepared with 3- and 3,5-substituted pyrazoles by the same or similar synthetic protocols.

Keywords: Copper; Pyrazole; Dinuclear complexes; Trinuclear complexes

1. Introduction

Triangular trinuclear copper(II)-complexes have been generating great interest due to their unusual magnetic and spectral properties [1], interesting redox chemistry [2] and the potential to model the active sites of several multicopper enzymes (e.g., ascorbate oxidase [3], laccase [3], ceruloplasmin [3], particulate methane monooxygenase [4]) [5]. Recently, we have shown that the nine-membered $(Cu–N–N)_3$ framework formed by three pyrazolato anions (pz) and three Cu(II)-centers can accommodate different μ_3-bridging anions (O^{2-}, HO^-, Cl^-, Br^-) [6]. The controlled interchange of these anions brings about an orderly transition from antiferromagnetic to ferromagnetic exchange among the copper centers [7]. Ferromagnetically coupled Cu_3-complexes are especially important as they are closely related to the also ferromagnetic active centers of particulate methane monooxygenase [8]. In order to further explore the possibilities of chemical diversification of trinuclear Cu(II)-pyrazolates, a synthetic and structural study on the peripheral substitution of the pyrazolate ligands has been undertaken. The outcome was expected to provide insight into the molecular and crystal structure, as well as physico-chemical properties of new trinuclear Cu(II)-pyrazolate complexes.

2. Experimental

2.1. Materials and methods

All commercially available reagents were used as received. Pyrazole, 4-methyl-pyrazole, 3-methyl-pyrazole and 3,5-dimethyl-pyrazole were purchased from Aldrich Chemical Company. 4-Chloro-pyrazole [9], 4-bromo-pyrazole [9], 3,5-diphenyl-pyrazole [10] and $Cu(CH_3CN)_4PF_6$ [11] were prepared according to the literature procedures. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared, NMR and UV–Vis spectra were recorded on a Nicolet FT-IR 6000, Bruker Advance DRX-500 and Varian Cary 500 Scan, respectively, at room temperature. Melting points were measured on an Electrothermal IA9100 apparatus and are reported without correction.

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0020-1693/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2004.03.016

X-ray diffraction data, collected at room temperature from a single crystal mounted atop a glass fiber with a Bruker AXS SMART 1K CCD diffractometer, graphite-monochromated Mo Kα radiation [12a], were corrected for Lorentz and polarization effects [12b]. The structures were solved employing the SHELXTL-direct methods program and refined by full-matrix least-squares methods on F^2 [12c]. Crystallographic details are summarized in Table 1.

2.2. Synthesis of 4-iodo-pyrazole

Pyrazole (5.00 g, 73 mmol) and anhydrous Na_2CO_3 (4.10 g, 39 mmol) are dissolved in 60 ml hot H_2O. A solution of I_2 (18.64 g, 73 mmol) and KI (26.00 g, 157 mmol) in 70 ml H_2O is added dropwise. The reaction mixture is kept at 100 °C for 30 min, 70 ml H_2O is added, it is brought to reflux and filtered hot. Slightly yellowish needles separate from the light red solution upon cooling to 0 °C, which are filtered out, washed with ice-cold water and air-dried. Yield: 11.26 g (79%). M.p. 105–107 °C. Recrystallization from water gives shiny, colorless needles of 4-iodo-pyrazole. ^{1}H NMR ($CDCl_3$, ppm): 7.64 (s, 2H, *H*-3 and *H*-5), 11.95 (s, br, 1H, N*H*). ^{13}C NMR ($CDCl_3$, ppm): 56.4 (*C*-3 and *C*-5), 138.6 (broad, *C*-4). IR (KBr pellet, cm^{-1}): 610s, 648w, 653w, 812s, 872s, 938s, 954m, 1033m, 1142m, 1178w, 1268w, 1321m, 1328m, 1365s, 1456w, 1475w, 1537m, 2788s, 2844s, 2909s, 2957s, 3040s, 3114s, 3123s.

2.3. Synthesis of 3(5)-methyl-5(3)-phenyl-pyrazole

The procedure for the preparation of 3,5-diphenyl-pyrazole is adopted for use here [10]. Benzoylacetone (19.26 g, 0.12 mol) is suspended in 40 ml EtOH 95% and hydrazine monohydrate (7.5 ml, 7.74 g, 0.15 mol) is added dropwise, under stirring. The solid quickly dissolves and a clear, yellowish solution is obtained. *CAUTION*! The reaction is highly exothermic and might cause vigorous boiling. The reaction mixture is refluxed for 30 min, then cooled to room temperature. A snow-white, voluminous, cotton-like solid forms, which is taken up as a suspension into 150 ml distilled water, filtered, washed thoroughly with water and dried in an oven. This material is sufficiently pure (as indicated by its clean ^{1}H NMR spectrum) and has been used without further purification. Yield: 17.98 g (96%). M.p. 128–129 °C. ^{1}H NMR ($CDCl_3$, ppm): 2.24 (s, 3H, C*H*$_3$), 6.33 (s, 1H, *H*-4$_{pz}$), 7.29 (t, 1H, *H*-para$_{Ph}$), 7.35 (t, 2H, *H*-meta$_{Ph}$), 7.72 (d, 2H, *H*-ortho$_{Ph}$), 11.78 (s, br, 1H, $w_{1/2}=$, N*H*). ^{13}C NMR ($CDCl_3$, ppm): 11.4 (*C*H$_3$), 101.9 (*C*-4$_{pz}$), 125.7 (*C*-ortho$_{Ph}$), 127.6 (*C*-para$_{Ph}$), 128.5 (*C*-meta$_{Ph}$), 132.6 (*C*-ipso$_{Ph}$), 142.93 (C_{pz}–CH_3), 149.9 (C_{pz}–Ph). The ^{13}C NMR assignments have been made according to previous results in different solvents [13]. IR (KBr pellet, cm^{-1}): 510w, 644w, 690s, 716w, 764s, 795w, 832w, 876w, 910w, 964m, 1032w, 1060w, 1077m, 1103w, 1153w, 1178w, 1204m, 1275w, 1294w, 1313w, 1329w, 1375w, 1409w, 1462m, 1515m, 1574m, 1580m, 1590s, 2756m, 2826m, 2855m, 2899m, 2952m, 2975m, 3012m, 3086s, 3128m, 3184m.

