Inorganica Chimica Acta, 201 (1992) 177–184

Copper(II) complexes with the tetraaza ligands resulting from single condensation between linear triamines and aromatic aldehydes. Crystal structure of [Cu(pyaDPT)I]I·MeOH, [Cu(pyaMeDPT)I]I·MeOH and [Cu(iqaMeDPT)I]I

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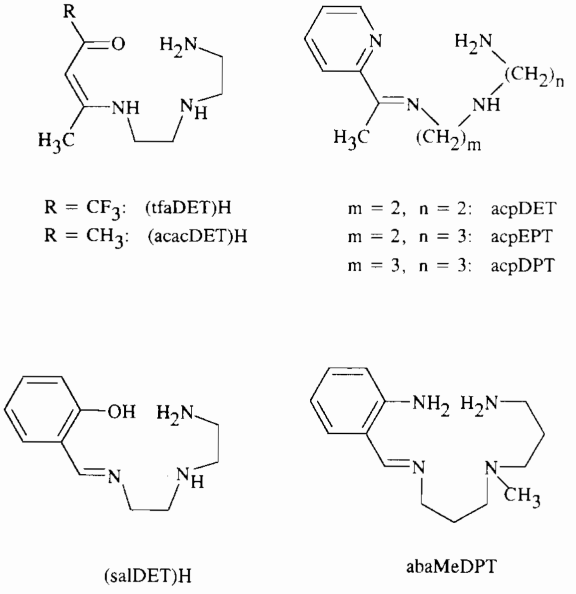
(Received March 13, 1992; revised June 1, 1992)

Abstract

The condensation of one primary amino group of the appropriate triamine: bis(2-aminoethyl)-amine (DET), bis(3-aminopropyl)-amine (DPT) or bis(3-aminopropyl)-methylamine (MeDPT), with the appropriate aldehyde: pyridine-2-carboxaldehyde (pya), 3-formylisoquinoline (iqa) or 2-aminobenzaldehyde (aba), has yielded six new quadridentate N_4-type ligands: pyaDET, pyaDPT, pyaMeDPT, iqaMeDPT, abaDET and abaDPT. The ligands have been isolated as corresponding copper (II) complexes of the general formula [CuLI]I or [CuLI]I·MeOH. The crystal structures of [Cu(pyaDPT)I]I·MeOH, [Cu(pyaMeDPT)I]I·MeOH and [Cu(iqaMeDPT)I]I complexes have been determined by single crystal X-ray diffraction techniques. The geometry around the copper center is intermediate between idealized square-pyramidal and trigonal-bipyramidal symmetry, with the trigonality increasing on going from [Cu(pyaDPT)I]I·MeOH to [Cu(iqaMeDPT)I]I. Crystallographic data: [Cu(pyaDPT)I]I·MeOH: triclinic, $P1$, $a=8.398(3)$, $b=9.503(3)$, $c=12.191(5)$ Å, $\alpha=86.96(3)$, $\beta=85.68(3)$, $\gamma=78.73(3)°$, $R=0.076$; [Cu(pyaMeDPT)I]I·MeOH: monoclinic, $P2_1/c$, $a=9.670(4)$, $b=12.351(6)$, $c=17.074(5)$ Å, $\beta=95.60(3)°$, $R=0.058$; [Cu(iqaMeDPT)I]I: monoclinic, $P2_1/n$, $a=11.210(3)$, $b=10.920(4)$, $c=17.323(5)$ Å, $\beta=96.11(2)°$, $R=0.045$.

Introduction

The monocondensation products of α,ω-diamines and carbonyl compounds, wherein one primary amino group forms an imine or enamine bond and the other one is unchanged and prone for the subsequent reactions, have been shown [1, 2] to have a good potential as the precursors for generation of unsymmetrical flexible ligands capable of binding transition metal ions. Little is known, however, about analogous monocondensation products derived from linear triamines. Wallis and Cummings [3] reported that the complexes $[M(tfaDET)]PF_6$ (M = Cu, Ni) incorporating the ligand (tfaDET)H (Scheme 1) formed upon partial hydrolysis of the corresponding symmetrical dicondensation product $(tfa)_2(DET)H_2$ in the presence of nickel(II) or copper(II) ions in alkaline or acidic medium. The complexes [M(acacDET)]X (M = Cu, Ni, X = I, PF_6) were obtained in a similar way in acidic medium [3].



Scheme 1.

