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# Unprecedented copper(II)-assisted acetal formation of a formyl-substituted bispyrazole. The X-ray structures of copper[1,2-bis-(3′-dimethoxymethylpyrazol-1′-yl)ethane] dichloride and dibromide

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The formation of two new acetal-containing ligands 1,2-bis(3′-dimethoxymethylpyrazol-1′-yl)ethane (bdmpe) and 1,2-bis(3′-diethoxymethylpyrazol-1′-yl)ethane (bdepe) in a Cu(II)-assisted alcoholysis of the initial ligand 1,2-bis(3′-formylpyrazol-1′-yl)ethane is described. The new ligands form polymeric complexes with Cu(II) salts of the general formula $[Cu(L)X_2]_x$, where L = bdmpe or bdepe, and X = Cl or Br. The single-crystal X-ray structures of $[Cu(bdmpe)Cl_2]_x$ and $[Cu(bdmpe)Br_2]_x$ show that two of the four oxygen atoms of the acetal fragments are axially semi-coordinated to the copper(II) ions, adjusting the coordination sphere around the metal ion to a very distorted octahedron. The coordination of the oxygen atoms of the acetal groups to the metal ion may well be the driving force for the transformation of the initial aldehyde groups into the acetal fragments. The equatorial plane in $[Cu(bdmpe)Cl_2]_x$ is a *trans*-$CuN_2Cl_2$ chromophore, while in $[Cu(bdmpe)Br_2]_x$ it is a *cis*-$CuN_2Br_2$ species with a large in-plane distortion.

## 1. Introduction

Coordination compounds of copper(II) with various azole-containing ligands have been intensively explored during the last decade.[1–4] The interest in this subject has been partly caused by the numerous interactions of copper ions with imidazole groups from histidine residues in many biological molecules and metalloproteins.[5–7] A variety of chelating ligands, mostly containing pyridine, pyrazole, or benzimidazole rings, have been used to model the imidazole–copper bonding in metalloproteins. Pyrazole derivatives, among all azoles, mimic imidazole most closely,[8] being isostructural and isoelectronic analogues of imidazole. This work reports the synthesis and structures of new copper(II) complexes with the pyrazole-containing ligands 1,2-bis(3′-dimethoxymethylpyrazol-1′-yl)ethane (bdmpe) and 1,2-bis(3′-diethoxymethylpyrazol-1′-yl)ethane (bdepe). Both ligands are formed during the process of crystallisation with copper(II) salts from the initial ligand 1,2-bis(3′-formylpyrazol-1′-yl)ethane (bape) due to the reaction of the aldehyde groups with the solvent.

The starting compound 1,2-bis(3′-formylpyrazol-1′-yl)ethane (bape) has been synthesised using a procedure similar to that described by Tarrago *et al*.[9] It consists of two pyrazole fragments containing aldehyde groups in the 3 positions, which are coupled by an aliphatic spacer (Fig. 1). Similar ligands, containing aliphatic substituents instead of the aldehyde groups, have been described previously.[10–13] Generally, they have been found to act as chelating didentate ligands,[11,12] but a few exceptions are known. The ligand 1,2-bis(3′,5′-dimethylpyrazol-1′-yl)-ethane (bmpze) in the copper(II) complex $[Cu(bmpze)Cl_2(H_2O)]$ acts as a monodentate ligand through one pyrazole group with the second heterocycle only involved in hydrogen-bonding interactions with an adjacent complex.[13] The same ligand acts as a bridging didentate species in the palladium(II) complex *trans*-$[Pd(bmpze)Cl_2]_3$, resulting in the formation of the "molecular tricorn" structure.[10] The carbonyl substituents on the azole ring provide the ligand bape with potentially additional coordinating atoms. For example, the ligand 4-methyl-5-imidazolecarboxaldehyde (4-Me-5-CHOIm), containing the formyl group in the 5 position, acts as a didentate chelating ligand in the copper(II) complex $[Cu(4\text{-Me-5-CHOIm})_4](NO_3)_2(H_2O)_2$. Here the coordination about the copper(II) ion may be described as a distorted dodecahedron in which four oxygen atoms from the carbonyl groups form an elongated tetrahedron about the central metal ion.[2] A few examples are known in which the carbonyl group acts as a bridging group between two metal ions.[14] However, no examples of the transformation of an aldehyde group into their acetals with the subsequent coordination of the latter to the metal ion have been hitherto described in the literature.