2.4. Synthesis of $Cu_3(3,5\text{-}Ph_2\text{-}pz)_3$

$Cu(CH_3CN)_4PF_6$ (3.579 g, 9.60 mmol) and 3,5-diphenyl-pyrazole (2.115 g, 9.60 mmol) are dissolved in 25 ml acetone with stirring to give a clear, slightly green solution. Dropwise addition of Et_3N (1.6 ml, 1.162 g, 11.48 mmol) induces the formation of a white precipitate, which is stirred for 30 min, then filtered, washed with three 5 ml portions of acetone and vacuum-dried. Yield: 2.701 g (99%). ^{1}H NMR ($CDCl_3$, ppm): 6.77 (s, 1H, *H*-4$_{pz}$), 7.08 (t, 4H, *H*-meta$_{Ph}$), 7.21 (t, 2H, *H*-para$_{Ph}$), 7.71 (d, 4H, *H*-ortho$_{Ph}$). ^{13}C NMR ($CDCl_3$, ppm): 102.2 (*C*-4$_{pz}$), 126.6 (*C*-ortho$_{Ph}$), 128.0(*C*-para$_{Ph}$), 128.6 (*C*-meta$_{Ph}$), 132.6 (*C*-ipso$_{Ph}$), 155.1 (*C*-3(5)$_{pz}$).

2.5. $(Bu_4N)_2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}4\text{-}Cl\text{-}pz)_3Cl_3]$ (**1**)

$CuCl_2 \cdot 2H_2O$ (128 mg, 0.75 mmol), 4-chloro-pyrazole (77 mg, 0.75 mmol), NaOH (30 mg, 0.75 mmol) and Bu_4NCl (139 mg, 0.5 mmol) are stirred in 10 ml CH_2Cl_2 for 12 h, at ambient temperature, and NaCl is filtered out. Treatment of the green filtrate with 50 ml Et_2O crushes out complex **1** as a green solid, which is filtered, washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O. Yield: 235 mg (81%). M.p. 175 °C. *Anal.* for $C_{41}H_{78}Cl_8Cu_3N_8$, calculated/found: C, 42.55/42.67; H, 6.81/6.79; N, 9.68/9.70%. ^{1}H NMR (CD_3CN, ppm): 38.99 ($w_{1/2} = 95.4$ Hz). IR (KBr pellet, cm^{-1}): 618s, 738m, 748m, 757m, 797m, 857s, 876m, 890m, 968vs, 996m, 1028w, 1052vs, 1105w, 1160m, 1201m, 1234w, 1305s, 1328w, 1347w, 1379s, 1400m, 1459s, 1487s, 2876s, 2943s, 2962vs, 3133m, 3141m. UV–Vis (CH_2Cl_2, cm^{-1}): ~12 600 (sh), 14 608, ~27 000 (sh), 35 718. Crystals suitable for X-ray diffraction are obtained by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **1**.

2.6. $(Bu_4N)_2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}4\text{-}Br\text{-}pz)_3Cl_3]$ (**2**)

A similar procedure using $CuCl_2 \cdot 2H_2O$ (980 mg, 5.75 mmol), 4-bromo-pyrazole (845 mg, 5.75 mmol), NaOH (230 mg, 5.75 mmol) and Bu_4NCl (1.065 g, 3.83 mmol) in 30 ml CH_2Cl_2 yields 2.390 g (97%) of **2**. M.p. 176 °C. *Anal.* for $C_{41}H_{78}Br_3Cl_5Cu_3N_8$, calculated/found: C, 38.15/38.31; H, 6.10/6.20; N, 8.68/8.56%. ^{1}H NMR (CD_3CN, ppm): 38.23 ($w_{1/2} = 85.5$ Hz). IR (KBr pellet, cm^{-1}): 452m, 615s, 737m, 748m, 756m, 797w, 858s, 876m, 888m, 952vs, 996m, 1027w, 1052vs, 1109w, 1162s, 1192m, 1232w, 1298s, 1332w, 1351w, 1379s, 1394m, 1459m, 1487s, 2875s, 2942s, 2960vs, 3132m. UV–Vis

Table 1
Crystallographic data

	1	**2**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{41}H_{78}Cl_8Cu_3N_8$	$C_{41}H_{78}Br_3Cl_5Cu_3N_8$	$C_{44}H_{87}Cl_5Cu_3N_8$	$C_{72}H_{162}Cl_6Cu_2N_8O_4$	$C_{25}H_{39}Cl_3Cu_2N_{10}$	$C_{50}H_{51}Cl_3Cu_2N_{10}O$	$C_{60}H_{48}Cl_4Cu_2N_8$
Formula weight	1157.33	1290.71	1096.09	1543.88	713.09	1041.44	1149.94
T (K)	298(2)	298(2)	293(2)	293(2)	298(2)	298(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	18.704(3)	18.880(4)	18.716(2)	10.389(3)	18.110(2)	11.548(2)	13.404(2)
b (Å)	18.674(3)	18.897(4)	18.559(2)	14.226(4)	15.348(2)	22.220(3)	15.162(2)
c (Å)	16.412(3)	16.545(3)	16.639(2)	16.488(5)	12.034(1)	19.744(2)	13.647(2)
α (°)	90	90	90	95.823(5)	90	90	90
β (°)	106.086(3)	106.588(4)	106.349(1)	101.868(5)	94.357(2)	103.095(2)	109.491(2)
γ (°)	90	90	90	98.706(5)	90	90	90
V (Å^3)	5507.9(15)	5657(2)	5546.0(8)	2335(1)	3335.1(6)	4934(1)	2614.7(5)
Z	4	4	4	1	4	4	2
D_{calc} (g cm^{-3})	1.396	1.516	1.313	1.098	1.420	1.402	1.461
μ (mm^{-1})	1.572	3.508	1.417	0.670	1.547	1.072	1.067
$F(000)$	2412	2628	842	2316	1472	2152	1180
Crystal size (mm)	0.20 × 0.14 × 0.03	0.12 × 0.10 × 0.06	0.30 × 0.26 × 0.18	0.38 × 0.10 × 0.09	0.18 × 0.16 × 0.12	0.18 × 0.12 × 0.06	0.12 × 0.10 × 0.06
Reflections collected	12 002	12 326	12 043	10 287	14 304	21 681	11 305
Unique reflections	3969	4083	4001	6709	4808	7106	3756
Observed reflections ($I > 2\sigma(I)$)	3019	2857	3378	5284	3826	4543	2800
θ range (°)	1.57–23.28	1.56–23.32	1.58–23.27	1.46–23.29	1.13–23.28	1.40–23.30	2.08–23.26
Data/restraints/parameter	3969/0/277	4083/0/277	4001/0/280	6709/0/442	4808/0/371	7106/0/602	3756/0/334
$R(F)$; $Rw(F)$ ($I > 2\sigma(I)$)	0.0335; 0.0697	0.0362; 0.0767	0.0252; 0.0710	0.0577; 0.1802	0.0272; 0.0682	0.0383; 0.0789	0.0292; 0.0639
Goodness-of-fit	1.045	0.962	1.077	1.047	1.033	0.986	0.949
Largest peak/hole (e Å^{-3})	0.363/−0.359	0.695/−0.606	0.231/−0.312	0.562/−0.296	0.228/−0.256	0.297/−0.246	0.205/−0.309

(CH_2Cl_2, cm^{-1}): $\sim$12 600 (sh), 14 598, $\sim$27 000 (sh), 36 048.

