Copper(II)- and Proton-Assisted Condensation Reactions of a Tetrapodal Pentaamine with Acetone: Formation of “Podand-cum-Macrocycle” Copper Complexes and a Protonated Bis(aminal)

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Dedicated to Professor Dieter Sellmann on the occasion of his 60th birthday

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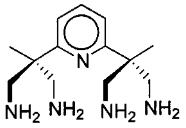
The tetrapodal pentaamine 2,6-$C_5H_3N[CMe(CH_2NH_2)_2]_2$ (pyN_4, **1**) forms mononuclear complexes with Cu^{II}, as shown for a series of compounds of the type $[(\mathbf{1})Cu]X_2$ (X = Br, SCN, PF_6, ClO_4). The coordination environment of the copper ion is square-pyramidal, with the pyridine nitrogen atom of **1** in the apical position. The axial bond Cu–N_{py} is significantly longer than the four Cu–N bonds at the base of the pyramid, average values being 2.16 Å and 2.03 Å, respectively. When $[(\mathbf{1})Cu]X_2$ (X = PF_6, ClO_4) is refluxed with an excess of acetone in methanol in the absence of base, the corresponding bis(isopropylideneimine) complexes $[\{(nac)_2pyN_4\}Cu]X_2$ are obtained, in which two diametrically opposite primary amino groups of **1** have condensed with the ketone. The complex cations, which are now chiral, again have square-pyramidal coordinated Cu^{II}. In the presence of sodium methoxide, the condensation of $[(\mathbf{1})Cu]X_2$ with acetone proceeds further, leading to the formation of one diacetone-amine-imine linkage in the product. A 12-membered 1,5,9-triazamacrocycle, incorporating the 2,6-disubstituted pyridine unit, is thus formed. Two podand nitrogen donors of the NN_4 set (which retains its square pyramidal topology) remain: a primary amine and an isopropylidene imine group. The product forms as a mixture of both conceivable isomers (azomethine groups at the base of the pyramid *cis* or *trans*), which were separated and structurally characterised as the tribromocuprate(I) and hexafluorophosphate salts, respectively. The condensation of metal-free **1** with acetone in the presence of two equivalents of HBr yields the bis(aminal) salt (2,6-$C_5H_3N\{CMe[\mathit{cyclo}\text{-}CH_2NH_2C(CH_3)_2NHCH_2\text{-}]\}_2)Br_2$, in which one of the secondary amino groups in each diazacyclohexane ring is protonated, as ascertained by X-ray crystallography. The aminal is a metal-free tautomer of the bis(isopropylideneimine) ligand $(nac)_2pyN_4$, to which it converts upon reaction with Cu^{II} under suitable conditions, providing an alternative synthetic route to complexes of the type $[\{(nac)_2pyN_4\}Cu]X_2$.

Introduction

The tetrapodal pentaamine **1** (pyN_4) forms mononuclear complexes with cobalt(III), nickel(II), and iron(II/III) in which all four arms of the ligand as well as the apical donor atom are coordinated to the metal centre.[1,2] A monodentate additional ligand completes the coordination octahedron. We are currently exploring ways to introduce a functional periphery into such complexes,[3,4] appended to the basal donor atoms of **1**, that will engage in secondary interactions with the monodentate ligand, so as to control its binding and reactivity. Ligand derivatives with: (a) one, (b) two, or (c) four modified sidearms have been obtained by Schiff base condensation with carbonyl compounds, such as: (a) salicylaldehyde, (b) acetone, or (c) cinnamaldehyde, and isolated in the form of their nickel(II) complexes, which are mononuclear.[4]

The spatial orientation of the secondary donor groups in the ligand periphery has to enable noncovalent interactions with the monodentate ligand; at the same time, the coordination of peripheral groups to the apical site (which would hinder the binding of an exogenous ligand) is to be precluded, and the periphery should not interfere with mononuclear NN_4 complex formation. These difficulties are illustrated by two derivatives of **1**: 1) the mono(salicylaldehyde) derivative, as obtained under (a), above, is hexadentate, its NN_4O donor set occupying all coordination sites in an octahedral complex;[4] 2) a related symmetrical ligand, with four uniformly modified sidearms and a potential NN_4O_4 donor set, adopts a dinucleating coordination mode in the case of nickel(II) and copper(II): each metal ion uses a square-planar disposed N_2O_2 donor subset, and the pyridine nitrogen atom remains uncoordinated.[5]



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A strategy to enforce a mononucleating NN_4 donor set in derivatives of **1** irrespective of the nature of the ligand periphery is to increase the rigidity (“juxtapositional fixedness”[6,7]) of the coordination cap. One possibility is to tie

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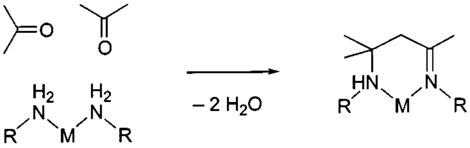
the 1,3-diaminoprop-2-yl sidearms together by bridges between equatorial amino groups, to give a macrocyclic ring "capped" by a pyridine unit. At a later stage, the bridges could carry donor groups pointing towards the sixth coordination site. In order to probe the viability of this approach, we chose a reaction known to furnish acetone-derived C_3 linkages between adjacent NH_2 groups in transition metal amine complexes (the Curtis reaction, Scheme 1).[8,9] In this contribution, we describe the copper(II) complex of **1**, and its reactivity, and that of partially protonated **1**, towards acetone.



Scheme 1. Condensation of adjacent primary amino groups in a metal complex with acetone to produce a diacetone-amine-imine linkage (Curtis reaction)

Results and Discussion

[(1)Cu]X$_2$ (X = Br, SCN, PF$_6$, ClO$_4$)

The bromide salt [(**1**)Cu]Br$_2$ formed in good yield as a microcrystalline purple solid upon refluxing a methanolic solution of equivalent amounts of the pentaamine **1**, prepared by neutralisation of **1**·4HBr·MeOH with four equivalents of LiOMe, and $CuCl_2·2H_2O$. Recrystallisation from methanol or methanol/water yielded the solvates [(**1**)Cu]Br$_2$·0.5MeOH (**2**), [(**1**)Cu]Br$_2$·2MeOH (**3**), and [(**1**)Cu]Br$_2$·3H$_2$O (**4**), and recrystallisation in the presence of NH_4SCN or NH_4PF_6 gave the thiocyanate and hexafluorophosphate salts [(**1**)Cu](SCN)$_2$·H$_2$O (**5**) and [(**1**)Cu](PF$_6$)$_2$ (**7**). The perchlorate [(**1**)Cu](ClO$_4$)$_2$ (**8**), which is soluble in acetone, was obtained directly from the reaction of **1** and [Cu(DMF)$_6$](ClO$_4$)$_2$ in methanol (see Experimental Section). The magnetic moment determined for **2** (Gouy balance, 1.7 μB) conforms to one unpaired electron, as expected for Cu^{II}, and a quasi-reversible redox wave in the cyclic voltammogram of this compound at $E_{1/2} = -0.62$ V (vs. NHE) is assigned to the [Cu^{II}/Cu^{I}] couple.[10]