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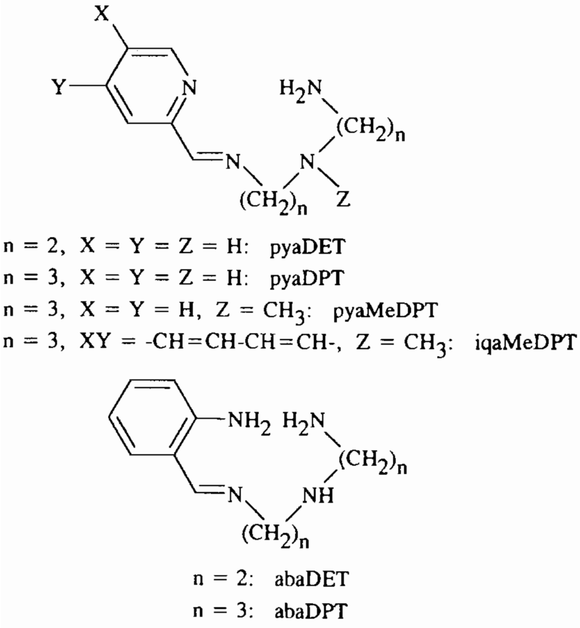
Prince and Stotter [4] prepared the complexes [Ni(acpDET)]$(ClO_4)_2$, [Ni(acpDPT)]$(ClO_4)_2$, Ni(acp-EPT)]$(ClO_4)_2$ and [Cd(acpDPT)Cl]ClO_4 by the *in situ* reaction of 2-acetylpyridine, the appropriate triamine and metal salt. Sheldrick and Stotter [5] grew monocrystals of the [Ni(acpDPT)]$(ClO_4)_2$ adduct with 2-acetylpyridine and determined its crystal and molecular structure, confirming the presence of monocondensation products incorporated into the complex molecule. Rotondo and Priolo [6] observed that the presence of copper(II) in the reaction mixture of salicylaldehyde and bis(2-aminoethyl)-amine favored the monocondensation, which led to the product [Cu(salDET)]PF_6. Very recently, we have shown [7] that the abaMeDPT ligand can be prepared by the direct condensation of 2-aminobenzaldehyde and bis(3-aminopropyl)-methylamine with no template metal ion present in the reaction mixture. The crystal structure of its copper complex [Cu(abaMeDPT)I]I showed an equatorial arrangement of the quadridentate ligand around the metal center in a distorted square-pyramidal geometry.

Scarcity of synthesized and structurally characterized metal complexes with monocondensation products derived from linear aliphatic triamines, and their interesting chemical and physical properties, prompted us to search for further compounds of this type. In this paper we report the synthesis and characterization of six new copper(II) complexes with the ligands depicted in Scheme 2. Crystal structures of the three complexes [Cu(pyaDPT)I]I·MeOH, [Cu(pyaMeDPT)I]I·MeOH and [Cu(iqaMeDPT)I]I have been determined.



Scheme 2.

Experimental

Reagents

Bis(2-aminoethyl)-amine (DET), bis(3-aminopropyl)-amine (DPT) and bis(3-aminopropyl)-methylamine (MeDPT) were dried over potassium hydroxide and distilled, fractions 116–117, 124–125 and 105–106 °C/8 Th being collected, respectively. Pyridine-2-carboxaldehyde (pya) was distilled, the fraction 61–62 °C/8 Th being collected. 3-Formylisoquinoline (iqa) and 2-aminobenzaldehyde (aba) were prepared by the literature methods [8, 9]. All other chemicals were reagent grade and used without further purification.

Complexes

Equimolar amounts (0.025 mol) of the appropriate aldehyde (pya, aba, iqa) and triamine (DET, DPT, MeDPT) were refluxed in methanol (70 ml) for 1 h. Copper sulfate pentahydrate (0.025 mol) in methanol (50 ml) was added to the resulting solution, followed by barium iodide (0.025 mol) in the same solvent (50 ml). The mixture was then stirred at reflux for 30 min and filtered while hot. A dark-green solid separated upon cooling and was removed by filtration. An additional portion of solid was obtained upon concentration of the filtrate. Both portions were combined and recrystallized from methanol to give a dark-green crystalline solid of the copper complex in 30–40% yield. The following complexes were prepared this way.

[Cu(pyaDET)I]I (1). Anal. Found: C, 23.6; H, 3.1; N, 10.8. Calc. for $C_{10}H_{16}CuI_2N_4$: C, 23.6; H, 3.2; N, 11.0%.

[Cu(pyaDPT)I]I·MeOH (2). Anal. Found: C, 27.2; H, 4.2; N, 9.6. Calc. for $C_{13}H_{24}CuI_2N_4O$: C, 27.4; H, 4.3; N, 9.8%.

[Cu(pyaMeDPT)I]I·MeOH (3). Anal. Found: C, 28.7; H, 4.5; N, 9.6. Calc. for $C_{14}H_{26}CuI_2N_4O$: C, 28.8; H, 4.5; N, 9.6%.

[Cu(iqaMeDPT)I]I (4). Anal. Found: C, 33.9; H, 4.0; N, 9.1. Calc. for $C_{17}H_{24}CuI_2N_4$: C, 33.9; H, 4.0; N, 9.3%.

[Cu(abaDET)I]I·MeOH (5). Anal. Found: C, 25.8; H, 4.0; N, 9.9. Calc. for $C_{12}H_{22}CuI_2N_4O$: C, 25.9; H, 4.0; N, 10.1%.

[Cu(abaDPT)I]I (6). Anal. Found: C, 28.5; H, 4.0; N, 10.1. Calc. for $C_{13}H_{22}CuI_2N_4$: C, 28.3; H, 4.0; N, 10.2%.

Physical measurements

Carbon, hydrogen and nitrogen contents were determined on a Carlo Erba elemental analyser MOD 1106. Field desorption mass spectra were recorded on a Varian Mat 711 spectrometer with accelerating voltage 8 kV, extracting voltage −3 kV, and emitter current 10 mA. IR spectra of the solid samples dispersed in Nujol and hexachlorobutadiene were run on a Perkin-Elmer 621, and electronic spectra on a Perkin-Elmer UV-Vis 402 spectrophotometer. Conductance measurements were performed on a K-58 conducting bridge constructed at the Technical University of Warsaw.