2.7. $(Bu_4N)_2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}4\text{-}I\text{-}pz)_3Cl_3]$ (**3**)

A similar procedure using $CuCl_2 \cdot 2H_2O$ (298 mg, 1.75 mmol), 4-iodo-pyrazole (845 mg, 1.75 mmol), NaOH (70 mg, 1.75 mmol) and Bu_4NCl (324 mg, 1.17 mmol) in 25 ml CH_2Cl_2 yields 2.390 g (98%) of **3**. M.p. 180 °C. *Anal.* for $C_{41}H_{78}Cl_5Cu_3I_3N_8$, calculated/found: C, 34.39/34.34; H, 5.50/5.50; N, 7.83/7.86%. ^1H NMR (CD_3CN, ppm): 37.62. IR (KBr pellet, cm^{-1}): 419s, 616s, 737m, 799w, 858s, 882s, 914vs, 995w, 1025w, 1055vs, 1106w, 1166s, 1183w, 1289s, 1322w, 1351w, 1378s, 1419w, 1462s, 1483s, 2873s, 2933s, 2961vs, 3129m. UV–Vis (CH_2Cl_2, cm^{-1}): $\sim$12 600 (sh), 14568, $\sim$27 000 (sh), 35578.

2.8. $(Bu_4N)_2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}4\text{-}Me\text{-}pz)_3Cl_3]$ (**4**)

A similar procedure using $CuCl_2 \cdot 2H_2O$ (469 mg, 2.75 mmol), 4-methyl-pyrazole (226 mg, 2.75 mmol), NaOH (110 mg, 2.75 mmol) and Bu_4NCl (510 mg, 1.84 mmol) in 10 ml CH_2Cl_2 yields 990 mg (99%) of **4**. M.p. 191 °C. *Anal.* for $C_{44}H_{87}Cl_5Cu_3N_8$, calculated/found: C, 48.20/48.14; H, 8.01/8.40; N, 10.22/10.26%. ^1H NMR (CD_3CN, ppm): 35.04. IR (KBr pellet, cm^{-1}): 405w, 630m, 678w, 748w, 799w, 851m, 860m, 876m, 887w, 990w, 1016s, 1030w, 1069vs, 1106w, 1156w, 1175m, 1318m, 1349w, 1378m, 1459m, 1486s, 2875s, 2941s, 2961vs, 2997m, 3093w, 3116w, 3136w. UV–Vis (CH_2Cl_2, cm^{-1}): $\sim$9759 (sh), $\sim$12 600 (sh), 14 608, $\sim$27 000 (sh), 30 488, $\sim$36 000 (sh).

2.9. $(Bu_4N)_4[Cu_2(\mu\text{-}3\text{-}Me\text{-}pz)_2Cl_4]Cl_2 \cdot 4H_2O$ (**5**)

$CuCl_2 \cdot 2H_2O$ (456 mg, 2.68 mmol), 3-methyl-pyrazole (220 mg, 2.68 mmol), NaOH (107 mg, 2.68 mmol) and Bu_4NCl (721 mg, 2.59 mmol) are stirred in 10 ml CH_2Cl_2 for 12 h, at ambient temperature, and the solution is filtered. Treatment of the green filtrate with 30 ml Et_2O crushes out a green oily material; the supernatant liquid is decanted, the oil washed with Et_2O and let in air. After several weeks the green oil transforms into a soft, orange crystalline mass. After a suitable crystal for X-ray diffraction is isolated, the solid is taken up into Et_2O, filtered and air-dried. Yield: 543 mg. M.p. 69 °C (the color of the melt is green). IR (KBr pellet, cm^{-1}): 405m, 516w, 641w, 661w, 673w, 739m, 759s, 794w, 886m, 924w, 955m, 1006w, 1030m, 1082m, 1125m, 1151w, 1168w, 1205w, 1284w, 1316w, 1346s, 1383s, 1469s, 1485s, 1496m, 1626w, 2874s, 2938s, 2961s, 3105w, 3122w, 3361m, 3444m. UV–Vis (CH_2Cl_2, cm^{-1}): $\sim$9100 (sh), 14 078, $\sim$26 500 (sh), $\sim$29 000 (sh), $\sim$36 000 (br), $\sim$39 500 (br).

2.10. $Cu_2(\mu\text{-}Cl)(\mu\text{-}3,5\text{-}Me_2\text{-}pzH)(3,5\text{-}Me_2\text{-}pzH)_4Cl_2$ (**6**)

$CuCl_2 \cdot 2H_2O$ (352 mg, 2.06 mmol), 3,5-dimethyl-pyrazole (198 mg, 2.06 mmol) and NaOH (110 mg, 2.75 mmol) are stirred in 10 ml THF for 15 h, at ambient temperature. The green solution is filtered and an equal volume of hexanes is added. A green solid is filtered out, washed with hexanes and dried at 90 °C. Crystals are obtained by layering an Et_2O solution with hexanes. Yield: 147 mg. M.p. 168 °C. IR (KBr pellet, cm^{-1}): 434m, 605m, 660m, 680m, 744w, 759m, 789s, 810s, 981w, 1027s, 1042s, 1117w, 1153m, 1174s, 1278s, 1345m, 1380m, 1417s, 1472s, 1528m, 1572vs, 1622w, 2860m, 2925s, 2958s, 3035m, 3111s, 3141s, 3265vs. UV–Vis (CH_2Cl_2, cm^{-1}): 13 508, $\sim$24 300 (sh), $\sim$28 500 (sh), 37 388.

2.11. $Cu_2(\mu\text{-}Cl)(\mu\text{-}OH)(3\text{-}Me\text{-}5\text{-}Ph\text{-}pzH)_4Cl_2 \cdot 3\text{-}Me\text{-}5\text{-}Ph\text{-}pzH$ (**7**)

A similar procedure using $CuCl_2 \cdot 2H_2O$ (336 mg, 1.97 mmol), 3-methyl-5-phenyl-pyrazole (311 mg, 1.97 mmol) and NaOH (105 mg, 2.63 mmol) yields crystals of **7** (178 mg) by slow evaporation of the filtered mother liquor. M.p. $\sim$190 °C (decomp.). IR (KBr pellet, cm^{-1}): 449w, 487w, 503w, 534w, 614m, 628m, 664m, 692s, 717m, 762vs, 794s, 802s, 913w, 962m, 1002m, 1029s, 1041s, 1073w, 1169m, 1205s, 1267s, 1294s, 1413m, 1473s, 1500s, 1565s, 1587w, 2871m, 2925m, 2965m, 3031m, 3057m, 3132s, 3241vs, 3445m. UV–Vis (CH_2Cl_2, cm^{-1}): $\sim$11 400 (br), $\sim$12 600 (br), $\sim$24 600 (sh), $\sim$28 500 (sh), 39 368.