X-ray structural data have been obtained for several compounds of composition [(**1**)Cu]X$_2$, showing the copper(II) ion to be present in a square-pyramidal coordination environment in all cases. The pyridine nitrogen atom of the pentaamine ligand occupies the axial position, while the primary amino groups are at the base of the pyramid. Without exception, the axial bond Cu−N$_{py}$ is significantly longer than the basal copper−nitrogen bonds, average values being 2.16 Å and 2.03 Å, respectively. While pentacoordinate Cu^{II} is not susceptible to first-order Jahn−Teller effects, such differences, which have been ascribed to a "plasticity effect", are a common feature in the structural chemistry of this ion.[11,12] The following discussion pertains to the cation in [(**1**)Cu](SCN)$_2$·H$_2$O (**5**), whose structure is shown in Figure 1. The complex has crystallographic C_1 symmetry. The basal Cu−N bond lengths are similar (Table 1), averaging 2.039(3) Å, while the axial Cu−N bond length is 2.207(2) Å. These values are similar to those determined for the corresponding bonds in the pentaammine copper(II) complex K[Cu(NH$_3$)$_5$](PF$_6$)$_3$.[13] All N$_{ax}$−Cu−N$_{bas}$ angles in **5** are close to 90°. A distortion of the ligand framework from ideal square-pyramidal geometry, which is probably due, in large measure, to crystal packing effects,[2] causes the pyridine ring to be tilted from the normal on the basal CuN$_4$ plane by 27.3(1)°, and the nonbonded distances C16···C21 and C17···C20 to be lengthened and shortened

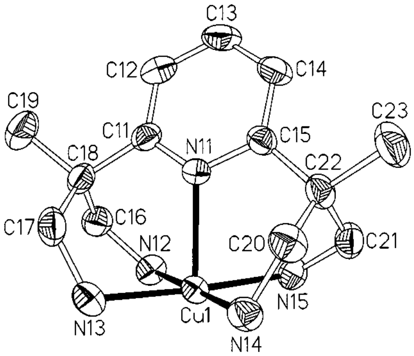


Figure 1. Molecular structure of the cation in **5** with thermal ellipsoids at the 50% probability level; hydrogen atoms have been omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for compounds **5**, **9**, **11**, and **12** with estimated standard deviations in parentheses; see also Table 2

Bond or angle	**5**	**9**	**11**	**12**
Cu1−N11	2.207(2)	2.105(4)	2.101(4)	2.141(7)
Cu1−N12	2.069(3)	2.008(2)	2.028(3)	2.001(7)
Cu1−N13	2.019(3)	2.046(2)	1.996(3)	2.022(8)
Cu1−N14	2.024(3)	−	2.028(3)	2.036(7)
Cu1−N15	2.045(3)	−	2.006(3)	2.038(7)
N12−C2	−	1.269(5)	−	−
N12−C5	−	−	−	1.32(1)
N12−C7	−	−	1.473(5)	−
N13−C2	−	−	1.277(5)	1.25(1)
N15−C5	−	−	1.290(5)	−
N15−C7	−	−	−	1.46(1)
N11−Cu1−N12	89.7(1)	94.8(1)	93.2(2)	89.3(3)
N11−Cu1−N13	91.5(1)	89.8(1)	94.0(2)	91.4(3)
N11−Cu1−N14	91.0(1)	−	93.2(2)	90.8(3)
N11−Cu1−N15	85.7(1)	−	90.0(2)	92.7(3)
N12−Cu1−N13	82.3(1)	84.99(9)	85.0(2)	86.8(3)
N14−Cu1−N15	87.0(1)	−	85.1(2)	86.3(3)
N13−Cu1−N14	97.2(1)	−	95.3(2)	92.8(3)
N12−Cu1−N15	93.6(1)	−	94.2(2)	94.1(3)
N12−Cu1−N13A	−	95.04(9)	−	−
N12−Cu1−N14	179.1(1)	−	173.6(2)	179.6(3)
N13−Cu1−N15	175.0(1)	−	176.0(2)	175.8(3)
N12−Cu1−N12A	−	170.3(2)	−	−
N13−Cu1−N13A	−	179.6(3)	−	−
Cu1−N11−C11	116.2(2)	118.7(2)	116.9(3)	116.5(7)
Cu1−N11−C15	116.3(2)	−	117.1(3)	114.7(6)
Cu1−N12−C2	−	126.0(3)	−	−
Cu1−N12−C5	−	−	−	123.4(6)
Cu1−N12−C7	−	−	119.1(3)	−
Cu1−N12−C16	117.0(2)	114.4(2)	114.0(2)	116.2(5)
Cu1−N13−C2	−	−	127.1(3)	128.8(8)
Cu1−N13−C17	112.2(2)	114.5(2)	112.6(3)	112.5(6)
Cu1−N15−C5	−	−	122.3(3)	−
Cu1−N15−C7	−	−	−	120.4(6)
Cu1−N15−C21	−	−	116.9(2)	113.7(5)

to 5.301(5) Å and 4.516(5) Å, respectively (Table 2). In the crystal lattice of **5**, one of the SCN^- counterions is oriented parallel to the basal CuN_4 plane of the cation; its sulfur atom approaches the copper ion to within 2.991(1) Å (sum of the van-der-Waals radii of Cu^{II} and S: 3.20 Å[14]), which may be the underlying reason why **5** has a different colour in the solid state (blue) than those complexes of the [(**1**)Cu]X_2 series where such Cu^{II}/anion contacts are not observed (purple).