X-ray crystallography

Single crystals of [Cu(pyaDPT)I]I·MeOH (**2**), [Cu(pyaMeDPT)I]I·MeOH (**3**) and [Cu(iqaMeDPT)I]I (**4**) were studied by X-ray diffraction techniques. An air stable crystal of the appropriate copper complex was mounted on a glass fiber with epoxy glue and mounted on a four-circle automated Siemens-Nicolet R3m/V diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal data for the three complexes are reported in Table 1. An ω–2θ scan mode was used for data collection and reflections with $3 < 2\theta < 50°$ for **3** and $3 < 2\theta < 54°$ for **2** and **4** were collected. A variable scan speed from 1.5 to 14.65° min^{-1} in ω and a constant scan width of 1.20° was used. With the acceptance criteria $F \geqslant 4\sigma(F)$, 2793 unique reflections were retained for **2**, 2713 for **3** and 3198 for **4**, respectively. Lorentz and polarization corrections were applied to the intensities and, only for **2**, an empirical absorption correction, based on measurements of six reflections at $\chi \cong 270°$ for different azimuthal angles (ψ-scan) was made, and the transmission factor ranged from 0.06 to 1.00. The structures were solved using three-dimensional Patterson and Fourier techniques and refined by full-matrix least-squares methods with anisotropic temperature factors for all the non-hydrogen atoms, excluding MeOH atoms for **2** and **3**. The positions of the hydrogen atoms were calculated geometrically and floated on the positions of the adjacent atoms, with a common refined temperature factor of 0.065, 0.070, and 0.076 Å in **2**, **3** and **4**, respectively. In the refinement procedure the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme of the type $w^{-1} = \sigma^2(F) + gF^2$, g being 0.0024, 0.0054 and 0.0008 for **2**, **3** and **4**, respectively. Final R and R_w indices were: 0.076 and 0.097 for **2**, 0.058 and 0.080 for **3**, and 0.045 and 0.054 for **4**, while the goodness-of-fit was 1.92, 0.99 and 1.39, respectively, and the corresponding data-to-parameter ratios were 15.9:1, 14.2:1, and 14.6:1, respectively. All calculations were carried out using the programs Siemens SHELXTL PLUS (Release 4.1) on a Digital® MicroVAX 3300 computer. The final atom coordinates are listed in Table 2.

Results and discussion

Refluxing equimolar amounts of the corresponding triamine and aldehyde in methanol in the absence of metal ions yields the monocondensation products pyaDET, pyaDPT, pyaMeDPT, iqaMeDPT, abaDET and abaDPT (Scheme 2) readily, as evidenced by observation of the molecular peak in FD mass spectrum of the reaction mixture. A subsequent *in situ* reaction

TABLE 1. Crystal data for the complexes [Cu(pyaDPT)I]I·MeOH (**2**), [Cu(pyaMeDPT)I]I·MeOH (**3**) and [Cu(iqaMeDPT)I]I (**4**)

Compound	[Cu(pyaDPT)I]I·MeOH (**2**)	[Cu(pyaMeDPT)I]I·MeOH (**3**)	[Cu(iqaMeDPT)I]I (**4**)
Empirical formula	$C_{13}H_{24}CuI_2N_4O$	$C_{14}H_{26}CuI_2N_4O$	$C_{17}H_{24}CuI_2N_4$
Color, habit	green, irregular shape	green parallelopipeds	green parallelopipeds
Size (mm)	0.2×0.2×0.03	0.16×0.16×0.24	0.12×0.12×0.16
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P1$	$P2_1/c$	$P2_1/n$
Unit cell dimensions			
a (Å)	8.398(3)	9.670(4)	11.210(3)
b (Å)	9.503(3)	12.351(6)	10.920(4)
c (Å)	12.191(5)	17.074(5)	17.323(5)
α (°)	86.96(3)		
β (°)	85.68(3)	95.60(3)	96.11(2)
γ (°)	78.73(3)		
Volume (Å^3)	950.7(6)	2029.5(14)	2108.6(11)
Z	2	4	4
Formula weight	565.7	579.7	600.7
Density (calc.) (Mg m^{-3})	1.976	1.897	1.892
Absorption coefficient (mm^{-1})	4.369	4.096	3.943
$F(000)$	538	1108	1152