2.12. $Cu_2(\mu\text{-}Cl)_2(3,5\text{-}Ph_2\text{-}pzH)_4Cl_2$ (**8**)

A similar procedure using $CuCl_2 \cdot 2H_2O$ (374 mg, 2.19 mmol), 3,5-diphenyl-pyrazole (483 mg, 2.19 mmol) and NaOH (117 mg, 2.93 mmol) yields crystals of **8** (280 mg) by layering a THF solution with hexanes. M.p. 207 °C. IR (KBr pellet, cm^{-1}): 549m, 628w, 659w, 668w, 692s, 760vs, 808w, 815w, 919w, 980m, 1001w, 1028w, 1060m, 1081m, 1103m, 1190s, 1257m, 1295w, 1321w, 1395w, 1414w, 1446m, 1458s, 1472s, 1486s, 1566s, 1611w, 3035m, 3048m, 3065m, 3137m, 3209s, 3431m. UV–Vis (CH_2Cl_2, cm^{-1}): 11 635, 23 158, 28 958, $\sim$40 000 (br).

3. Results and discussion

3.1. Synthesis

The trinuclear complexes **1**–**4** are prepared similarly as the parent compound, $(Bu_4N)_2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}pz)_3Cl_3]$ (**9**) [6]. In a typical synthesis, equimolar amounts of $CuCl_2 \cdot 2H_2O$, 4-substituted pyrazole (4-R-pzH; R = H, Cl, Br, I, Me, NO_2), NaOH and Bu_4NCl

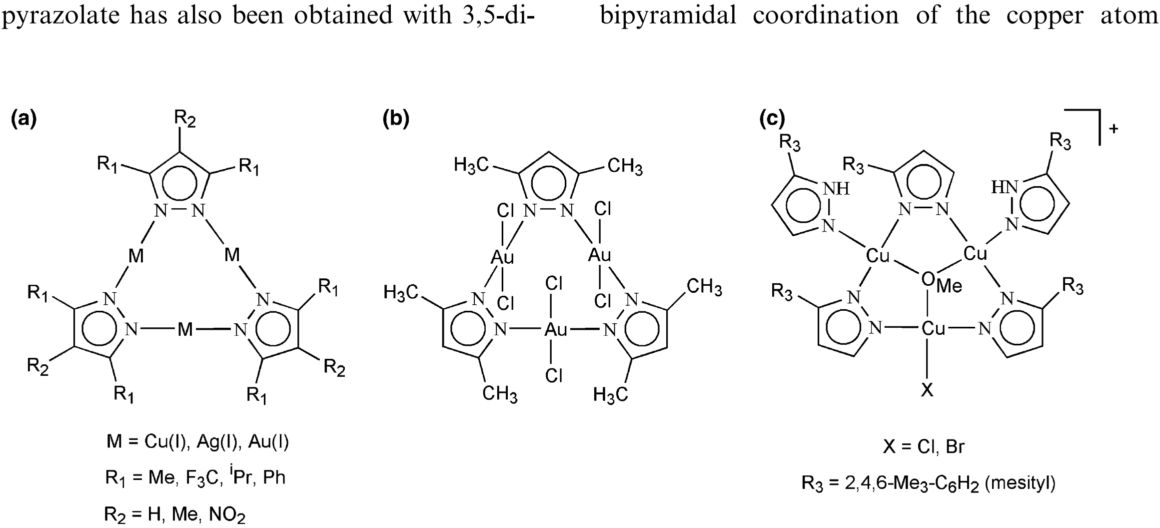
are stirred together in dichloromethane, to give the corresponding trinuclear complex in nearly quantitative yield. Under the same experimental conditions, however, 3- and 3,5-substituted pyrazoles fail to provide similar complexes. The product of the reaction employing 3-methyl-pyrazole has been crystallized and shown by X-ray crystallography to be a dinuclear complex. Since trinuclear Cu(II)-pyrazolates with unsubstituted pyrazole can easily be obtained under several different conditions and in various solvents [6], two alternative procedures have also been tried using 3,5-disubstituted pyrazoles. In one procedure, $CuCl_2 \cdot 2H_2O$ is reacted with the corresponding 3,5-disubstituted pyrazole (3,5-Me_2-pzH, 3-Me-5-Ph-pzH or 3,5-Ph_2-pzH) and NaOH in a 3:3:4 molar ratio in tetrahydrofuran. In each case, the product of the reaction has been identified to be a dinuclear complex. In the other procedure, the copper(I)-trimer Cu_3(3,5-Ph-pz)$_3$ is oxidized with aqueous H_2O_2 in the presence of Bu_4NCl. Again, the isolated product of the reaction is the dinuclear complex **8**.

A possible explanation for this observation is that there is a steric hindrance between the 3- or 3,5-substituents of the pyrazole ligands and the terminal chlorine atoms attached to the copper centers. The deformation of the copper-pyrazolate framework, in order to avoid that repulsion, seems unfavorable over the formation of dinuclear structures. A fact that supports this presumption is that several two-coordinate Cu(I)$_3$- [14], as well as Ag(I)$_3$- [14e,15] and Au(I)$_3$-pyrazolates [15a,16] with various 3,5-substituted pyrazoles (no terminal halogen ligands) are known (Scheme 1(a)). [M(μ-3,5-R_2-pz)]$_3$ frameworks of four-coordinate M-centers are known only with the two additional ligands perpendicular to the (M–N–N)$_3$-plane (Scheme 1(b)): in Cu_3[μ-3,5-(F_3C)$_2$-pz]$_5$, the four-coordination around the two Cu(II) centers is completed by two extra bridging 3,5-(F_3C)$_2$-pz ligands, one on either side of the planar Cu(II)$_2$Cu(I)[(F_3C)$_2$pz]$_3^{2+}$ framework [17]. Moreover, a Au(III)$_3$-pyrazolate has also been obtained with 3,5-dimethyl-pyrazole; in this case the Au-Cl bonds are oriented above and below, not *in* the plane of the Au_3-trimer, thus allowing sufficient space for the pyrazolate ligands' methyl substituents [18]. In the recently reported [Cu_3(μ_3-OMe)(μ-3-R-pz)$_3$X(3-R-pzH)$_2$]X (R = mesityl, X = Cl, Br), only one copper atom bears a halogen ligand; the two adjacent pyrazole groups orient their mesityl substituents away from it, in order to avoid steric crowding (Scheme 1(c)). This trinuclear structure does not persist in solution, however [19].

