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Stability of disubstituted copper complexes in the gas phase analyzed by electrospray ionization mass spectrometry

Ines Starke, Stefan Kammer, Hans-Jürgen Holdt and Erich Kleinpeter*
Chemisches Institut, Universität Potsdam, Karl-Liebknecht-Str. 24–25, D-14476 Potsdam (Golm), Germany

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A series of nitrogen ligand (L)/copper complexes of the type $[Cu^{I}L]^{+}$, $[Cu^{II}L(X)]^{+}$ and $[Cu^{I}L_2]^{+}$ ($X = Cl^{-}$, BF_4^{-}, $acac^{-}$, CH_3COO^{-} and $SO_3CF_3^{-}$) was studied in the gas phase by electrospray ionization mass spectrometry. The following ligands (L) were employed: 1,12-diazaperylene (*dap*), 1,1′-bisisoquinoline (*bis*), 2,2′-bipyridine (*bpy*), 1,10-phenanthroline (*phen*), 2,11-disubstituted 1,12-diazaperylenes (*dap*), 3,3′-disubstituted 1,1′- bisisoquinoline (*bis*), 5,8-dimethoxy-substituted diazaperylene (*meodap*), 6,6′- dimethoxy-substituted bisisoquinoline (*meobis*) and 2,9-dimethyl-1,10-phenanthroline (*dmphen*). Collision-induced decomposition measurements were applied to evaluate the relative stabilities of the different copper complexes. The influence of the spatial arrangement of the ligands, of the type of substituents and of the counter ion of the copper salts employed for the complexation was examined. Correlations were found between the binding constants of the $[ML_2]^{+}$ complexes in solution and the relative stabilities of the analogous complexes in the gas phase. Furthermore, complexation with the ligands 2,11-dialkylated 1,12-diazaperylenes [alkyl = ethyl (*dedap*) and isopropyl (*dipdap*)] was studied in the solvents CH_3OH and CH_3CN. Copyright © 2010 John Wiley & Sons, Ltd.

A large number of metal complexes with 1,10-phenanthroline (*phen*) and its derivatives have been synthesized and display promising properties in a variety of fields, such as electron transfer processes in biological systems and self-assembly of supramolecular architectures.[1–6] In particular, copper complexes of 2,9-dimethyl-1,10-phenanthroline ligands are of great interest because of their photoluminescent behaviour and DNA/RNA binding properties.[7,8]

Solution studies of the relative stability of copper complexes with various nitrogen ligands have been performed.[9–14] Especially, the nitrogen heterocycles 1,10-phenanthroline (*phen*), 2,2′-bipyridine (*bpy*) and 2,9-dimethyl-1,10-phenanthroline (*dmphen*) have been studied as chelate ligands in solution and by electrospray ionization mass spectrometry (ESI-MS) in the gas phase.[15–19]

Detailed insight into the structure and binding interactions of transition metal complexes can be obtained by collision-induced dissociation (CID).[20–29] There is particular interest in the formation and dissociation of transition metal complexes with two or more different ligands which are simultaneously bound to one metal ion; in this connection the disassembly of these complexes is dependent on the binding interactions of the various ligands.[30–32]

The planar 'large surface' ligand *dap* as a phenanthroline analogue with increased π-delocalization was synthesized by Schmelz and coworkers.[33] The complexation of 1,1′-bis(isoquinoline) *bis* and *dap* in competition with other pyridyl containing ligands has been studied in detail.[34–37] The synthesis and physicochemical properties of Cu^{I} complexes with the nonplanar *bis* were described by Jahng *et al*.[38] Furthermore, it has been shown that substituents at the phenanthroline ring in positions close to the donor nitrogen atoms can have significant influences on the structure and properties of copper complexes.[39–42] Copper(I) complexes of the general formula $[Cu^{I}L_2]^{+}$ (L = 2,9-disubstituted-phenanthroline) display interesting photophysical properties resulting from metal-to-ligand charge transfer (MLCT).[43] A synthetic goal has been to maximize the size of the substituents at positions 2 and 9 of the phenanthroline ligand, while retaining the two bidentate ligands on the metal center which give rise to the MLCT. Recently, a number of 2,11-dialkylated 1,12-diazaperlyenes [alkyl = methyl (*dmdap*), ethyl (*dedap*) and isopropyl (*dipdap*)], have been synthesized by reductive cyclization of the corresponding 3,3′-dialkylated 1,1′-bisisoquinolines *dmbis*, *debis*, and *dipbis* which are the first copper(I) complexes with 'large surface' ligands.[44]