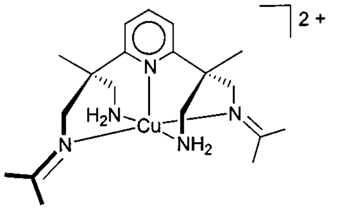
Table 2. Intramolecular angles [°] and distances [Å] quantifying the distortions of the ligand cap in complexes **5**, **11** and **12** (with estimated standard deviations in parentheses); compound **9** does not show these distortions owing to crystallographically imposed symmetry; see footnote and text for definitions of angles

Angle or distance	5	11	12
ε[a]	30.7(2)	24.1(3)	29.9(6)
ζ[b]	9.3(1)	7.4(2)	9.0(5)
η[c]	24.6(2)	20.2(2)	25.9(4)
d(C16···C21)[d]	5.301(5)	5.238(6)	5.37(2)
d(C17···C20)[d]	4.516(5)	4.585(7)	4.50(2)

[a] Angle ε between the least-squares planes defined by the pyridine ring (N11, C11, C12, C13, C14, C15) and the quaternary and methyl carbon atoms C18/C19/C22/C23. – [b] Angle ζ between the least-squares planes defined by the equatorial nitrogen atoms N12/N13/N14/N15 and the methylene carbon atoms C16/C17/C20/C21. – [c] Angle η subtended by the lines N11···C13 and N11–Cu1 at N11. – [d] The corresponding distance is 4.965(5) Å in **9.**

[{(nac)$_2$pyN$_4$}Cu](PF$_6$)$_2$

When a suspension of [(**1**)Cu](PF_6)$_2$ (**7**) in methanol is refluxed with a large excess of acetone in the absence of base, a mononuclear copper(II) complex is obtained cleanly and in good yield as a blue-violet solid which contains the bis(acetoneimine) derivative of the ligand, as verified by an X-ray structure analysis, i.e. [{(nac)$_2$pyN$_4$}Cu](PF_6)$_2$·$Me_2(C{=}O)$ (**9**).[15] Heating the mixture to reflux is essential for the reaction to take place; in a separate experiment under otherwise identical conditions, stirring a solution of **7** in acetone at room temperature led to quantitative re-isolation of the starting material upon workup.



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The IR spectrum of **9** has absorptions between 3400 and 3000 cm^{-1} (ν_{N-H} str) and at 1582 cm^{-1} (ν_{N-H} def), characteristic of coordinated primary amine groups, and a new strong absorption at 1658 cm^{-1} assigned to the C=N stretching vibration. The spectrum is similar to that of a nickel(II) complex of the same ligand previously isolated from *basic* mixtures of **1** and acetone upon addition of a suitable nickel(II) salt.[4] In the same manner as has been observed for the nickel(II) complex, reacting [(**1**)Cu](PF_6)$_2$ (**7**) in neat acetone does not lead to more highly condensed products. The generation of **9** parallels the formation of a copper(II) bis(isopropylideneimine) complex from bis(1,3-propanediamine)copper(II) perchlorate and acetone under base-free conditions, as reported by Curtis and House.[16] A *trans* arrangement of the coordinated *N*-isopropylidene groups was inferred on the basis of circumstantial evidence for this complex, whose hydrolytic instability, however, precluded structural characterisation. The complex was isolated as an intermediate from a reaction which, upon prolonged standing and without added base, produced a square planar 16-membered macrocyclic copper(II) species. Contrary to these observations, compound **9**, which is remarkably stable towards hydrolysis, shows no further reaction with acetone in the absence of base.

The structure of the cation in **9** is shown in Figure 2. The molecule is C_2-symmetrical, with the metal ion, the pyridine nitrogen atom N11, and the pyridine carbon atom C13 lying on the rotation axis. The pyridine, primary amine, and isopropylidene-imine nitrogen atoms define a square pyramid, which is distorted slightly in the sense that, while one basal *trans* N–Cu–N unit is strictly linear [∠(N13–Cu1–N13A) = 179.6(3)°], the other is bent at an angle of ∠(N12–Cu1–N12A) = 170.3(2)° (Table 1). Of the basal Cu–N bonds, those involving the sp^2 nitrogen atoms are shorter [d(Cu1–N12) = 2.008(2) Å], as expected, than those involving the primary amine groups [d(Cu1–N13) = 2.046(2) Å]. Again, the axial Cu–N bond is longer [d(Cu1–N11) = 2.105(4) Å] than the bonds at the base of the pyramid. Overall, the structure resembles that of a related pentacoordinate nickel(II) complex of the same ligand, except that in the latter the $M-N_{ax}$ bond is the shortest of all metal–nitrogen bonds.[4] Complexes of this topology are chiral, the aliphatic quaternary carbon atoms being stereogenic centres as a consequence of asymmetric substitution of the basal N_4 donor set. Compound **9** crystallises in the noncentrosymmetric space group *C*2, which indicates spontaneous resolution of enantiomers upon crystallisation.[17]

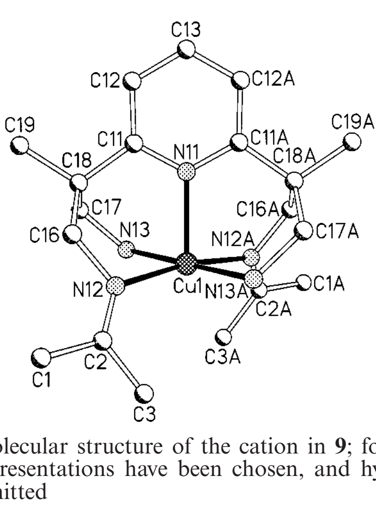


Figure 2. Molecular structure of the cation in **9**; for clarity, ball-and-stick representations have been chosen, and hydrogen atoms have been omitted

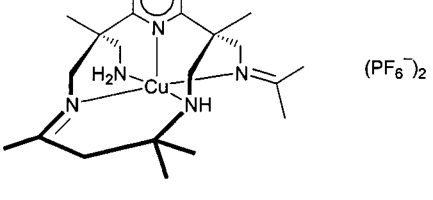
Copper(II) Pentaamine Complexes Containing an Acetone-Derived C_3 Bridge and an Isopropylidene-Imine Unit

Whereas refluxing mixtures of [(**1**)Cu]X_2 and acetone in methanol, in the absence of base, yield the *trans*-bis(isopropylideneimine) derivative (compounds **9** and **10**, above), an excess of sodium methoxide in such solutions causes the condensation to proceed further, leading to the formation of one diacetone-amine-imine linkage. A 12-membered 1,5,9-triazamacrocycle, incorporating the pyridine nitrogen atom, is thus formed. Two "podand" nitrogen donors remain of the NN_4 set, viz. a primary amine and an isopropylidene imine group (podand-cum-macrocycle). The condensation parallels the formation of an isolable intermediate in the Ni^{II}/ethylenediamine system, which also contains one diacetone-amine-imine bridge beside an isopropylideneimine and an NH_2 group.[16] In our case, with Cu^{II}, complete cyclisation involving all basal N donors, in a manner similar to the formation of a 16-membered tetraazamacrocycle from the Cu^{II} complex of 1,3-diaminopropane,[8] has so far not been observed. Two regioisomeric forms are possible for the condensation product of **1**, depending on whether the C=N double bonds are *cis* or *trans* with respect to the pyridine ring plane. Indeed, the product initially forms as a mixture of both isomers, which have been separately obtained as the hexafluorophosphate (*trans*, **11**) and tribromocuprate(I) salts (*cis*, **12**), by a combination of fractional crystallisation and temperature-induced isomerisation (see Experimental Section). In the case of **12**, the reducing agent responsible for the formation of $[Cu^IBr_3]^{2-}$ is as yet unidentified. However, the pentaamine **1** has been shown to act partially as a reducing agent in the case of some cobalt(III) complexes.[1]