Compounds **1**–**4**, **9** and the NO_2-substituted analogue (Bu_4N)$_2$[Cu_3(μ_3-Cl)$_2$(μ-4-NO_2-pz)$_3$$Cl_3$] (**10**) [7], are insoluble in cold or boiling diethyl ether, hexane, benzene, toluene and ethyl acetate (exception is **10** which is soluble in ethyl acetate). They are sparingly soluble in cold THF, chloroform and ethanol, fairly soluble in cold methanol, dichloromethane and acetone and very soluble in cold acetonitrile, nitromethane, dimethylsulfoxide and *N*,*N*-dimethylformamide. The solubilities increase in the order: **1** < **2** < **3** < **9** < **4** < **10**. Only **9** is soluble in water. **5**–**8** are soluble in polar organic solvents and **6** is also very soluble in diethyl ether.

3.2. Description of the crystal structures

Compounds **1**, **2** and **4** are isostructural. They crystallize in the same space group, *C*2/*c*, as the parent compound **9**, but are not isostructural with it. Their structures consist of a nine-membered (Cu–N–N)$_3$ metallacycle, with a C_2-axis running through a terminal Cl–Cu bond and bisecting the pyrazolate ring on the opposite side of the metallacycle (Fig. 1). The three Cu-atoms, three terminal chlorides and one pyrazolate ring form a planar unit; the remaining two pyrazolate rings are bent one above and one below this plane (Fig. 2). Two unsymmetrically capping chlorine atoms, one on either side of the metallacycle (at 1.666–1.681 Å from the Cu_3-plane), complete the distorted trigonal bipyramidal coordination of the copper atoms. The



Scheme 1.

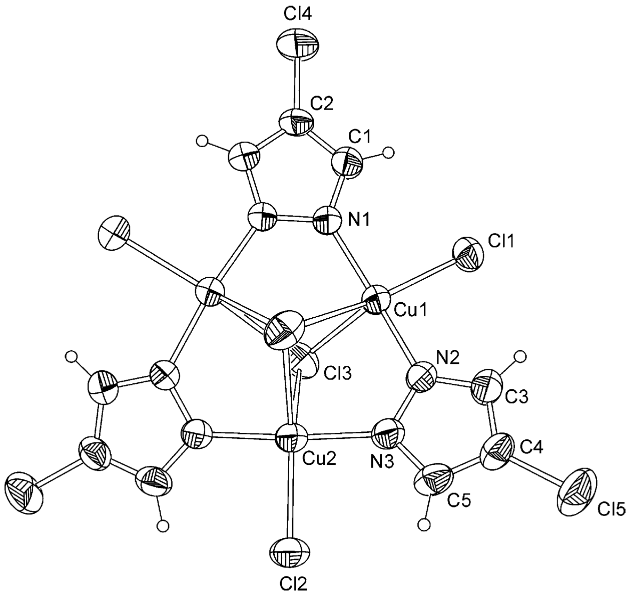


Fig. 1. ORTEP drawing for compound **1**, viewed perpendicular to the C_2-axis. Thermal ellipsoids are shown at the 50% probability level.

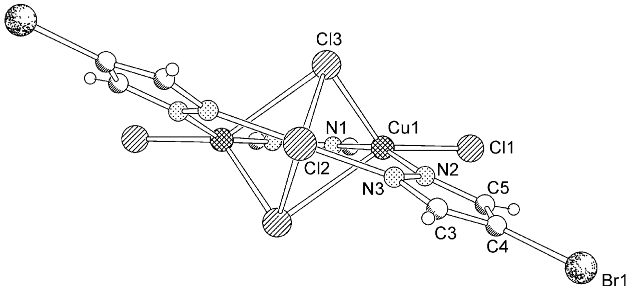


Fig. 2. Ball-and-stick representation for compound **2**, viewed along the C_2-axis.

intramolecular Cu–Cu distances range from 3.3962(8) to 3.4864(6) Å. There are no significant intermolecular interactions between the trinuclear units.

Bond lengths and angles for **1**, **2** and **4** (Table 2) do not vary significantly with substitution of the pyrazole 4-position with Cl, Br or Me groups, as compared with the unsubstituted **9** [6]. Although similar bond lengths are also observed in the case of **10** [7], there are two notable differences between the structure of the latter and **1**, **2**, **4**, **9**. First, the $[Cu(4\text{-}NO_2\text{-}pz)]_3$ framework of **10** is almost planar, with a slight bowl-shaped deformation. Second, both capping chlorine atoms are symmetrically placed at 2.501(1)–2.628(1) Å from the three copper centers.

A crystal structure analysis is not yet available for **3**, but its trinuclear nature, similar to those of other members of this series, is clearly established based on elemental analysis, IR, ^1H NMR and UV–Vis spectroscopy.

Table 2
Selected bond lengths (Å) and angles (°) for **1**, **2** and **4**

	1	**2**	**4**
Cu(1)···Cu(2)	3.3962(8)	3.4052(9)	3.4045(5)
Cu(1)···Cu(1′)	3.453(1)	3.473(1)	3.4864(6)
Cu(1)–N(1)	1.942(3)	1.944(3)	1.942(2)
Cu(1)–N(2)	1.941(3)	1.940(3)	1.938(2)
Cu(2)–N(3)	1.946(3)	1.947(3)	1.941(2)
Cu(1)–Cl(1)	2.281(1)	2.280(1)	2.3021(7)
Cu(1)–Cl(3)	2.359(1)	2.361(1)	2.3539(7)
Cu(2)–Cl(2)	2.286(1)	2.283(1)	2.301(1)
Cu(2)–Cl(3)	2.545(1)	2.549(1)	2.5602(7)
Cu(1′)–Cl(3)	2.923(1)	2.931(1)	2.9773(7)
N(2)–Cu(1)–N(1)	162.8(1)	162.3(2)	161.37(9)
N(2)–Cu(1)–Cl(1)	92.99(9)	93.4(1)	93.58(6)
N(1)–Cu(1)–Cl(1)	93.82(8)	93.84(9)	94.06(6)
N(2)–Cu(1)–Cl(3)	92.81(9)	92.4(1)	92.72(6)
N(1)–Cu(1)–Cl(3)	94.49(9)	94.6(1)	94.67(6)
Cl(1)–Cu(1)–Cl(3)	131.36(4)	132.32(5)	132.22(3)
Cl(3)–Cu(1)–Cl(3′)	80.67(4)	80.41(4)	81.02(2)
N(3′)–Cu(2)–N(3)	175.5(2)	175.1(2)	174.9(1)
N(3)–Cu(2)–Cl(2)	92.25(9)	92.43(9)	92.55(5)
N(3′)–Cu(2)–Cl(3)	86.87(9)	86.7(1)	86.92(6)
N(3)–Cu(2)–Cl(3)	89.82(9)	89.8(1)	89.35(6)
Cl(2)–Cu(2)–Cl(3)	137.40(2)	137.50(3)	136.95(2)
Cl(3)–Cu(2)–Cl(3′)	85.20(5)	85.00(6)	86.10(3)
Cu(1)–Cl(3)–Cu(2)	87.58(3)	87.73(4)	87.60(2)
Cu(1)–Cl(3)–Cu(1′)	80.88(3)	81.26(4)	80.76(2)

While the few known stable triangular Cu(II)-pyrazolates all involve unsubstituted pyrazoles [6,20] **1**–**4** and **10** are the first examples of such complexes with 4-substituted pyrazoles.