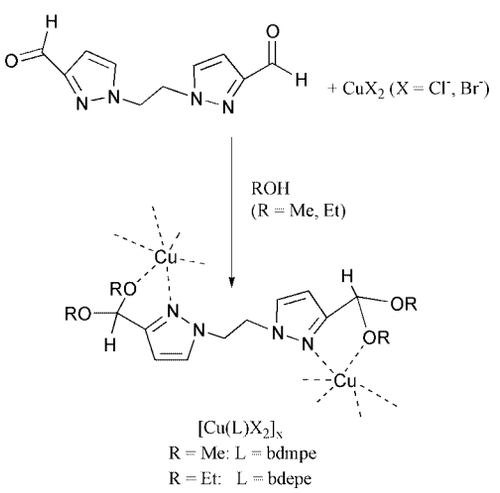


**Fig. 1** Schematic presentation of the aldehyde transformation.

## 2. Results and discussion

### 2.1 General

The crystallisation of the new pyrazole-containing ligand bape with the copper(II) salts in alcohol solution (methanol or ethanol) leads to the formation of coordination compounds

**Table 1** Spectroscopic data for bape, $[Cu(bdmpe)Cl_2]_x$, $[Cu(bdmpe)Br_2]_x$ and $[Cu(bdepe)Cl_2]_x$

| | bape | $[Cu(bdmpe)Cl_2]_x$ | $[Cu(bdmpe)Br_2]_x$ | $[Cu(bdepe)Cl_2]_x$ |
|---|---|---|---|---|
| IR/cm$^{-1}$ | 2861 $\nu$(C–H) aliph<br>1682 $\nu$(C=O) | 2939, 2836 $\nu$(C–H)<br>1048, 1033 $\nu$(C–O) | 2972, 2833 $\nu$(C–H) aliph<br>1053, 1033 $\nu$(C–O) | 2970, 2928, 2883 $\nu$(C–H) aliph<br>1035 (d) $\nu$(C–O) |
| LF/cm$^{-1}$ | — | 14700 (18000 sh) | 13280 (10900 sh), 24300, 19850 | 14900 (17540 sh) |
| EPR | — | $g_1 = 2.16$<br>$g_2 = 2.13$<br>$g_3 = 2.05$ | $g = 2.12$ | $g_1 = 2.27$<br>$g_2 = 2.12$<br>$g_3 = 2.06$ |

with two new ligands, bdmpe and bdepe (Fig. 1). These ligands are formed as the result of the reaction of aldehyde groups of the initial ligand bape with the solvent and their subsequent transformation into acetal fragments. A transformation of this kind, despite being widely known for organic reactions, has never been reported to occur during the synthesis of coordination compounds. The reaction is generally catalysed by inorganic (anhydrous) acids,[15] but in this case it can be regarded as caused by the presence of the copper ions. The Cu(II) ion has the electronic configuration $4s^0 3d^9$ and is a typical example of a 3d metal ion whose complexes show the presence of a Jahn–Teller effect. The crystal structures of $[Cu(bdmpe)Cl_2]_x$ and $[Cu(bdmpe)Br_2]_x$ indicate that in both complexes two of the four oxygen atoms of the acetals are semi-coordinated to the copper ions, adjusting the coordination sphere around the metal ion to a very distorted elongated octahedron, with oxygen atoms occupying the axial positions. Presumably, the formation of the acetal fragments allows the coordination of the oxygen atoms to the Cu(II) ion, which in turn stabilises the complex formed. Facts, supporting this assumption, are that no transformation occurs during the recrystallisation of the free ligand bape from an alcohol solution. In this case both NMR and IR spectra still show the presence of the aldehyde groups. Furthermore, attempts to obtain complexes of the ligand bape with other 3d metal ions (Zn(II), Co(II), Ni(II)) were not successful. This also indicates that the stability of the Cu(II) complexes is influenced by the presence of an additional Cu–O interaction. A large deviation from a regular octahedral geometry would be abnormal for ions other than Cu(II). Also, coordination compounds of copper(II) salts of the weakly and non-coordinating anions nitrate and tetrafluoroborate could not be obtained.