The ligands *meodap* and *meobis*, synthesized for the first time, have two methoxy groups in positions 5 and 8, and 6 and 6′, respectively. This substitution should influence the π-acceptor properties of these ligands; reduced stabilities of *meodap* and *meobis* complexes were expected.[45]

The copper complexes containing phenanthroline ligands with aryl substituents in positions 2 and 9 are of special interest because of existing, long-living excited states at room temperature; in addition, steric hindrance can provide highly

*Correspondence to: E. Kleinpeter, Chemisches Institut, Universität Potsdam, Karl-Liebknecht-Str. 24–25, D-14476 Potsdam (Golm), Germany.
E-mail: ekleinp@uni-potsdam.de

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protected rigid coordination spheres for metal ions.[46,47] Intensive steric interactions between aryl substituents and conformationally flexible ligands can result in a hard twist of the aryl moieties while the structure of phenanthroline remains almost or completely planar.[48–50] There has been considerable interest in the use of metal ions to control the self-assembly of topologically novel molecular structures. For example, minimum requirements for ligands bearing helical structures are two separate bidentate metal-binding sites which must be either linked directly or connected by a suitable spacer group. However, Constable *et al.*[51] have shown that the ligand 2,2′:6′,2″:6″,2‴-quaterpyridine (*qtpy*) generally forms mononuclear non-helical complexes with transition metal di- or trications.[52]

Both complex formation and stability of the unsubstituted ligands *dap*, *bis*, *bpy* and *phen* with transition metal ions in the gas phase have been studied by ESI-MS and CID measurements.[53] In this paper, we extend our studies to the gas-phase complexation of non-substituted ligands to copper complexes with disubstituted ligands (*dmdap*, *dmbis*, *dedap*, *debis*, *dipdap*, *dipbis*, *meodap*, *meobis*, *phbis* – R = Ph, *pybis* – R = pyridine and *dmphen*; see Scheme 1). In addition, we evaluate both the dissociation and the stability of the various homoleptic or heteroleptic copper complexes by energy-variable CID experiments. The complexes of interest incorporate either one or two of the new ligands in competition with pre-existing ligands *phen*, *bpy* and *dmphen*. In addition, the effect of the steric hindrance of various substituents in positions 2 and 11 will be studied by measuring the relative stabilities of complexes containing the ligands *dap*, *dmdap*, *dedap*, and *dipdap*.

The solution-binding constants of the *phen* ligands are typically larger than those of *bpy* and its analogues because the rigidity of *phen* generates a higher degree of preorganization.[54]

In order to investigate comprehensively the importance of this fact, the stability of rigid 2,11-dialkylated 1,12-diazaperlyene ligand complexes were compared with that of the 3,3′-disubstituted 1,1′-bis(isoquinoline) analogues *dmbis*, *debis*, *dipbis* and the complexes with *meodap* and *meobis* (with R = MeO at the position 5,8 and 6,6′, respectively) as ligands.

In addition, the new ligand *phbis*, with the sterically ambitious substituent phenyl, and the pyridyl ligand *pybis*, were chosen to investigate the effect of both the replacement of the alkyl substituent for phenyl and pyridyl and, in the case of *pybis*, the ability to coordinate the copper ion in tetradentate mode.

EXPERIMENTAL

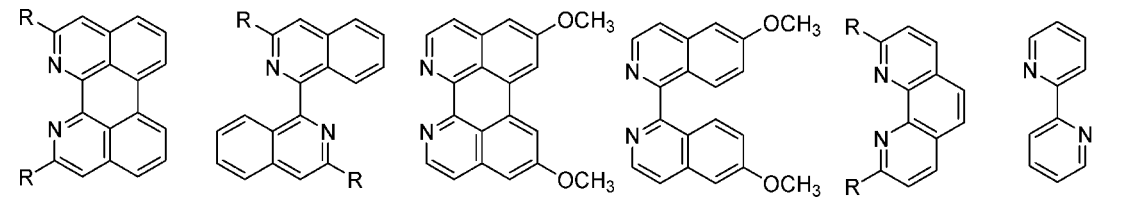
Syntheses

The ligands 1,12-diazaperylene[55] (*dap*) and bis(isoquinoline)[56] (*bis*), and the 2,11-dialkylated 1,12-diazaperylene (alkyl = Me, ethyl, and isopropyl), were synthesized by reductive cyclization of the corresponding 3,3′-dialkylated 1,1′-bisisoquinolines. The 3,3′-alkyl-1,1′-bisisoquinolines were synthesized by homocoupling the corresponding 1-chloro-3-alkylisoquinolines.[44]