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

[Cu(pyaDPT)I]I·MeOH (2)					[Cu(pyaMeDPT)I]I·MeOH (3)					[Cu(iqaMeDPT)I]I (4)				
	x	*y*	*z*	U^a		*x*	*y*	*z*	U^a		*x*	*y*	*z*	U^a
I(1)	770(1)	667(1)	1937(1)	37(1)	I(1)	9342(1)	2003(1)	490(1)	51(1)	I(1)	−3157(1)	4486(1)	−726(1)	59(1)
I(2)	2760(1)	3665(1)	4418(1)	53(1)	I(2)	5864(1)	345(1)	6516(1)	73(1)	I(2)	−867(1)	−928(1)	1774(1)	53(1)
Cu	−2018(2)	2715(1)	2509(1)	29(1)	Cu	7498(1)	2475(1)	−806(1)	39(1)	Cu	−2734(1)	3368(1)	707(1)	40(1)
O	−4189(18)	4528(16)	−2036(13)	89(4)	O	4221(15)	2213(12)	1691(10)	149(5)	N(1)	−4075(5)	2104(5)	961(3)	41(2)
N(1)	−1458(12)	4717(10)	1965(8)	37(3)	N(1)	5488(7)	1841(6)	−658(5)	51(2)	N(2)	−2096(5)	1842(5)	290(3)	42(2)
N(2)	−2806(12)	2912(11)	985(8)	36(3)	N(2)	7628(7)	1013(5)	−1277(4)	47(2)	N(3)	−999(5)	3756(5)	1254(3)	49(2)
N(3)	−3616(11)	1375(10)	3106(9)	36(3)	N(3)	8689(7)	3159(5)	−1655(4)	46(2)	N(4)	−3541(5)	4696(5)	1233(3)	50(2)
N(4)	−1389(13)	3033(10)	4022(8)	40(3)	N(4)	6962(7)	3915(6)	−400(4)	48(2)	C(1)	−5068(6)	2260(7)	1285(4)	48(2)
C(1)	−752(17)	5619(13)	2469(11)	44(4)	C(1)	4411(10)	2267(9)	−341(7)	63(4)	C(2)	−5829(6)	1285(7)	1460(4)	53(2)
C(2)	−464(18)	6920(14)	1978(14)	56(5)	C(2)	3196(10)	1728(11)	−273(8)	78(4)	C(3)	−5494(6)	76(7)	1274(4)	50(2)
C(3)	−956(19)	7270(17)	937(13)	56(3)	C(3)	3017(12)	730(12)	−588(8)	82(5)	C(4)	−4423(7)	−86(7)	921(4)	49(2)
C(4)	−1672(16)	6377(13)	408(11)	44(4)	C(4)	4102(12)	260(9)	−950(7)	69(4)	C(5)	−3766(6)	917(6)	779(3)	41(2)
C(5)	−1925(14)	5077(12)	938(9)	35(3)	C(5)	5321(9)	859(7)	−972(5)	54(3)	C(6)	−2662(6)	851(7)	395(3)	46(2)
C(6)	−2689(17)	4062(15)	465(10)	47(4)	C(6)	6567(10)	416(7)	−1294(6)	56(3)	C(7)	−982(6)	1790(7)	−90(4)	54(2)
C(7)	−3542(18)	1835(17)	500(12)	53(5)	C(7)	8942(13)	602(9)	−1567(7)	75(4)	C(8)	46(7)	2158(8)	475(5)	64(3)
C(8)	−4827(17)	1386(18)	1287(13)	57(5)	C(8)	9424(12)	1350(9)	−2184(7)	70(4)	C(9)	−13(7)	3450(8)	765(5)	64(3)
C(9)	−4176(17)	531(16)	2273(12)	52(5)	C(9)	9796(10)	2433(9)	−1887(7)	62(3)	C(10)	−782(8)	5069(7)	1488(5)	68(3)
C(10)	−3031(15)	407(13)	4030(10)	41(4)	C(10)	9423(10)	4173(8)	−1390(7)	61(3)	C(11)	−1736(9)	5651(7)	1904(5)	70(3)
C(11)	−2699(16)	1199(16)	5036(10)	50(4)	C(11)	8513(12)	5068(7)	−1079(7)	68(4)	C(12)	−2908(9)	5853(7)	1404(5)	67(3)
C(12)	−1234(17)	1858(14)	4858(10)	45(4)	C(12)	7958(11)	4815(8)	−336(6)	62(3)	C(13)	−892(7)	2969(7)	1966(4)	58(3)
C(13)	−4554(25)	3303(22)	−2526(18)	82(5)	C(13)	7670(11)	3376(9)	−2361(6)	65(3)	C(14)	−6881(7)	1500(10)	1816(5)	69(3)
					C(14)	3272(20)	2451(16)	2267(11)	123(6)	C(15)	−7614(8)	546(12)	1967(5)	83(4)
										C(16)	−7297(9)	−655(11)	1784(5)	81(4)
										C(17)	−6276(8)	−906(9)	1436(4)	65(3)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

of the ligands with copper(II) sulfate and barium iodide affords the complexes **1–6** (Table 3) of the general formula [Cu(L)I]I or [Cu(L)I]I·MeOH. The complexes are moderately soluble in methanol, acetone, acetonitrile and dimethylformamide.

In the IR spectra of the copper complexes (Table 3) several absorption bands in the 3030–3300 cm^{-1} region are observed. These bands, assigned to the ν(N–H) vibrations, appear at lower frequencies than for non-hydrogen-bonded primary and secondary amines, due to the involvement of amino groups in the coordination of the central metal ion. Three complexes, **2**, **3** and **5**, predicted as methanol solvates on the basis of elemental analysis, show additional broad bands at 3400–3470 cm^{-1} resulting from the methanol OH stretching modes. Absorption bands assignable to the ν(C=N) vibrations appear at 1630–1660 cm^{-1}.