Up to this moment it has not been possible to obtain crystals of $[Cu(bdepe)Cl_2]_x$ suitable for X-ray structure determination. However, the spectroscopic data clearly indicate that the coordination sphere around the metal ions in both chloride complexes is very similar, if not identical. Spectral data for all compounds are presented in Table 1.

### 2.2 Crystal structure descriptions

PLUTON[16] projections of parts of the crystal structures of $[Cu(bdmpe)Cl_2]_x$ and $[Cu(bdmpe)Br_2]_x$ are shown in Fig. 2 and 3, respectively. Crystallographic data for both compounds are presented in Table 4 (see later) with selected bond lengths and angles listed in Tables 2 and 3. Both complexes have polymeric structures, with the ligands forming bridges between two copper(II) ions. The coordination sphere around Cu(II) can be described best as very distorted elongated octahedral $CuN_2X_2O_2$ ($X = Cl^-$, $Br^-$), with the two oxygen atoms from the acetal fragments in opposite positions.

In $[Cu(bdmpe)Cl_2]_x$ the copper ion lies on an inversion centre. The equatorial plane is formed by *trans*-chloride ions and two nitrogen atoms from two different ligand molecules with Cu–N and Cu–Cl distances of 2.009(3) and 2.2557(14) Å, which are in the normal range for similar $CuCl_2N_2$ chromophores.[4,17] The long Cu–O distances of 2.885(3) Å show the presence of a common Jahn–Teller distortion in the complex, comparable with Cu–O bonds in complexes with weakly binding ligands, such as carbonyl groups.[2,4]