We were successful in preparing *meodap* by using the 1,1′-biisoquinoline precursor *meobis* bearing the methoxy groups in the desired position. This precursor was synthesized by homocoupling of the corresponding 1-chloro-6-methoxyisoquinoline.[57] The 6,6′-dimethoxy-1,1′-biisoquinoline was converted into the corresponding disubstituted *dap* by reductive cyclization with potassium following the protocol of Schmelz *et al.*[55] for the synthesis of the unsubstituted *dap*. The ligands *phbis* and *pybis* were synthesized by the same procedure from 1-chloro-3-phenylisoquinoline[58] and 1-chloro-3-(2-pyridyl)isoquinoline,[59] respectively. The subsequent reaction with potassium did not, however, give rise to the desired ligands *phdap* and *pydap*.

1,1′-Bisisoquinolines

To a stirred, deep blue solution of nickel(II) chloride hexahydrate ($NiCl_2.6H_2O$; 7.27 g; 30.6 mmol) and triphenylphosphine (32.1 g; 122.4 mmol) in dimethylformamide (150 mL) under nitrogen at 50°C, zinc powder (2 g, 30.6 mmol) was added. After 2 h, the color of the mixture changed to reddish brown and the corresponding 1-chloroisoquinoline (30.6 mmol) was added. After being stirred overnight at 50°C, the mixture was poured into dilute ammonia solution and stirred under a stream of air for a further 30 min until the mixture turned blue. The solid was collected by filtration, dried over $CaCl_2$ and chromatographed through a silica gel column. After the elution of large amounts of triphenylphosphine and a small amount of triphenylphosphine oxide, the 3,3′-dialkyl-1,1′-biisoquinolines were obtained.



Scheme 1.

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Meobis

From 5.93 g 1-chloro-6-methoxyisoquinoline (30.6 mmol). For further purification the product was crystallized from acetone/hexane. Eluent: $CHCl_3/CH_3OH$ 9:1 $R_f = 0.8$. Yield: 3.1 g (10.1 mmol) 64%. Smp. 213–215°C. $C_{20}H_{16}N_2O_2$ (316.36): calc.: C 75.93, H 5.1, N 8.85; found: C 76.21, H 5.51, N 8.78. ^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 8.60$ (d, $^3J_{H,H} = 5.7$ Hz, 1 H, 3-H), 7.66 (m, 2 H, 4, 5-H), 7.15 (d, $^3J_{H,H} = 2.4$ Hz, 1 H, 8-H), 7.08 (m, 1 H, 7-H) 3.94 (s, 3 H, 9–CH_3) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) $\delta = 160.6$ (C6), 157.5 (C1), 142.4 (C3), 138.8 (C4a), 129.0 (C5), 123.5 (C8a), 120.4 (C7), 120.2 (C4), 104.3 (C8), 55.5 (9-CH_3). EI-MS: m/z (%) = 315 $[M–H]^+$ (100), 285 [M-OCH_3] (50). IR (KBr): $\tilde{\nu} = 3070$ (w, C-H aromatic), 1613 (s, -C = N aromatic), 824 (w, C-H aromatic) cm^{-1}.

Phbis

From 7.3 g 1-chloro-3-phenylisoquinoline (30.6 mmol). Eluent: $CHCl_3$, $R_f = 0.7$. Yield: 3.9 g (9.6 mmol) 64%. Smp. 203–206°C. $C_{30}H_{20}N_2$ (408.5): calc.: C 88.21, H 4.93, N 6.86; found: C 87.9, H 4.81, N 6.78. ^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 8.11$ (m, 3 H, 6, 10, 14-H), 7.89 (m, 2 H, 8, 5-H), 7.59 (m, 1 H, 7-H), 7.33 (m, 4 H, 4, 11, 13, 12-H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) $\delta = 157.9$, 149.8, 139.5, 138.0, 130.3, 128.7, 128.5, 127.5, 127.3, 127.1, 127.14, 116.9, 116.8 ppm. MS (EI) m/z (%) = 407 $[M–H]^+$ (100), 204 $[M–C_{15}H_{10}N]^+$ (50). IR (KBr): $\tilde{\nu}$= 3037 (w, C-H aromatic), 1559 (s, -C = N aromatic), 736 (s, C-H aromatic) cm^{-1}.