The complexes behave as 1:1 electrolytes in methanol solution. At the concentration of 1×10^{-3} mol dm^{-3} the molar conductance of five complexes, **1–4** and **6** (Table 3) is contained within the 80–115 Ω^{-1} cm^2 mol^{-1} range proposed for 1:1 electrolytes dissolved in methanol [10]. The slightly higher value obtained for **5** (123 Ω^{-1} cm^2 mol^{-1} probably reflects a subsequent partial dissociation of the $[\text{Cu(L)I}]^+$ cation.

UV–Vis spectra of the copper complexes recorded in solid state as Nujol mulls show no gross differences from the solution spectra, except for marked broadening of the absorption bands. In solution, each complex displays a single d–d transition band in the visible region. The position of this band varies from 575 to 807 nm depending on the ligand, and suggests that even minor changes within the ligand molecule may affect the overall coordination geometry around the copper center. Since a square-pyramidal geometry has been found for the recently reported [Cu(abaMeDPT)I]I complex having a d–d transition band at 622 nm [7], we focused our attention on molecular structure determination of the complexes **2**, **3** and **4**, absorbing at higher wavelengths.

TABLE 3. Spectral data and molar conductances for the copper complexes

Compound	ν^{a} (cm^{-1})			$\lambda_{\max}{}^{b}$ (nm) (log ε)	$\Lambda_M{}^{c}$ (Ω^{-1} cm^2 mol^{-1})
	ν(O–H)	ν(N–H)	ν(C=N), ν(C=C) δ(N–H)		
[Cu(pyaDET)I]I (**1**)		3240 3160 3080	1662 1602 1582	220(4.60) 279sh 280(3.88) 294sh 625(2.25)	114
[Cu(pyaDPT)I]I·MeOH (**2**)	3420	3240 3180 3105	1650 1630 1608	218(4.63) 289(4.06) 345sh 746(2.38)	107
[Cu(pyaMeDPT)I]I·MeOH (**3**)	3395	3190 3165 3085	1650 1605 1567	216(4.58) 286(4.02) 333sh 807(2.65)	96
[Cu(iqaMeDPT)I]I (**4**)		3222 3168 3075	1647 1633 1600	220(4.60) 262(4.07) 365sh 420sh 685(2.15)	94
[Cu(abaDET)I]I·MeOH (**5**)	3470	3280 3150 3070	1650 1615 1580 1560	220(4.69) 244sh 258(4.23) 417sh 575(2.17)	123
[Cu(abaDPT)I]I (**6**)		3210 3120 3030	1640 1615 1575 1530	220(4.60) 262(4.07) 365sh 420sh 685(2.15)	100

[a] Prominent IR absorption bands in 1500–1700 and 3000–3500 cm^{-1} regions. [b] UV–Vis spectra in acetonitrile for **4** and in methanol for the other compounds, sh denotes shoulder. [c] Molar conductances in 1×10^{-3} mol dm^{-3} methanol solution.

TABLE 4. Selected bond lengths (Å)

[Cu(pyaDPT)I]I·MeOH (**2**)		[Cu(pyaMeDPT)I]I·MeOH (**3**)		[Cu(iqaMeDPT)I]I (**4**)	
I(1)–Cu	2.806(2)	I(1)–Cu	2.766(2)	I(1)–Cu	2.761(1)
Cu–N(1)	2.109(10)	Cu–N(1)	2.133(7)	Cu–N(1)	2.121(5)
Cu–N(2)	2.007(10)	Cu–N(2)	1.986(7)	Cu–N(2)	1.979(6)
Cu–N(3)	2.091(10)	Cu–N(3)	2.113(7)	Cu–N(3)	2.115(6)
Cu–N(4)	2.011(11)	Cu–N(4)	1.995(7)	Cu–N(4)	1.982(6)
N(1)–C(5)	1.347(15)	N(1)–C(5)	1.331(12)	N(1)–C(5)	1.387(8)
N(2)–C(6)	1.251(17)	N(2)–C(6)	1.261(12)	N(2)–C(6)	1.278(9)
N(2)–C(7)	1.464(20)	N(2)–C(7)	1.496(15)	N(2)–C(7)	1.473(9)
N(3)–C(9)	1.484(19)	N(3)–C(9)	1.479(13)	N(3)–C(9)	1.500(10)
N(3)–C(10)	1.467(15)	N(3)–C(10)	1.488(12)	N(3)–C(10)	1.503(10)
N(4)–C(12)	1.464(16)	N(3)–C(13)	1.506(12)	N(3)–C(13)	1.497(9)
C(5)–C(6)	1.424(20)	N(4)–C(12)	1.467(12)	N(4)–C(12)	1.464(10)
C(7)–C(8)	1.499(21)	C(5)–C(6)	1.477(14)	C(5)–C(6)	1.469(10)
C(8)–C(9)	1.492(21)	C(7)–C(8)	1.509(17)	C(7)–C(8)	1.486(10)
C(10)–C(11)	1.543(19)	C(8)–C(9)	1.463(15)	C(8)–C(9)	1.501(12)
C(11)–C(12)	1.483(21)	C(10)–C(11)	1.539(15)	C(10)–C(11)	1.493(13)
		C(11)–C(12)	1.459(17)	C(11)–C(12)	1.512(13)