Figure 3 shows the crystal structures of the cations in **11** and **12**. Both complexes, which are chiral, crystallise in centrosymmetric space groups (Table 3). The coordination geometry of the Cu^{II} ion is square-pyramidal in both cases, with a similar tilt of the pyridine ring (Table 2). The $Cu-N_{ax}$ and $Cu-N_{bas}$ bond lengths do not differ markedly from those determined for the bis(isopropylideneimine) complex **9** (Table 1). The diacetone-amine-imine linkage runs alongside the pyridine ring, spanning a pair of *cis*-positioned nitrogen atoms of both 1,3-diaminoprop-2-yl sidearms. The conformation of the bridge is the same in both structures, only its orientation is inverted on going from **11** (C=N *trans*) to **12** (C=N *cis*). Isomerism at the secondary amine centres due to restricted inversion is not observed. Neither structure is significantly strained, as judged from the bond lengths and angles in the ligand framework; in particular, the bond angles in the 12-membered triazamacrocycle incorporating the acetone-derived bridge and the *ortho*-disubstituted pyridine unit are within the range for sp^2- and sp^3-hybridised carbon and nitrogen atoms. The conformation of the triazamacrocycle in **11** and **12** is similar to that found in Cu^{II} and Ni^{II} complexes of 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene, which may be obtained by the metal-templated condensation of dipropylenetriamine with acetone.[18,19] It therefore seems unlikely that the formation of a second diacetone-amine-imine linkage in **11** or **12** is inhibited purely for reasons of ring strain that would otherwise ensue; rather, the nucleophilicity of the last remaining primary amino group appears to be significantly reduced, and a stronger base may be required to produce an amido ligand in sufficient concentration to allow the second ring closure to proceed.[20]

A Bis(aminal) Derivative From the Reaction of 1·2HBr with Acetone

Beside transition metal ions such as Ni^{II} and Cu^{II}, protons have also been used as a templating agent (and acid catalyst) in macrocyclisations involving C=N bond formation.[3,21] Metal-free condensation products are attractive as they provide indirect access to macrocyclic complexes not otherwise accessible, either by a metal-template reaction or by transmetallation. In the case of 1,2-diaminoethane, with acetone as the carbonyl component, the formation of a macrocyclic product is observed only when the diamine is employed in its monoprotonated form, $H_2NCH_2CH_2NH_2{\cdot}HX$.[22,23] The macrocycle, which separates as the diprotonated salt, is assembled from two equivalents of diamine and four equivalents of acetone, containing two diacetone-amine-imine bridges. The same product forms when mesityloxide (4-methyl-3-pentene-2-one) is used as the carbonyl component. In the case of monoprotonated 1,3-diaminopropane, instead of macrocycle formation, the reaction with acetone may lead preferentially to the aminal derivative, which is a six-membered hexahydropyrimidine ring.[24–27] The intermediate formation of aminals has been invoked as the controlling process in the assembly of a Schiff base tetramacrocycle from **1** and a difunctional aldehyde in the presence of protons,[3] and a bis(aminal) product has been isolated from the reaction of **1** with two equivalents of ferrocenecarbaldehyde.[5] In view



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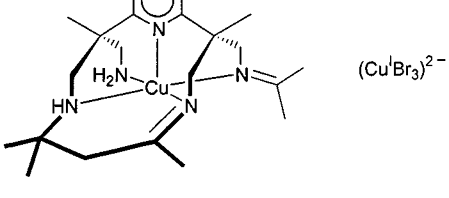

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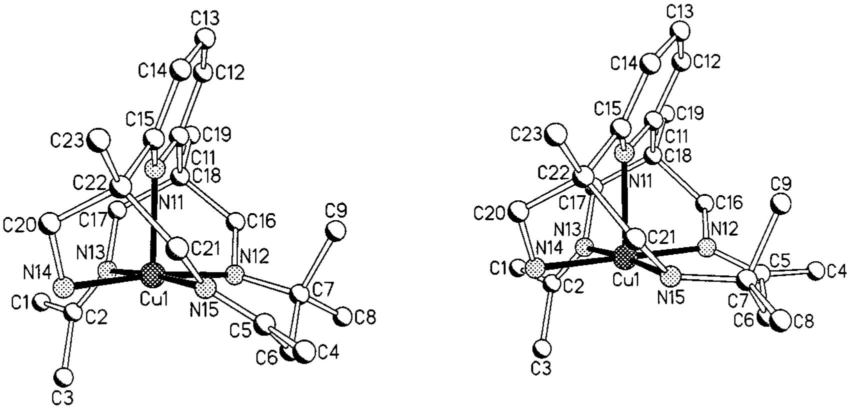


Figure 3. Molecular structures of the two isomeric complexes arising from the condensation of [(**1**)Cu]X_2 with acetone in the presence of base; the orientation of the C=N double bonds is *trans* in **11** (left), and *cis* in **12** (right)

Table 3. Crystallographic data for compounds **5**, **9**, **11**, **12** and **13**