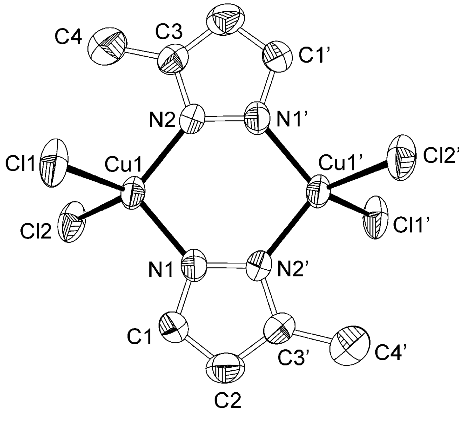


Fig. 3. ORTEP drawing for compound **5**, showing the atom labeling scheme. Thermal ellipsoids at the 30% probability level. Hydrogen atoms omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for **5**

Cu(1)···Cu(1′)	3.810(1)	N(1)–Cu(1)–N(2)	101.3(1)
Cu(1)–N(1)	1.946(3)	N(1)–Cu(1)–Cl(2)	100.3(1)
Cu(1)–N(2)	1.947(3)	N(2)–Cu(1)–Cl(2)	128.2(1)
Cu(1)–Cl(1)	2.260(1)	N(1)–Cu(1)–Cl(1)	127.5(1)
Cu(1)–Cl(2)	2.256(1)	N(2)–Cu(1)–Cl(1)	101.2(1)
		Cl(2)–Cu(1)–Cl(1)	101.76(5)

The structure of **5** (Fig. 3) lies on an inversion center and consists of two Cu atoms held at 3.810(1) Å by two bridging 3-methyl-pyrazolate ligands (crystallographically imposed dihedral angle between pyrazole planes: 180°). Each copper atom bears two terminal chlorine atoms and has a distorted tetrahedral coordination geometry, with angles of 100.3(1)–128.2(1)° (Table 3). The structure of this complex should be different in solution

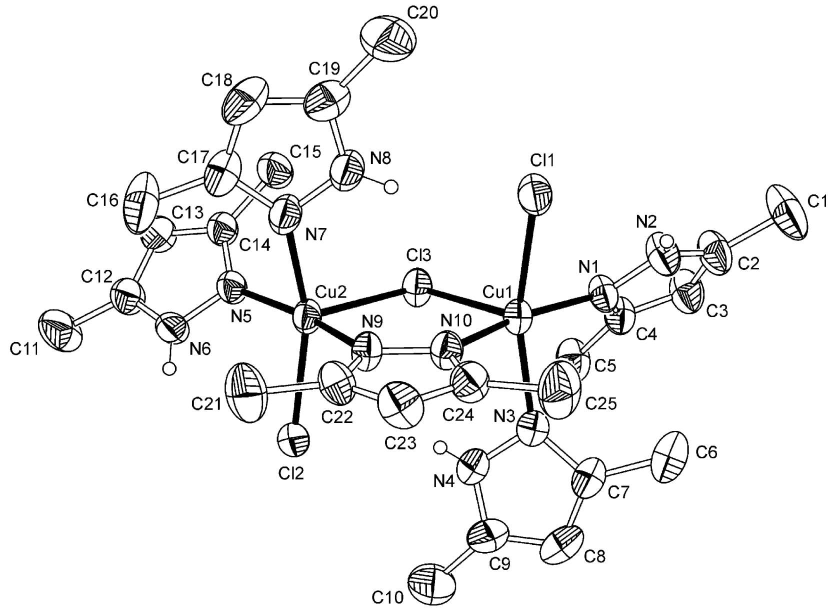


Fig. 4. ORTEP drawing for compound **6**, showing the atom labeling scheme. Thermal ellipsoids at the 50% probability level. C–H hydrogen atoms omitted for clarity.

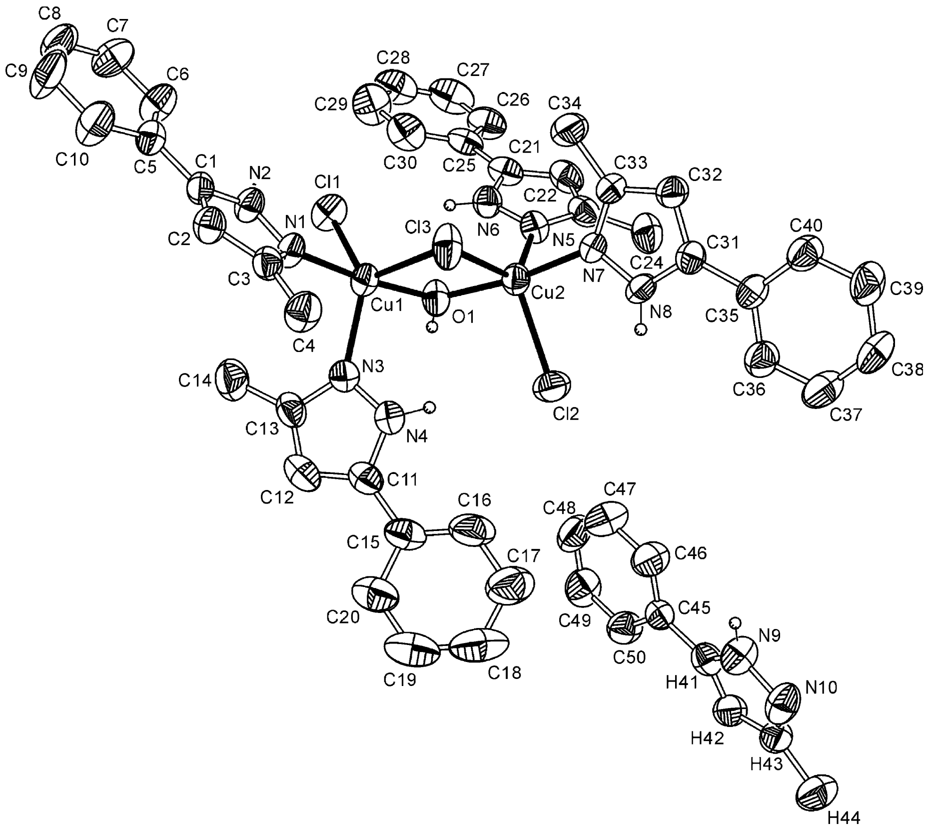


Fig. 5. ORTEP drawing for compound **7**, showing the atom labeling scheme. Thermal ellipsoids at the 50% probability level. C–H hydrogen atoms omitted for clarity.