TABLE 5. Selected bond angles (°)

[Cu(pyaDPT)I]I·MeOH (**2**)		[Cu(pyaMeDPT)I]I·MeOH (**3**)		[Cu(iqaMeDPT)I]I (**4**)	
I(1)–Cu–N(1)	105.6(3)	I(1)–Cu–N(1)	110.5(2)	I(1)–Cu–N(1)	114.7(1)
I(1)–Cu–N(2)	94.0(3)	I(1)–Cu–N(2)	94.0(2)	I(1)–Cu–N(2)	94.5(1)
N(1)–Cu–N(2)	78.8(4)	N(1)–Cu–N(2)	79.0(3)	N(1)–Cu–N(2)	79.6(2)
I(1)–Cu–N(3)	100.6(2)	I(1)–Cu–N(3)	106.3(2)	I(1)–Cu–N(3)	112.1(2)
N(1)–Cu–N(3)	153.3(3)	N(1)–Cu–N(3)	142.4(3)	N(1)–Cu–N(3)	132.5(2)
N(2)–Cu–N(3)	94.1(4)	N(2)–Cu–N(3)	91.5(3)	N(2)–Cu–N(3)	88.9(2)
I(1)–Cu–N(4)	96.1(3)	I(1)–Cu–N(4)	94.5(2)	I(1)–Cu–N(4)	92.7(2)
N(1)–Cu–N(4)	89.5(4)	N(1)–Cu–N(4)	90.9(3)	N(1)–Cu–N(4)	90.7(2)
N(2)–Cu–N(4)	166.2(4)	N(2)–Cu–N(4)	168.6(3)	N(2)–Cu–N(4)	169.7(2)
N(3)–Cu–N(4)	93.2(4)	N(3)–Cu–N(4)	93.4(3)	N(3)–Cu–N(4)	95.2(2)
Cu–N(1)–C(1)	130.6(8)	Cu–N(1)–C(1)	131.5(7)	Cu–N(1)–C(1)	131.1(5)
Cu–N(1)–C(5)	111.0(8)	Cu–N(1)–C(5)	111.3(6)	Cu–N(1)–C(5)	111.2(4)
Cu–N(2)–C(6)	115.5(9)	Cu–N(2)–C(6)	117.2(6)	Cu–N(2)–C(6)	117.2(5)
Cu–N(2)–C(7)	123.8(8)	Cu–N(2)–C(7)	122.1(6)	Cu–N(2)–C(7)	123.5(4)
C(6)–N(2)–C(7)	120.6(11)	C(6)–N(2)–C(7)	120.6(8)	C(6)–N(2)–C(7)	119.2(6)
Cu–N(3)–C(9)	115.9(8)	Cu–N(3)–C(9)	113.5(6)	Cu–N(3)–C(9)	113.6(4)
Cu–N(3)–C(10)	114.1(8)	Cu–N(3)–C(10)	113.8(6)	Cu–N(3)–C(10)	115.3(5)
C(9)–N(3)–C(10)	108.9(10)	C(9)–N(3)–C(10)	104.8(7)	C(9)–N(3)–C(10)	104.9(6)
Cu–N(4)–C(12)	120.0(8)	Cu–N(3)–C(13)	105.2(6)	Cu–N(3)–C(13)	104.1(4)
N(1)–C(5)–C(6)	114.8(10)	C(9)–N(3)–C(13)	109.1(7)	C(9)–N(3)–C(13)	109.7(6)
C(4)–C(5)–C(6)	124.4(11)	C(10)–N(3)–C(13)	110.4(7)	C(10)–N(3)–C(13)	109.2(6)
N(2)–C(6)–C(5)	119.7(12)	Cu–N(4)–C(12)	120.7(6)	Cu–N(4)–C(12)	119.3(5)
N(2)–C(7)–C(8)	110.5(12)	N(1)–C(5)–C(6)	114.6(8)	N(1)–C(5)–C(6)	113.0(6)
C(7)–C(8)–C(9)	114.0(12)	C(4)–C(5)–C(6)	122.4(9)	C(4)–C(5)–C(6)	122.9(6)
N(3)–C(9)–C(8)	114.8(13)	N(2)–C(6)–C(5)	117.8(8)	N(2)–C(6)–C(5)	118.6(6)
N(3)–C(10)–C(11)	113.5(10)	N(2)–C(7)–C(8)	110.7(9)	N(2)–C(7)–C(8)	109.2(6)
C(10)–C(11)–C(12)	113.3(10)	C(7)–C(8)–C(9)	113.6(10)	C(7)–C(8)–C(9)	114.6(7)
N(4)–C(12)–C(11)	113.7(11)	N(3)–C(9)–C(8)	119.2(8)	N(3)–C(9)–C(8)	117.4(7)
		N(3)–C(10)–C(11)	115.9(8)	N(3)–C(10)–C(11)	115.7(7)
		C(10)–C(11)–C(12)	114.7(8)	C(10)–C(11)–C(12)	114.1(7)
		N(4)–C(12)–C(11)	113.1(8)	N(4)–C(12)–C(11)	111.3(6)