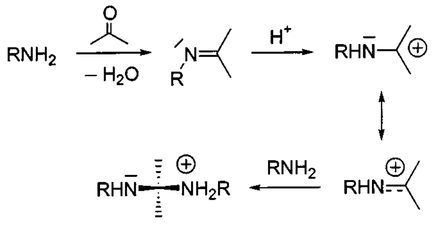
	5	**9**	**11**	**12**	**13**
Empirical formula	$C_{15}H_{25}CuN_7S_2 \cdot H_2O$	$C_{19}H_{33}CuF_{12}N_5P_2 \cdot C_3H_6O$	$C_{22}H_{37}CuF_{12}N_5P_2$	$C_{22}H_{37}Br_3Cu_2N_5 \cdot CH_4O$	$C_{19}H_{35}Br_2N_5 \cdot CH_4O$
Molecular weight	449.10	743.06	725.05	770.42	525.38
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
Space group (no.)	$P2_1/n$ (no. 14)	$C2$ (no. 5)	Pbca (no. 61)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a [Å]	14.466(3)	14.367(4)	13.496(3)	9.824(2)	11.977(2)
b [Å]	9.242(2)	10.829(3)	12.663(3)	9.989(2)	12.514(1)
c [Å]	15.102(4)	11.269(4)	34.491(8)	15.404(5)	16.680(3)
α [°]	90	90	90	103.50(2)	90
β [°]	90.69(2)	114.52(2)	90	98.97(2)	104.52(1)
γ [°]	90	90	90	95.72(2)	90
Z	4	2	8	2	4
V [Å^3]	2018.9(8)	1595.1(8)	5895(2)	1437.2(6)	2420.2(6)
$\rho_{calcd.}$ [g cm^{-3}]	1.478	1.547	1.634	1.780	1.442
Diffractometer	Nicolet R3m/V	Nicolet R3m/V	Siemens P4	Nicolet R3m/V	Siemens P4
λ[a] [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal size [mm^3]	0.45 × 0.32 × 0.20	0.50 × 0.38 × 0.32	0.76 × 0.60 × 0.36	0.28 × 0.24 × 0.12	0.55 × 0.50 × 0.40
T [°C]	298(2)	298(2)	200(2)	298(2)	210(2)
Absorption correction	Psi-scan	Psi-scan	Psi-scan	Psi-scan	Psi-scan
T_{min}/T_{max}	0.334/0.403	0.589/0.665	0.214/0.255	0.077/0.138	0.029/0.084
Scan	ω	ω	ω	ω	ω
2Θ range	$4 \leq 2\Theta \leq 54$	$4 \leq 2\Theta \leq 54$	$4 \leq 2\Theta \leq 54$	$4 \leq 2\Theta \leq 54$	$4 \leq 2\Theta \leq 54$
Measured reflections	5525	2760	7834	6986	6610
Unique reflections	4412	2212	6425	6266	5289
Observed reflections[b]	2706	2051	4733	2292	3825
μ(Mo-K_α) [mm^{-1}]	1.308	0.881	0.949	5.675	3.369
Refined parameters	310	238	379	309	254
Data/parameter ratio	14.2	9.3	17.0	20.3	20.8
$wR2$ (all data)[c]	0.0778	0.0737	0.1493	0.1784	0.1228
R 1 (obs. data)[d]	0.0368	0.0316	0.0611	0.0647	0.0500
ρ_{fin}(max/min.) [e Å^{-3}]	0.334/−0.362	0.292/−0.217	1.116/−0.766	1.014/−0.773	0.611/−0.610
Weighting scheme[e]	$k = 0.0340/l = 0$	$k = 0.0489/l = 0$	$k = 0.0523/l = 19.0627$	$k = 0.0803/l = 0$	$k = 0.0536/l = 2.2687$
Abs. struct. parameter	–	0.013(14)	–	–	–

[a] Mo-K_α, graphite monochromator. – [b] with $F_o \geq 4\sigma(F)$. – [c] $wR2 = (\{\Sigma[w(F_o^2 - F_c^2)^2]\}/\{\Sigma[w(F_o^2)^2]\})^{0.5}$. – [d] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F > 4\sigma(F)$. – [e] $w = 1/[\sigma^2(F_o^2) + (k \cdot P)^2] + l \cdot P$and $P = (F_o^2 + 2F_c^2)/3$.

of the fact that the pentaamine **1** contains two 1,3-diaminopropyl residues in close proximity, thereby perhaps favouring macrocyclisation, we studied the reactivity of **1** towards acetone in the presence of two equivalents of hydrogen bromide.

When a methanolic solution of **1**·2 HBr, prepared in situ from the pentaamine tetrahydrobromide by addition of the required amount of LiOMe, is refluxed with an excess of acetone, the mixture soon deposits a colourless precipitate (52% isolated yield). Bands characteristic of a C=N stretching vibration are absent in the IR spectrum of this product, ruling out Schiff base formation. Instead, the combined elemental analysis, NMR and mass spectroscopic data show the material to be a bis(aminal) dihydrobromide/methanol solvate (**13**), formed by condensation of **1**·2HBr with two equivalents of acetone, by the classical mechanism shown in Scheme 2. The same product is obtained, again exclusively, when reacting **1**·2HBr with mesityloxide (4-methyl-3-

pentene-2-one), H^+ apparently catalysing hydrolysis of the latter after its carbonyl group has formed the Schiff base, with concomitant liberation of water.



Scheme 2. Formation of the protonated aminal moiety in **13**, involving acetone and two equivalents of primary amine

Single crystals of **13** were of sufficient quality to allow the determination of its solid-state structure, and in particular the hydrogen atom positions, all of which could be deduced from a difference Fourier synthesis. The structure of the dication, which has crystallographic C_1 symmetry, is shown in Figure 4. Each diazacyclohexane ring contains one nitrogen atom carrying two protons and hence a formal positive charge (N13, N15), and one nitrogen atom with a single proton (N12, N14). The diazacyclohexane rings both have a chair conformation, and are held in relative proximity by weak intramolecular/interionic hydrogen bonded contacts between aminal NH/NH_2 groups and one bromide counterion [Figure 4; d(N13−H13B···N14) = 3.230(5) Å, ∠(NHN) = 141.3(4)°, van der Waals radius of N: 1.55 Å;[14] d(N13−H13A···Br1) = 3.223(3) Å, ∠(NHBr) = 160.1(4)°; d(N14−H14B···Br1) = 3.587(3) Å, ∠(NHBr) = 150.8(4)°, sum of van der Waals radii of N and Br: 3.4 Å[14]]. As a consequence of the intramolecular contacts, the "single" proton H14B adopts an equatorial position, while H12B is in an axial position. The nitrogen−carbon bonds involving the NH_2^+ groups are slightly but significantly longer than the corresponding bonds involving NH (see the legend to Figure 4), as has been found for other amine/ammonium pairs.[28] The nitrogen atom N12 has a hydrogen-bonded contact with the OH group of the solvate methanol molecule. Bond lengths and angles in the diazacyclohexane and pyridine rings are in the normal range.