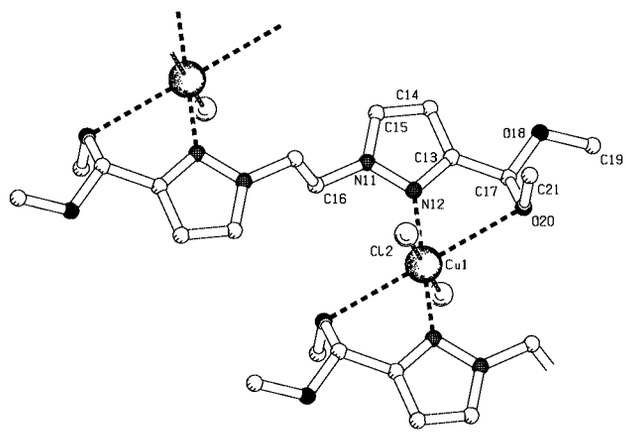


**Fig. 2** PLUTON[16] plot of the molecular structure of $[Cu(bdmpeCl_2]_x$. Hydrogen atoms are omitted for clarity.

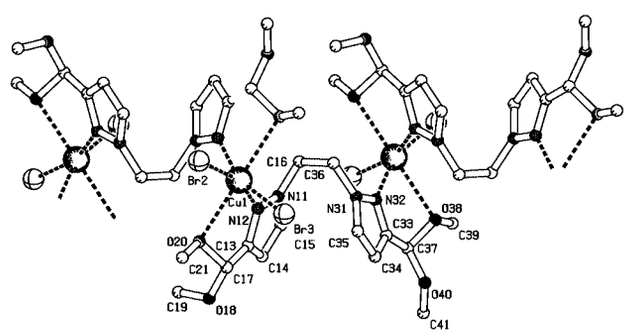


**Fig. 3** PLUTON[16] plot of the molecular structure of $[Cu(bdmpe)Br_2]_x$. Hydrogen atoms are omitted for clarity.

In $[Cu(bdmpe)Br_2]_x$ the equatorial square plane is not planar, with a dihedral angle between the $CuBr_2$ and $CuN_2$ planes of 20.17°, and with the four in-plane '90 degree' angles summing up to 367.4°. This distortion can be ascribed to factors like the large size of the bromide anions as well as pyrazole stacking and/or chelation constraints. The two bromides and the two nitrogen atoms in $[Cu(bdmpe)Br_2]_x$ are located in *cis*-positions to each other. The Cu–O distances are somewhat shorter in $[Cu(bdmpe)Br_2]_x$, *viz.* 2.604(16) to 2.673(16) Å, also indicative for a Jahn–Teller distortion.

The very small N–Cu–O coordination angles in both compounds (respectively of 68.43(11)° and of 70.2(6) and 68.6(6)°) are due to the restriction imposed by the three-bond ligand bite and the long Cu–O (semi-)coordination distance.

The crystal lattice of $[Cu(bdmpe)Br_2]_x$ is stabilised by the stacking of the pyrazole groups with the shortest ring–ring distances of 3.696 Å. For $[Cu(bdmpe)Cl_2]_x$ no stacking or hydrogen bonding is observed.

### 2.3 Spectroscopic data

The most important features of the IR spectra are given in Table 1. In all spectra of the coordination compounds the intense band in the region ≈1680 cm$^{-1}$, which is observed in the spectrum of the initial bape and corresponds to the C=O

stretching, is absent. Instead two intense bands appear around 1050 $cm^{-1}$. Apparently, the band at the highest frequency belongs to the non-coordinated acetal moiety, while the other band corresponds to the acetal fragment which is bound to the copper(II) ion. No bands are present in the region 3600 $cm^{-1}$ which indicates the absence of any O–H bonds and proves the formation of a "normal" acetal instead of a half-acetal.[18]

Visible-NIR reflectance spectra (Table 1) show the expected bands for octahedrally based Cu(II) complexes. The broad and asymmetric band around 15000 $cm^{-1}$ observed in both chloride complexes corresponds to a $^3T_{2g} \longleftarrow {}^2E_{1g}$ transition for the Cu(II) ion and is typical for 4 + 2 tetragonal ("square-plane") copper(II) complexes with a $CuN_2Cl_2$ chromophore group.[19] In the spectrum of $[Cu(bdmpe)Br_2]_x$ the band corresponding to the d–d transition is observed at a somewhat lower frequency (at 13280 $cm^{-1}$ with a shoulder at 10900 $cm^{-1}$); but two other bands are also present (24300 and 19850 $cm^{-1}$) which correspond to LMCT transitions Cu(II) $\longleftarrow \pi$Br.[19]

EPR powder spectra of the two chloride complexes taken at room temperature appear to be rather similar, both showing three signals ($g_1 = 2.16$, $g_2 = 2.13$, $g_3 = 2.05$ for $[Cu(bdmpe)Cl_2]_x$ and $g_1 = 2.27$, $g_2 = 2.12$, $g_3 = 2.06$ for $[Cu(bdepe)Cl_2]_x$), consistent with elongated rhombic-octahedral systems in a $d_{x^2-y^2}$ ground state.[20] The EPR spectra of chloride and bromide complexes are quite different. The EPR spectrum of $[Cu(bdmpe)Br_2]_x$ at room temperature and at 77 K shows only one broad signal with $g = 2.12$, apparently due to some minor exchange interactions leading to unresolved spectra.