The three structures, **2**, **3** and **4**, consist of a discrete $[Cu(L)I]^+$ complex cation, an uncoordinated iodide anion, and in the case of **2** and **3** of a methanol solvent molecule. Selected bond distances are given in Table 4, selected bond angles in Table 5, and views of the complex cations in Fig. 1. In each cation a copper center is coordinated by a neutral ligand molecule through its four nitrogen atoms plus an iodide anion

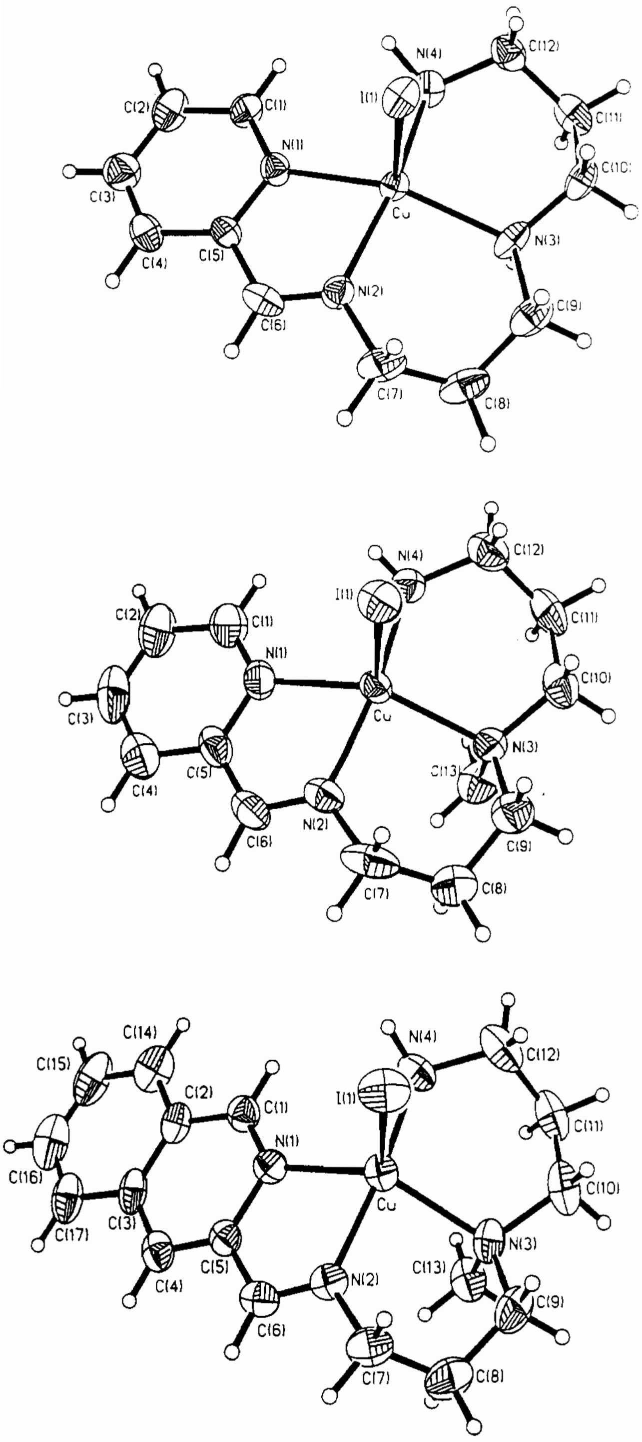


Fig. 1. Perspective views of the complex cations showing the atom-labelling system and thermal ellipsoids at the 50% probability for [Cu(pyaDPT)I]I·MeOH (**2**) (top), Cu(pyaMeDPT)·MeOH (**3**) (center) and Cu(iqaMeDPT) (**4**) (bottom).

at the fifth coordination site. The stereochemistry of the CuN_4I core is transient between square-pyramidal and trigonal-bipyramidal symmetry, with the trigonality increasing in the order **2**, **3** and **4** (Reedijk's structural parameter τ [11] 0.21, 0.44 and 0.62, respectively). For the sake of uniformity, it is viewed in this paper as a distortion from trigonal-bipyramidal symmetry with N(1), N(3) and I(1) atoms occupying the equatorial coordination sites, and with N(2) and N(4) as apical atoms. The main distortions from the bipyramidal configuration for the three complexes results from the non-linearity of the N(2)–Cu–N(4) axis (mean 168.2°). Moreover, the angle N(1)–Cu–N(3) in the equatorial plane exhibits a dramatic distortion from the ideal trigonal angle of 120° (153.3, 142.4 and 132.5° for **2**, **3** and **4**, respectively), and consequently the N(1)...N(3) separation is very large (4.09, 4.02 and 3.88 Å, respectively). The mean N(1)–Cu–N(2) 'bite' angle is only 79.2° and in the three complexes the Cu atom lies *c.* 0.10 Å out of the trigonal plane towards N(4). In the coordination polyhedron the N_4 ligand forms three (5,6,6)-membered chelate rings adopting the planar–chair–chair conformation. The average in-plane Cu–N distances 2.100, 2.123 and 2.118 Å for **2**, **3** and **4**, are *c.* 0.1 Å larger than the average Cu–N out-of-plane distances Cu–N(2) and Cu–N(4) (2.009, 1.991 and 1.981 Å, respectively), and are similar to those observed previously for other trigonal-bipyramidal copper(II) monocationic complexes containing four nitrogen donor atoms [12–24]. In the three complexes the Cu–I(1) bond distance (2.806, 2.766 and 2.761 Å for **2**, **3** and **4**, respectively) is longer than the Cu–I covalent bond (1.33 + 1.35 Å), and those found, for example in $[Cu(bipy)_2I]^+$ (2.675 Å [16] and 2.697 Å [24]) or in $[Cu(phen)_2I]^+$ (2.672 Å [22]), which have almost a regular set of trigonal-bipyramidal angles. The structures of the three complexes are strictly analogous as shown by fitting of the CuN_4I core of **3** with that of **4** (weighted r.m.s. deviations are only 0.103 Å) and with that of **2** (weighted r.m.s. 0.104 Å), while superimposition of the common skeleton yields the corresponding deviations of 0.208 and 0.145 Å, respectively (see 'Supplementary material' for views of the fittings). Besides the ionic forces due to the ionic character of the structure, the cohesion of the crystals is achieved through usual van der Waals interactions, even if a short contact between uncoordinated counter-anion I(2) and methanol oxygen atom (3.54 and 3.44 Å in **2** and **3**, respectively) could suggest that the solvent is strongly associated with the iodide ion. The closest approach of I(2) to the copper center is 4.75, 4.88 and 4.85 Å in **2**, **3** and **4**, respectively.