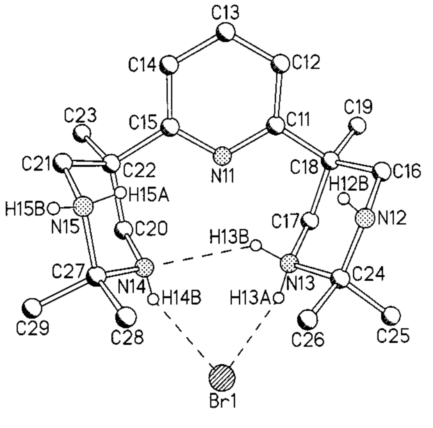
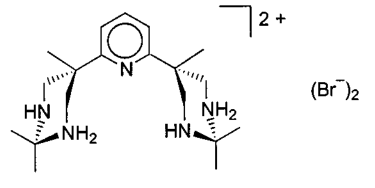


Figure 4. Molecular structure of the doubly protonated bis(aminal) which forms as the dibromide salt **13** when condensing **1**·2HBr with acetone. The positions of all hydrogen atoms have been located in a difference Fourier synthesis, but only the nitrogen-bonded protons are shown for clarity; some structural parameters are: N12−C16 = 1.468(6) Å, N12−C24 = 1.461(6) Å, N13−C17 = 1.501(5) Å, N13−C24 = 1.533(6) Å; C16−N12−C24 = 114.9(4)°, C17−N13−C24 = 114.0(3)°, N12−C24−N13 = 109.2(3)°



13

The bis(aminal) **13**, when deprotonated, is a metal-free tautomer of the bis(isopropylideneimine) ligand as found in complexes **9** or **10**. Indeed, the reaction of **13** with $[Cu(DMF)_6](ClO_4)_2$, after addition of two equivalents of LiOMe, yields **10** as the exclusive product, as identified by elemental analysis and IR spectroscopy. Compound **13** may thus serve as a metal-free equivalent of this chiral ligand, and work is currently under way to extend its coordination chemistry to other transition metals.

Conclusion

Reaction of the copper(II) template $[(\mathbf{1})Cu]^{2+}$ with acetone does not furnish a symmetrical condensation product in which all basal N donors have been incorporated into a macrocyclic ring, spanned by a 2,6-disubstituted pyridine unit, to give a reinforced coordination cap as outlined in the Introduction. The $[(\mathbf{1})Cu]^{2+}$/acetone system may, however, be controlled to provide the chiral bis(isopropylideneimine) ligand $\{(nac)_2pyN_4\}$ exclusively, and other transition metal complexes of this ligand should be accessible by an indirect route, via the diprotonated bis(aminal) of **1** formed in the reaction of **1**·2HBr with acetone. Current work addresses the question whether the metal-free condensation reaction can be extended to other carbonyl compounds, to give a series of chiral square pyramidal coordination caps derived from **1** with two substituted sidearms.

Experimental Section

CAUTION! Although no problems were encountered in this work, transition metal perchlorate complexes with organic ligands are potentially explosive and should be handled with due precautions.

Materials and Instrumentation: Manipulations were performed under dinitrogen using standard Schlenk techniques and freshly dried solvents. Reagents were AR grade or better and were purchased from Merck, Fluka, and Aldrich. **1**·4HBr·MeOH and $[Cu(DMF)_6](ClO_4)_2$ were prepared as described previously.[29,30] IR (KBr discs) and UV/Vis spectra (solvent: DMSO) were recorded on Perkin−Elmer 16PC FT-IR and Shimadzu UV-3101 PC instruments. Cyclic voltammograms were recorded using an EG & G potentiostat PAR model 264A and a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum auxiliary electrode and a Ag/AgCl reference electrode (room temperature; solvent: DMSO; scan rate: 50 mV s^{-1}; supporting electrolyte: NBu_4PF_6 [10^{-1} M]; internal standard: ferrocene,

E(Fc/Fc$^+$) = +0.4 V vs. NHE[31]). NMR spectra were measured on a JEOL JNM-EX 270 spectrometer, and mass spectra were obtained on JEOL MSTATION 700 and Micromass ZABSpecE spectrometers. Magnetic moments were measured using a Johnson-Matthey Gouy balance, with diamagnetic corrections calculated from Pascal's constants.[32] Elemental analyses were performed using Carlo Erba Elemental Analysers 1106 and 1108.

X-ray Crystallography: Crystal data for compounds **5**, **9**, **11**, **12** and **13** are given in Table 3, and selected distances and angles are listed in Table 1 and 2. Cation structures are presented in Figure 1−4. Structural data for other compounds containing the copper complex [Cu(**1**)]$^{2+}$ have been deposited with the Cambridge Crystallographic Data Centre {[Cu(**1**)](Br)$_2$·2MeOH (**3**), [Cu(**1**)](Br)$_2$·3H$_2$O (**4**), [Cu(**1**)](Br)(PF$_6$)·MeOH (**6**), [Cu(**1**)](ClO$_4$)$_2$ (**8**), [{(nac)$_2$pyN$_4$}Cu](ClO$_4$)$_2$ (**10**)}; the cation parameters resemble those determined for **5**. All structures discussed in this contribution were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXTL NT 5.10 (Bruker AXS, 1998). All non-hydrogen atoms were refined anisotropically.

Treatment of Hydrogen Atoms: All hydrogen atom positions in compounds **5**, **11**, **13** were obtained from a difference Fourier synthesis. For the structure of **5**, the positional H atom parameters were refined while a common isotropic displacement parameter was kept constant. In the case of the solvate water molecule in **5** and for the entire structures of **11** and **13**, both positional and common isotropic displacement parameters were kept constant during refinement.

The hydrogen atoms in compounds **9**, **12** were geometrically positioned and allowed to ride on their carrier atoms during refinement; their isotropic displacement parameters were tied to those of the adjacent atoms by a factor of 1.2 or 1.5.

Other Remarks: The disorder of the hexafluorophosphate anions in compound **9** could be resolved into two preferred orientations [occupancy factors 0.86(2) and 0.14(2)].

The maximum of the residual electron density in compound **11** is located within the ligand framework, indicating that a small percentage of the other isomer is present in the crystal structure. In preliminary X-ray structural analyses of product used "as-obtained" (no treatment subsequent to synthesis; see details below), the presence of both isomers in approximately equal amounts led to the determination of identical C−N single and C=N double bond lengths. In the structure of **11**, these distances are distinctly different [N12−C7: 1.473(5) Å, N15−C5: 1.290(5) Å]; for this reason, no allowance was made for the possible presence of the other isomer.