**Table 2** Selected bond distances (Å) and angles (°) for $[Cu(bdmpe)Cl_2]_x$

| | | | |
|---|---|---|---|
| Cu(1)–Cl(2) | 2.2557(14) | Cl(2)–Cu(1)–N(12) | 90.35(10) |
| Cu(1)–N(12) | 2.009(3) | Cl(2)–Cu(1)–O(20) | 92.82(8) |
| Cu(1)–O(20) | 2.885(3) | N(12)–Cu(1)–O(20) | 68.43(11) |

### 2.4 Magnetic susceptibility

The magnetic susceptibility of $[Cu(bdmpe)Cl_2]_x$ and $[Cu(dbmpe)Br_2]_x$ has been determined in the temperature range 5–150 K. The magnetic interaction calculated from the Curie–Weiss law[21] results in a Weiss constant $\theta = 0$ K for both compounds indicating that no ferro- or antiferro-magnetic couplings are present in the systems. This is in agreement with the long distances between the copper ions, which are 7.523(3) Å for the chloride and 7.147(5) Å for the bromide complex, and indicates the absence of any exchange pathways between metal ions in the crystal lattice.

The Curie constant for $[Cu(bdmpe)Cl_2]_x$ is $C_{Cl} = 0.402$ and for $[Cu(bdmpe)Br_2]_x$ is $C_{Br} = 0.414$. The magnetic susceptibility results in $\mu_{B\ Cl} = 1.80$ B.M. and $\mu_{B\ Br} = 1.82$ B.M, which are normal values for complexes with one unpaired electron, as is in a copper $d^9$ system.[22] The $g$ values determined from the Curie constant[22] $g_{Cl} = 2.07$ and $g_{Br} = 2.10$ are in good agreement with the average $g$ values from the EPR measurements.

## 3. Concluding remarks

The first example of the transformation of an aldehyde group into acetal moieties due to the copper(II) assisted reaction with

**Table 3** Selected bond distances (Å) and angles (°) for $[Cu(bdmpe)Br_2]_x$

| | | | |
|---|---|---|---|
| Cu(1)–Br(2) | 2.388(4) | Cu(1)–N(32)b | 2.05(2) |
| Cu(1)–Br(3) | 2.412(4) | Cu(1)–O(20) | 2.604(16) |
| Cu(1)–N(12) | 2.039(16) | Cu(1)–O(38)b | 2.673(16) |
| | | | |
| Br(2)–Cu(1)–Br(3) | 96.11(13) | Br(3)–Cu(1)–N(32)b | 158.3(5) |
| N(12)–Cu(1)– N(32)b | 90.9(6) | Br(3)–Cu(1)–O(20) | 90.7(4) |
| O(20)–Cu(1)–O(38)b | 178.0(5) | Br(3)–Cu(1)–O(38)b | 90.7(3) |
| Br(2)–Cu(1)–N(12) | 160.1(5) | N(12)–Cu(1)–O(20) | 70.2(6) |
| Br(2)–Cu(1)–N(32)b | 90.6(4) | N(12)–Cu(1)–O(38)b | 108.2(6) |
| Br(2)–Cu(1)–O(20) | 90.6(3) | N(32)b–Cu(1)–O(20) | 109.9(6) |
| Br(2)–Cu(1)–O(38)b | 90.8(3) | N(32)b–Cu(1)–O(38)b | 68.6(6) |
| Br(3)–Cu(1)–N(12) | 89.8(5) | | |

Symmetry operation: b = 2 − $x$, 1/2 + $y$, 1/2 − $z$.