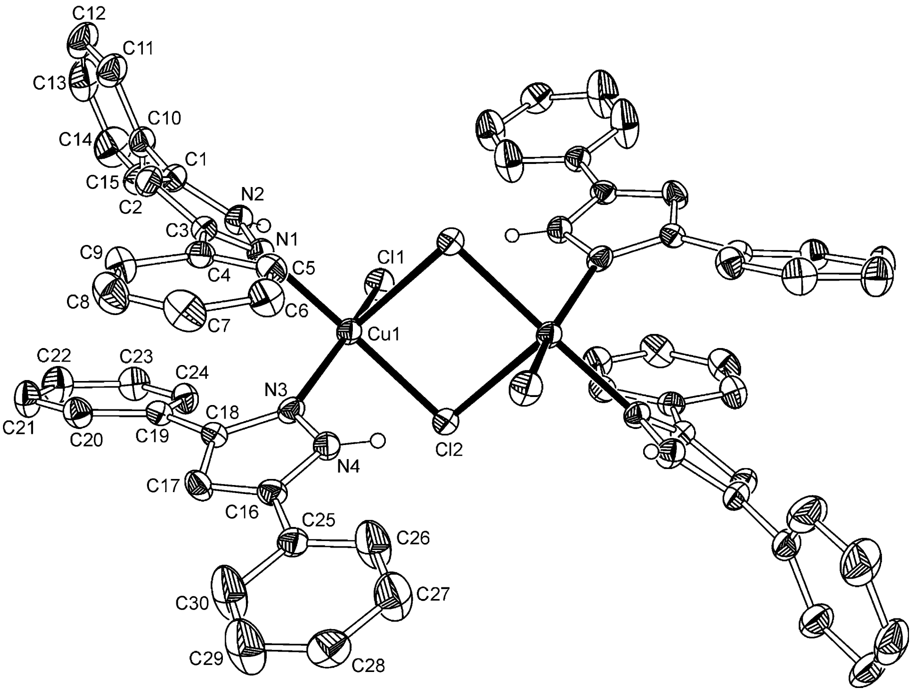


Fig. 6. ORTEP drawing for compound **8**, showing the atom labeling scheme. Thermal ellipsoids at the 30% probability level. C–H hydrogen atoms omitted for clarity.

and molten state, since the latter are green but the crystals are orange.

In the structures of **6**–**8** (Figs. 4–6), each Cu atom has two terminal, protonated pyrazole ligands and a terminal Cl atom coordinated. [1] The two ligands bridging the two copper centers are in each case different: a 3,5-dimethyl-pyrazolate and a chloride for **6**, a hydroxide and a chloride for **7** and two chlorides for **8**. This is reflected in different Cu–Cu separations, from 3.1963(7) Å in **7**, through 3.5253(7) Å in **8**, to 3.7543(6) Å in **6** (Tables 4–6). The coordination geometries of the copper atoms are in between ideal square-pyramidal and trigonal-bipyramidal, closer to the former in **6** and **8**, but closer to the latter in **7**. A particularity of structure **7** is the inclusion of a free 3-methyl-5-phenyl-pyrazole ligand molecule, which is integrated in the crystal lattice by N–H···Cl and O–H···N hydrogen bonds, π···π and C–H···π interactions. Intra- and/or intermolecular N–H···Cl hydrogen bonds are also observed in the structures of **6** and **8**.

While structural analogues of **8** with other pyrazoles (3,5-Me$_2$-pzH [22], 3,5-Et$_2$-4-Me-pzH [23], 3,4-Me$_2$-5-Ph-pzH [24]) have been reported, **5**–**7** are unique examples of dinuclear Cu(II)-pyrazole complexes. Other similar complexes with two bridging fluoride [25] or bromide [26] ligands are also known.

Table 4
Selected bond lengths (Å) and angles (°) for **6**

Cu(1)···Cu(2)	3.7543(6)	N(10)–Cu(1)–N(1)	166.6(1)
Cu(1)–N(1)	2.009(2)	N(10)–Cu(1)–N(3)	86.74(9)
Cu(1)–N(3)	2.057(2)	N(1)–Cu(1)–N(3)	89.37(9)
Cu(1)–N(10)	1.974(2)	N(10)–Cu(1)–Cl(1)	89.76(9)
Cu(1)–Cl(1)	2.3809(8)	N(1)–Cu(1)–Cl(1)	89.18(7)
Cu(1)–Cl(3)	2.4593(8)	N(3)–Cu(1)–Cl(1)	158.46(7)
Cu(2)–N(5)	2.006(2)	N(10)–Cu(1)–Cl(3)	92.91(7)
Cu(2)–N(7)	2.083(2)	N(1)–Cu(1)–Cl(3)	100.39(7)
Cu(2)–N(9)	1.971(2)	N(3)–Cu(1)–Cl(3)	101.24(7)
Cu(2)–Cl(2)	2.3661(8)	Cl(1)–Cu(1)–Cl(3)	100.15(3)
Cu(2)–Cl(3)	2.4665(8)	N(9)–Cu(2)–N(5)	167.07(9)
		N(9)–Cu(2)–N(7)	87.00(9)
		N(5)–Cu(2)–N(7)	88.93(9)
		N(9)–Cu(2)–Cl(2)	90.42(7)
		N(5)–Cu(2)–Cl(2)	88.98(7)
		N(7)–Cu(2)–Cl(2)	158.95(7)
		N(9)–Cu(2)–Cl(3)	93.21(7)
		N(5)–Cu(2)–Cl(3)	99.67(7)
		N(7)–Cu(2)–Cl(3)	102.92(7)
		Cl(2)–Cu(2)–Cl(3)	98.08(3)
		Cu(1)–Cl(3)–Cu(2)	99.31(3)

3.3. Spectroscopic results

^{1}H NMR shows that the trinuclear structures of **1**–**4** are maintained in solution, as indicated by the presence of a single downfield shifted pyrazole signal, at 38.99,

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[1] The structure of **8**, refined as a disordered model, has been previously reported [21]. Our use of Mo Kα radiation and CCD area detector improved the refinement and structural parameters, leading to a non-disordered model with better *R* values and lower esd's.