The structure of **12** is unremarkable in this respect, the maximum of the residual electron density being located at the copper atom.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-149662−149665 (**3**−**6**) and CCDC-149666−149671 (**8**−**13**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[(1)Cu](X)$_2$·solv (X = Br, solv = 0.5MeOH; 2): To a stirred suspension of **1**·4HBr·MeOH (1.24 g, 2.04 mmol) in methanol (20 mL) was added a solution of LiOMe (0.310 g, 8.16 mmol) in MeOH (5 mL) in one portion, to give a clear solution after ca. 15 min. at room temperature. To this was added a solution of CuCl$_2$·2H$_2$O (0.347 g, 2.04 mmol) in methanol (15 mL), and the mixture refluxed overnight. The solution changed colour from brown through blue to purple, and deposited a purple microcrystalline precipitate, which was collected on a glass frit, washed with methanol (3 × 10 mL), and dried in vacuo (0.65 g, 65%). Recrystallisation from methanol or methanol/water, with or without an added anion source (NH$_4$SCN, NH$_4$PF$_6$) and/or diethyl ether, yielded the compounds [(**1**)Cu](Br)$_2$·2MeOH (**3**), [(**1**)Cu](Br)$_2$·3H$_2$O (**4**), [(**1**)Cu](SCN)$_2$·H$_2$O (**5**), [(**1**)Cu](Br)(PF$_6$)·MeOH (**6**), and [(**1**)Cu](PF$_6$)$_2$ (**7**), in most cases as single crystals. All compounds are purple, with the exception of compound **5**, which is blue. The following analytical data were obtained for compound **2**: $C_{13}H_{25}Br_2CuN_5$·0.5CH$_4$O (490.8): calcd. C 33.04, H 5.55, N 14.27; found C 33.14, H 5.95, N 14.53. − IR (KBr): ṽ = 3442 cm^{-1}, 3432, 3303, 3213, 2982, 2926, 1600, 1584, 1470, 1455, 1250, 1088, 1011, 822, 768, 624. − MS (FAB, *p*-NBA): *m*/*z* (%) = 314 [(**1**)Cu]$^+$ (100), 395 {[(**1**)Cu]Br}$^+$ (65). − μ_{Eff} (spin only) = 1.71 BM. − Cyclic voltammetry (room temp., 10^{-3} M soln. in abs. DMSO): $E_{1/2}$ (Cu^{II}/Cu^{I}) = −0.62 V. − UV/Vis: λ_{max} (ε) = 530 nm (61 dm^3·mol^{-1}·cm^{-1}).

[(1)Cu](ClO$_4$)$_2$ (8): In contrast to the bromide salts **2**, **3** and **4**, the perchlorate salt **8** is soluble in acetone. It was prepared from the free pentaamine ligand **1** as follows: A suspension of **1**·4 HBr·MeOH (1.20 g, 1.98 mmol) in MeOH was neutralised by addition of 4 equiv. LiOMe. The resulting solution was taken to dryness, extracted with CH$_2$Cl$_2$ to remove LiBr, and the dichloromethane extract taken to dryness to leave **1** as a pale yellow oil. Addition of MeOH (15 mL) gave a clear solution, to which was added in one portion a faint blue solution of [Cu(DMF)$_6$](ClO$_4$)$_2$ in MeOH (15 mL). A purple solution formed immediately, which was refluxed for 1 h and subsequently reduced in volume to ca. 20 mL by applying a stream of dry dinitrogen. When crystallisation set in, the mixture was filtered, and diethyl ether allowed to diffuse into the filtrate. The single crystals obtained in this manner were separated by filtration, washed with MeOH, and dried in a stream of dinitrogen (0.21 g, 21%). Additional crops of **8** were obtained by allowing the mother liquor to stand in air. − $C_{13}H_{25}Cl_2CuN_5O_8$ (513.8): calcd. C 30.39, H 4.90, N 13.63; found C 30.68, H 4.96, N 13.75. − IR (KBr): ṽ = 3303 cm^{-1}, 3216, 3137, 2963, 2927, 2881, 1601, 1585, 1471, 1456, 1399, 1261, 1084 (br), 1012, 822, 802, 769, 625. − MS (FD): *m*/*z* (%) = 315 [(**1**)Cu]$^+$ (100), 413 {[(**1**)Cu](ClO$_4$)}$^+$ (80).

[{(nac)$_2$pyN$_4$}Cu](X)$_2$ (X = PF$_6$: 9): To a suspension of [(**1**)Cu](PF$_6$)$_2$ (0.20 g, 0.33 mmol) in methanol (30 mL) was added acetone in large excess (1 mL), and the mixture refluxed overnight to give a purple solution. Diffusion of diethyl ether into this solution produced single crystals of the acetone solvate [{(nac)$_2$pyN$_4$}Cu](PF$_6$)$_2$·H$_3$C(C=O)CH$_3$ (0.15 g, 62%). − $C_{19}H_{33}CuF_{12}N_5P_2$·C$_3H_6$O (743.1): calcd. C 35.56, H 5.29, N 9.43; found C 35.26, H 5.64, N 9.32. − IR (KBr): ṽ = 3371 cm^{-1}, 3316, 3214, 3113, 2958, 1729 (acetone), 1658 (C=N), 1582, 1469, 1374, 1265, 1122, 1014, 836 (PF$_6$), 557. − MS (FAB, *p*-NBA): *m*/*z* (%) = 394 [{(nac)$_2$-pyN$_4$}Cu]$^+$ (100), 475 {[{(nac)$_2$-pyN$_4$}Cu]Br}$^+$ (35). − μ_{Eff} (spin only) = 1.60(3) BM. − UV/Vis: λ_{max} (ε) = 528 nm (125 dm^3·mol^{-1}·cm^{-1}).

X = ClO$_4$ (10): The perchlorate salt [(**1**)Cu](ClO$_4$)$_2$ (**8**), when treated in a similar manner with an excess of acetone in MeOH/acetone at reflux under base-free conditions, gave the corresponding bis(isopropylideneimine) complex **10** as an unsolvated solid. − $C_{19}H_{33}Cl_2CuN_5O_8$ (594.0): calcd. C 38.42, H 5.60, N 11.79; found C 37.92, H 5.95, N 11.70. − IR (KBr): ṽ = 3321 cm^{-1}, 3273, 3214, 3113, 2981, 1661 (C=N), 1592, 1469, 1374, 1266, 1088 (br, ClO$_4$), 818, 624. − MS (FD): *m*/*z* (%) = 395 [{(nac)$_2$-pyN$_4$}Cu]$^+$ (20), 494 {[{(nac)$_2$-pyN$_4$}Cu]ClO$_4$}$^+$ (100). Compound **10** may also be obtained by first reacting a methanolic solution of **1** with acetone under reflux, followed by addition of $[Cu(DMF)_6](ClO_4)_2$ in MeOH. Finally, **10** was obtained from the diprotonated bis(aminal) **13** (see below) as follows: To a solution of **13** in methanol was first added LiOMe (2 equiv.), then $[Cu(DMF)_6](ClO_4)_2$ (1 equiv.) in MeOH, and the mixture refluxed overnight to give a purple solution. Isothermal diffusion of ether into this solution produced a purple crystalline precipitate identified as **10** by IR spectroscopy and elemental analysis.