**Table 4** Crystallographic data for $[Cu(bdmpe)Cl_2]_x$ and $[Cu(bdmpe)Br_2]_x$

| Crystal data | $[Cu(bdmpe)Cl_2]_x$ | $[Cu(bdmpe)Br_2]_x$ |
|---|---|---|
| Formula | $C_{14}H_{22}Cl_2CuN_4O_4$ | $C_{14}H_{22}Br_2CuN_4O_4$ |
| Formula weight | 444.81 | 533.71 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/n$ (no. 14) | $P2_12_12_1$ (no. 19) |
| $a$/Å | 12.788(5) | 10.448(6) |
| $b$/Å | 7.523(2) | 11.215(3) |
| $c$/Å | 9.691(4) | 16.851(3) |
| $\beta$/° | 93.76(5) | 90 |
| $V$/$A^3$ | 930.3(6) | 1974.5(13) |
| $Z$ | 2 | 4 |
| $D_c$/g $cm^{-3}$ | 1.588 | 1.795 |
| $F$(000) | 458 | 1060 |
| $\mu$/$mm^{-1}$ | 1.5 | 5.2 |
| Crystal dimensions/mm | 0.6 × 0.25 × 0.15 | 0.5 × 0.15 × 0.15 |
| Crystal habit | Plate | Rod |
| Crystal colour | Blue | Orange |
| Temperature/K | 293 | 293 |
| $\theta_{min,max}$/° | 2.6, 29.8 | 2.2, 23.9 |
| Reflections: total, unique, observed | 6573, 2681, 2314 | 1759, 1759, 885 |
| $R_{int}$ | 0.077 | — |
| $N_{ref}$, $N_{par}$ | 1835, 148 | 852, 116 |
| $R$, $wR$, $S$ | 0.0470, 0.0640, 2.61 | 0.0480, 0.0570, 1.64 |
| $\Delta\rho_{min,max}$/e $A^{-3}$ | −1.12, 1.06 | −1.80, 1.60 |

the solvent and subsequent semi-coordination of the acetals to the copper(II) ion is presented. The transformation of the initial ligand 1,2-bis(3′-formylpyrazol-1′-yl)ethane (bape) rendered the new ligands 1,2-bis(3′-dimethoxymethylpyrazol-1-yl)ethane (bdmpe) and 1,2-bis(3′-diethoxymethylpyrazol-1-yl)ethane (bdepe), which form polymeric copper(II) complexes with the oxygen atoms from the acetal fragments semi-coordinated to the copper ions, adjusting the coordination sphere to a very distorted octahedron. This special coordination, only possible for the Jahn–Teller effect in Cu(II) complexes, is considered to be the driving force for the transformation of the aldehyde groups of the initial ligand into the acetal fragments.

## 4. Experimental

### 4.1 Materials and methods

All starting materials were commercially available and used as purchased. Tetrahydrofuran for the ligand synthesis was dried on sodium and distilled under $N_2$ prior to use.

Metal analyses were carried out on a Perkin-Elmer 3100 atomic absorption (AAS) and flame emission spectrometer using a linear calibration method. C,H,N-analyses were performed on a Perkin-Elmer 2400 series. Infrared spectra in the 4000–300 $cm^{-1}$ range were recorded on a Bruker 330V IR spectrophotometer equipped with a Golden Gate Diamond. Ligand field spectra of the solids (300–2000 nm, diffuse reflectance) were taken on a Perkin-Elmer 330 spectrophotometer equipped with a data station. NMR spectra of the ligands were recorded on a JNF-FX 200 spectrometer. X-Band electron paramagnetic resonance (EPR) measurements were performed at room temperature and at 77 K in the solid state on a Jeol RE2x electron spin resonance spectrometer using dpph (diphenylpicrylhydrazine, $g$ = 2.0036) as a standard. Magnetic susceptibility was measured in the temperature range 2–300 K at 0.5 T with a MPMS 5S Quantum Design SQUID susceptometer. Data were corrected for magnetization of the sample holder and diamagnetic contributions, which were estimated from the Pascal constants.[23]