Supplementary material

The supplementary material is available upon request from author G.B. and includes: full tables of bond lengths (Table 4A) and angles (Table 5A), selected relevant mean-planes data (Table 6), calculated hydrogen-atom positions (Table 7), anisotropic temperature factors (Table 8), observed/calculated structure factors (Table 9), tetragonal-pyramidal versus trigonal-bipyramidal view of CuN_4I core (Fig. 2), views of coordination arrangement around the individual copper centers (Fig. 3), fitting of **3** with **2**, and with **4** (Fig. 4), and molecular packing scheme viewed down the *b* axis (Fig. 5).

Acknowledgement

This work was supported by Grant 2-1349-91-01 from the Polish Scientific Research Council, KBN (M.K., E.K. and A.O.).

References

1 M. Kwiatkowski, E. Kwiatkowski, A. Olechnowicz, D. M. Ho and E. Deutsch, *Inorg. Chim. Acta, 150* (1988) 65, and refs. therein.

2 M. Kwiatkowski, E. Kwiatkowski, A. Olechnowicz, D. M. Ho and E. Deutsch, *J. Chem. Soc., Dalton Trans.*, (1990) 2497 and 3063.

3 W. N. Wallis and S. C. Cummings, *Inorg. Chem., 13* (1974) 988.

4 R. H. Prince and D. A. Stotter, *Inorg. Chim. Acta, 10* (1974) 89.

5 G. M. Sheldrick and D. A. Stotter, *J. Chem. Soc., Dalton Trans.*, (1975) 666.

6 E. Rotondo and F. C. Priolo, *J. Chem. Soc. Dalton Trans.*, (1982) 1825.

7 E. Kwiatkowski, M. Kwiatkowski, A. Olechnowicz, T. Ossowski, B. Kościuszko and U. Dettlaff-Weglikowska, *J. Crystallogr. Spectrosc. Res., 21* (1991) 75.

8 C. E. Teague and A. Roe, *J. Am. Chem. Soc., 73* (1951) 688.

9 L. E. Smith and J. W. Opie, *Org. Synth. Collect., 3* (1956) 56.

10 W. J. Geary, *Coord. Chem. Rev., 7* (1971) 81.

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

12 N. J. Ray, L. Hulett, R. Sheahan and B. J. Hathaway, *J. Chem. Soc. Dalton Trans.*, (1981) 1463.

13 F. Huq and A. C. Shapski, *J. Chem. Soc. A*, (1971) 1927.

14 A. M. Manotti Lanfredi, A. Tiripicchio, M. Ghedini and G. De Munno, *Acta Crystallogr., Sect. B, 38* (1982) 1165.

15 D. Boys, C. Escobar and S. Martinez-Carrera, *Acta Crystallogr., Sect. B, 37* (1981) 351.

16 B. J. Hathaway and A. Murphy, *Acta Crystallogr., Sect. B, 36* (1980) 295.

17 M. A. Khan and D. G. Tuck, *Acta Crystallogr., Sect. B, 37* (1981) 1409.

18 W. P. Jensen and R. A. Jacobson, *Inorg. Chim. Acta, 49* (1981) 199.

19 S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, (1983) 199.

20 P. J. Burke, K. Henrick and D. R. McMillin, *Inorg. Chem., 21* (1982) 1881.

21 P. J. Burke, D. R. McMillin and W. R. Robinson, *Inorg. Chem., 19* (1980) 1211.

22 T. W. Hambley, C. L. Raston and A. H. White, *Aust. J. Chem., 30* (1977) 1965.

23 G. R. Newkome, V. K. Gupta and F. R. Fronczek, *Inorg. Chem., 22* (1983) 171.

24 G. A. Barclay, B. F. Hoskins and C. H. L. Kennard, *J. Chem. Soc.*, (1963) 5691.