Preparation of Copper(II) Complexes of 1 Containing an Acetone-Derived C_3 Bridge and an Isopropylidene-Imine Unit: To a stirred suspension of $1{\cdot}4HBr{\cdot}MeOH$ (0.766 g, 1.26 mmol) in methanol (20 mL) was added a slight excess of sodium metal (0.125 g, 5.23 mmol). After the evolution of H_2 had ceased, acetone (5 mL) was added to the clear solution, and the mixture refluxed for 1 h. After cooling to room temperature, $CuCl_2{\cdot}2H_2O$ (0.215 g, 1.26 mmol) was added as a solid in one portion, and the mixture refluxed overnight to give a purple solution. To this was added solid $NaPF_6$ to produce a purple precipitate, which was isolated and dried in vacuo (A). Preliminary X-ray data of this material indicated a mixture of two structural isomers (see text and X-ray Crystallography, above) originating from the condensation of $[(\mathbf{1})Cu]^{2+}$ with three equivalents of acetone. Elemental analysis data are in agreement with this formulation: $C_{22}H_{37}CuF_{12}N_5P_2$ (725.0): calcd. C 36.45, H 5.14, N 9.66; found C 36.50, H 5.33, N 9.62. The mother liquor of this preparation was taken to dryness, leaving a reddish-brown solid (B). Both isomers were obtained separately as follows:

Isomer with *trans*-Oriented C=N Double Bonds (11): The crystalline solid obtained under (A), above, was taken up in an acetone/methanol mixture (1:1, 20 mL), and the mixture refluxed overnight to give an intensely coloured purple solution. Cooling to room temperature produced a purple precipitate of single crystals and a faintly pink supernatant. Elemental analysis, although as yet unsatisfactory, and mass spectrometric data indicate a compound of composition $C_{22}H_{37}CuF_{12}N_5P_2$ [bis(hexafluorophosphate) salt, 725.0]: calcd. C 36.45, H 5.14, N 9.66; found C 35.57, H 5.04, N 8.92. − ESI: *m/z* (%) = 434 $[C_{22}H_{37}N_5Cu]^+$ (100). − IR (KBr): $\tilde{\nu}$ = 3356 cm^{-1}, 3307, 3270, 2983, 2939, 2357, 2338, 1660 (C=N), 1589, 1471, 1375, 1243, 1127, 1020, 984, 843 (PF_6), 556.

Isomer with *cis*-Oriented C=N Double Bonds (12): The solid obtained under (B) above was likewise taken up in an acetone/methanol mixture (1:1, 20 mL), and the mixture refluxed overnight. The purple solution, upon cooling to room temperature, deposited reddish-purple single crystals, leaving a strongly coloured purple supernatant. Elemental analysis data best agree with the solid being a monomethanol solvate of composition $C_{22}H_{37}Br_3Cu_2N_5{\cdot}CH_4O$ (tribromocuprate salt, 770.4): calcd. C 35.86, H 5.36, N 9.09; found C 34.60, H 6.11, N 8.73. − FAB: *m/z* (%) = 434 $[C_{22}H_{37}N_5Cu]^+$ (100). − IR (KBr): $\tilde{\nu}$ = 3442 cm^{-1}, 3212, 3136, 2969, 2368, 2344, 1645 (C=N), 1585, 1572, 1466, 1446, 1420, 1372, 1356, 1241, 1219, 1152, 1095, 1012, 834, 821, 764, 659, 597, 416.

Preparation of the Bis(aminal)dihydrobromide 13: Solid $1{\cdot}4HBr{\cdot}MeOH$ (0.67 g, 1.1 mmol) was treated with 2 equivalents of LiOMe (1 M solution in methanol, 2.2 mL, 2.2 mmol), giving a clear solution after stirring at room temperature for 5 min. To this was added a large excess of anhydrous acetone (30 mL), and the mixture heated to reflux. A colourless precipitate began to form after a few minutes. Refluxing was continued for 1 h; the mixture was then allowed to cool to room temperature, filtered (G4 glass frit), the obtained solid washed with acetone (2 × 8 mL), and dried in vacuo overnight (0.30 g, 52%). Single crystals of **13** (methanol solvate) were obtained by allowing diethyl ether to diffuse into a methanolic solution of the salt at room temperature. − $C_{19}H_{35}Br_2N_5{\cdot}CH_4O$ (525.4): calcd. C 45.72, H 7.48, N 13.33; found C 45.92, H 7.30, N 13.25. − ^1H NMR ([D_6]DMSO, room temp.): δ = 8.35 (br. s, 6 H, NH), 7.84 [AB_2, 3 lines, $^3J(HH)$ = 7.9 Hz, 1 H, py-H^4], 7.45 [AB_2, 2 lines, $^3J(HH)$ = 7.9 Hz, 2 H, py-$H^{3,5}$], 4.12 [br. s, 1 H, OH (methanol)], 3.47 (br. m, 4 H, $-C\mathit{H}H-$), 3.15 [s, 3 H, CH_3 (methanol)], 3.11 (br. m, 4 H, $-CH\mathit{H}-$), 1.52 [s, 6 H, $C(CH_3)_2$], 1.42 [s, 6 H, $C(CH_3)_2$], 1.37 (s, 6 H, py$-C-CH_3$). − ^{13}C NMR ([D_6]DMSO, room temp.): δ = 161.86 (s, C2/6), 138.19 (s, C4), 119.23 (s, C3/5), 69.63 (s, aminal $\mathit{C}Me_2$), 48.58 (s, CH_3OH), 46.94 (s, $-CH_2-$), 37.00 (s, py-$\mathit{C}-$Me), 25 [br, aminal $C(\mathit{C}H_3)_2$], 23.01 (py$-C-\mathit{C}H_3$). − FD: *m/z* (%) = 253 $[py(NH_2)_2(NH_3)_2]^+$ (25), 293 $[py(NH_2)(NH_3)(NHC(CH_3)_2NH_2)]^+$ (30), 333 $[py\{NHC(CH_3)_2NH_2\}_2]^+$ (50). − IR (KBr): $\tilde{\nu}$ = 3244 cm^{-1}, 2961, 1585, 1566, 1500, 1470, 1390, 1238, 1123, 1034, 983, 944, 914, 900, 883, 813, 761, 715, 643, 632, 525, 496, 484, 442. A similar reaction of $1{\cdot}2HBr$ in methanol with two equivalents of mesityloxide (4-methyl-3-pentene-2-one, $C_6H_{10}O$), after stirring at room temperature for 3 days, produced **13** as the exclusive product, as identified by elemental analysis and mass spectrometry. Further, mass spectra show the bis(aminal) (*m/z* = 333) to form also when reacting unprotonated **1**, prepared by addition of 4 equiv. of LiOMe to a suspension of $1{\cdot}4HBr{\cdot}MeOH$ in methanol, with acetone or mesityloxide (3 days, room temperature).

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[15] $[(\mathbf{1})Cu](ClO_4)_2$ (**8**) gives the same reaction, yielding the corresponding perchlorate salt $[\{(nac)_2\text{-}pyN_4\}Cu](ClO_4)_2$ (**10**), as

long as base-free conditions are maintained and the mixture is heated to reflux.

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