Table 5
Selected bond lengths (Å) and angles (°) for **7**

Cu(1)···Cu(2)	3.1963(7)	O(1)–Cu(1)–N(1)	173.8(1)
Cu(1)–O(1)	1.903(3)	O(1)–Cu(1)–N(3)	90.8(1)
Cu(1)–N(1)	1.987(3)	N(1)–Cu(1)–N(3)	95.1(1)
Cu(1)–N(3)	2.059(3)	O(1)–Cu(1)–Cl(3)	82.33(9)
Cu(1)–Cl(1)	2.445(1)	N(1)–Cu(1)–Cl(3)	93.8(1)
Cu(1)–Cl(3)	2.409(1)	N(3)–Cu(1)–Cl(3)	111.3(1)
Cu(2)–O(1)	1.905(3)	O(1)–Cu(1)–Cl(1)	87.64(8)
Cu(2)–N(5)	2.074(3)	N(1)–Cu(1)–Cl(1)	90.5(1)
Cu(2)–N(7)	1.980(3)	N(3)–Cu(1)–Cl(1)	125.0(1)
Cu(2)–Cl(2)	2.384(1)	Cl(3)–Cu(1)–Cl(1)	122.86(5)
Cu(2)–Cl(3)	2.450(1)	O(1)–Cu(2)–N(7)	169.1(1)
		O(1)–Cu(2)–N(5)	88.7(1)
		N(7)–Cu(2)–N(5)	94.1(1)
		O(1)–Cu(2)–Cl(2)	95.4(1)
		N(7)–Cu(2)–Cl(2)	92.6(1)
		N(5)–Cu(2)–Cl(2)	118.2(1)
		O(1)–Cu(2)–Cl(3)	81.21(9)
		N(7)–Cu(2)–Cl(3)	88.7(1)
		N(5)–Cu(2)–Cl(3)	126.8(1)
		Cl(2)–Cu(2)–Cl(3)	114.69(5)
		Cu(1)–Cl(3)–Cu(2)	82.27(4)
		Cu(1)–O(1)–Cu(2)	114.2(2)

Table 6
Selected bond lengths (Å) and angles (°) for **8**

Cu(1)···Cu(1′)	3.5253(7)	N(3)–Cu(1)–N(1)	90.37(8)
Cu(1)–N(1)	2.055(2)	N(3)–Cu(1)–Cl(2)	87.85(6)
Cu(1)–N(3)	2.009(2)	N(1)–Cu(1)–Cl(2)	178.16(6)
Cu(1)–Cl(1)	2.3296(8)	N(3)–Cu(1)–Cl(1)	150.96(7)
Cu(1)–Cl(2)	2.3009(8)	N(1)–Cu(1)–Cl(1)	92.24(6)
Cu(1)–Cl(2′)	2.5930(8)	Cl(2)–Cu(1)–Cl(1)	89.54(3)
		N(3)–Cu(1)–Cl(2′)	114.87(7)
		N(1)–Cu(1)–Cl(2′)	92.31(6)
		Cl(2)–Cu(1)–Cl(2′)	88.03(2)
		Cl(1)–Cu(1)–Cl(2′)	93.92(3)
		Cu(1)–Cl(2)–Cu(1′)	91.97(2)

38.23, 37.62 and 35.04 ppm for **1**, **2**, **3** and **4**, respectively. The observed trend is in agreement with the decreasing electronegativity of the substituent attached to the pyrazole ligand. Signals for the tetrabutylammonium counterion appear in the normal region for saturated hydrocarbons. Due to the presence of paramagnetic copper centers, pyrazole C-atoms could not be detected by ^{13}C NMR spectroscopy.

In the IR spectra of **1**–**3**, the C–Cl, C–Br and C–I stretching vibrations produce strong absorption bands at 968, 952 and 941 cm^{-1}, respectively. For **1**–**4**, the strongest absorption peaks attributed to the pyrazole ligands have been assigned as follows: 615–618 (630 for **4**) cm^{-1}, out-of-plane ring bending; 851–858 cm^{-1}, out-of-plane C–H bending; 1052–1055 (1069 for **4**) cm^{-1}, in-plane C–H bending; 1289–1300 and 1483–1487 cm^{-1}, ring stretching; 3093–3140 cm^{-1}, C–H stretching. The presence of tetrabutylammonium groups is indicated by strong absorptions at 2875 and 2962 cm^{-1} (ν_s and ν_{as} CH$_3$), 2942 cm^{-1} (ν_{as} CH$_2$), 1379 cm^{-1} (δ_s CH$_3$) and 1459 cm^{-1} (δ_{as} CH$_3$ and δ_s CH$_2$-scissoring) [27].

In the spectra of dinuclear complexes **6**–**8**, a very strong, broad band with several maxima between 3100 and 3300 cm^{-1} is indicative of N–H groups involved in hydrogen bonding. The absence of this band in the spectrum of **5** confirms the deprotonated nature of the 3-methyl-pyrazole ligands. For **5**–**7**, the presence of the pyrazole ligands' methyl-substituent is indicated by bands at ≈2870, 2925 and 2958 cm^{-1}. In the case of **5**, these bands are overlapped by the very strong Bu$_4$N-bands. For the latter compound, the presence of lattice H$_2$O-molecules is indicated by broad bands with maxima at 3361 and 3444 cm^{-1} (ν_s and ν_{as} OH), and at 1626 cm^{-1} (HOH bending). Absorptions between 3030 and 3065 cm^{-1} for **6**–**8** and 3105 and 3122 cm^{-1} for **5** are due to pyrazole and phenyl C–H stretching vibrations.

4. Conclusions

Here, we have demonstrated that the established procedure for the preparation of the parent compound, (Bu$_4$N)$_2$[Cu$_3$(μ_3-Cl)$_2$(μ-pz)$_3$Cl$_3$], can also be applied for the preparation of other trinuclear Cu(II)-pyrazolates with 4-substituted pyrazoles. This peripheral substitution with different electron-withdrawing or-releasing groups (Cl, Br, I, Me, NO$_2$) does not induce any significant change on the bond lengths of the trinuclear Cu(II)-pyrazolates studied. As for their three-dimensional molecular structure, the Cl-, Br- and Me-derivatives are identical to the parent compound, with a distorted [Cu(4-R-pz)]$_3$ framework, while the NO$_2$-analogue is approximately planar.

All attempts to extend this synthetic protocol for the preparation of similar trinuclear complexes with 3- or 3,5-substituted pyrazoles failed; dinuclear complexes were obtained instead. The reason for these results is assumed to be related to a steric repulsion between the pyrazole ligands' 3- or 3,5-substituents and the terminal chlorine atoms attached to the copper(II)-pyrazolate framework. The dinuclear complexes obtained provide, however, several new motifs in Cu(II) pyrazole- and pyrazolate-chemistry.

5. Supplementary material

CCDC 232032–232038 contain the supplementary crystallographic data for **1**, **2**, **4**–**8**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033. Tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, ORTEP drawings for **2** and **4** are available from the authors by request.

Acknowledgements

G.M. acknowledges a doctoral fellowship from NSF-EPSCoR (Grant No. EPS-9874782).

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