### 4.2 Synthesis of 1,2-bis(3′-formylpyrazol-1′-yl)ethane (bape)

Under an argon atmosphere, 2.00 g (0.02 mol) of 3-formylpyrazole were dissolved in 150 mL of thf while heating at reflux. The resulting solution was cooled to −40 °C, and the suspensions of 3.70 g (0.01 mol) of 1,2-ditosylate-ethane in 50 mL of thf and 2.24 g KOt-Bu (0.02 mol) in 30 mL of thf were added subsequently. The resulting white suspension was allowed to warm to room temperature over 6 h and was refluxed for 3 h. After filtration, the residue was washed with dichloromethane, and the resulting thf–$CH_2Cl_2$ solution was evaporated, yielding a yellow solid. Washing with $Et_2O$ gave 1.35 g of pure compound. Yield: 62% (0.06 mol). $^1$H-NMR (DMSO-d$^6$, 200 MHz): $\delta$ = 9.83 (s, 2H, C(O)*H*); 7.69 (d, 2H, 4′-pz-*H*); 6.70 (d, 2H, 3′-pz-*H*); 4.75 (s, 4H, pz–C*H*$_2$C*H*$_2$–pz); (Found: C, 54,6; H, 4.9; N, 25.7. $C_{10}H_{10}N_4O_2$ requires: C, 55.0; H, 4.6; N, 25.7%).

### 4.3 Syntheses of the coordination compounds

**[Cu(bdmpe)Cl$_2$]$_x$.** A solution of bape (0.131 g, 0.60 mmol) in 10 mL MeOH was slowly added to an equimolar solution of $CuCl_2 \cdot 2H_2O$ (0.102 g, 0.60 mmol) in 10 mL MeOH. Dark-blue rectangular crystals suitable for X-ray structure determination appeared the next day. Yield: 78% (0.208 g, 0.47 mmol); (Found: C, 37.5; H, 4.8; N, 12.4; Cu, 14.2. $C_{14}H_{22}N_4O_4CuCl_2$ requires: C, 37.8; H, 5.0; N, 12.6; Cu, 14.3%).

**[Cu(bdmpe)Br$_2$]$_x$.** A solution of bape (0.131 g, 0.6 mmol) in 10 mL MeOH was added to a solution of $CuBr_2$ (0.134 g, 0.6 mmol) in 10 mL MeOH. Very thin dark-orange needles appeared within a few hours. Yield: 82% (0.26 g, 0.49 mmol); (Found: C, 31.8; H, 4.1; N, 10.2; Cu, 11.9. $C_{14}H_{22}N_4O_4CuBr_2$ requires: C, 31.5; H, 4.2; N, 10.50; Cu, 11.9%). Crystals suitable for X-ray structure determination were obtained by slow diffusion of the reagents using a Y-shaped tube.

**[Cu(bdepe)Cl$_2$]$_x$.** A solution of bape (0.131 g, 0.6 mmol) in 10 mL EtOH was slowly added to an equimolar solution of $CuCl_2 \cdot 2H_2O$ (0.102 g, 0.6 mmol) in 10 mL EtOH. Very small blue crystals precipitated within a few hours. Yield: 69% (0.207 g, 0.41 mmol); (Found: C, 42.4; H, 6.0; N, 11.2; Cu, 12.6. $C_{18}H_{30}N_4O_4CuCl_2$ requires: C, 43.2; H, 6.0; N, 11.2; Cu, 12.68%).

### 4.4 X-Ray structure determinations

The reflection intensities were measured on a four-circle Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The cell dimensions were determined using 24 independent reflections. Intensities were corrected for Lorentz and polarization effects. Absorption correction was not applied. The positions of heavy atoms were determined from a Patterson map (DIRDIF).[24] The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[25] The remainder of the non-hydrogen atoms were located in subsequent difference Fourier syntheses. Full-matrix least-squares refinement on $F$ using the XTAL3.4 set of programs[26] with the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2$ ($F$). Positional refinement of the non-hydrogen atoms, anisotropic for all non-hydrogen atoms of [Cu(bdmpe)Cl$_2$]$_x$ but only for Cu and Br of [Cu(bdmpe)Br$_2$]$_x$ due to a limited dataset, fixed isotropic displacement parameters for the hydrogens, which were placed at a calculated distance of 0.95 Å from their parent atoms. Geometric calculations and molecular graphics were performed with the PLATON package.[16] For all structures a selection of the crystal data and additional parameters are presented in Table 4. Selected bond distances and bond angles are given in Tables 2 and 3.

CCDC reference numbers 164041 and 164042.

See http://www.rsc.org/suppdata/dt/b1/b104655c/ for crystallographic data in CIF or other electronic format.

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