Pybis

From 7.4 g 1-chloro-3-(2-pyridyl)isoquinoline (30.6 mmol). Eluent: $CHCl_3/CH_3OH$ 93:7 $R_f = 0.4$. Yield: 3.3 g (8.1 mmol) 53%. Smp. 342–345°C (decomp.). $C_{28}H_{18}N_4$ (410.5): calc.: C 81.93, H 4.42, N 13.65; found: C 82.12, H 4.85, N 14.23. ^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 9.00$ (s, 1 H, 4-H) 8.77 (m, 1 H, 11-H), 8.53 (d, $^3J_{H,H} = 7.5$ Hz, 1 H, 14-H), 8.11 (d, $^3J_{H,H} = 8.3$ Hz, 1 H, 8-H), 7.96 (d, $^3J_{H,H} = 8.5$ Hz, 1 H, 5-H), 7.76 (m, 2 H, 6, 12-H), 7.51 (m, 1 H, 13-H), 7.31 (m, 1 H, 7-H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) $\delta = 157.5$, 156.3, 149.1, 148.3, 137.9, 137.1, 130.4, 128.2, 128.1, 127.8, 127.5, 123.4, 121.8, 118.2 ppm. EI-MS: m/z (%) = 409 $[M–H]^+$ (100), 205 $[M–C_{14}H_9N_2]^+$ (50). IR (KBr): $\tilde{\nu}$= 3050 (w, C-H aromatic), 1587 (s, -C = N aromatic), 745 (s, C-H aromatic) cm^{-1}.

Meodap

In a Schlenk tube under a stream of argon, 6,6′-dimethoxy-1,1′-biisoquinoline (475 mg, 1.5 mmol) was dissolved in dry 1,2-dimethoxyethane (20 mL); potassium (0.82 g, 21 mmol), which was separated from its oxide layer and shredded into small pieces, was further added. The intensely colored blue mixture was stirred at room temperature for 16 h and the remaining potassium removed subsequently under argon. The solution was diluted with dry tetrahydrofuran (100 mL) and stirred under a stream of dry air for a further 4 h. The solvent was evaporated and the residue chromatographed on neutral Al_2O_3 to give the 5,8-dimethoxy-1,12-diazaperylenes as yellow solids (eluent: $CHCl_3/CH_3OH$ 9:1). Yield: 235.8 mg (0.75 mmol) 50%. Smp. 235–238°C (decomp.). $C_{20}H_{14}N_2O_2$ (314.34) calc.: C 76.42, H 4.49, N 8.91; found: C 76.51, H 4.35, N 8.73. ^{1}H-NMR (300 MHz, DMSO-d_6): $\delta = 8.51$ (d, $^3J_{H,H} = 5.6$ Hz, 1 H, 2-H), 7.87 (s, 1 H, 6-H), 7.60 (d, $^3J_{H,H} = 5.6$ Hz, 1 H, 3-H), 7.21 (s, 1 H, 4-H), 3.90 (s, 3 H, 13–CH_3) ppm. ^{13}C-NMR (75 MHz, DMSO-d_6) $\delta = 160.3$ (C5), 149.2 (C12c), 144.4 (C2), 138.4 (C6a), 131.1 (C3a), 120.7 (C4), 120.1 (C12b), 114.6 (C3), 106.0 (C6), 55.5 (13-CH_3) ppm. EI-MS: m/z (%) = 314 $[M]^+$ (100). IR (KBr): $\tilde{\nu} = 2923$ (s, -H_2C-H aliphatic), 1605 (s, -C = N- aromatic), 852 (s, C-H aromatic) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε/$M^{-1} \cdot cm^{-1}$) = 430 (15000), 405 (14000), 385 (9200), 360 (4000) nm.

The copper salts [$CuCl_2$ (× H_2O), $Cu(BF_4)_2$, $Cu(OAc)_2$, $Cu(acac)_2$, and $Cu(OTf)_2$], 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 2,2′-bipyridine, methanol (HPLC-grade) and $CHCl_3$ (suprasolv) were purchased from Sigma Aldrich Chemie (Taufkirchen, Germany) and used without further purification.

Stock solutions of the ligands in CH_3OH and of the metal salts in CH_3OH (10^{-3} M each) were prepared prior to dilution to 10^{-5} M for the MS investigations. The complexes were prepared by mixing metal and ligand solutions of appropriate stoichiometric quantities.

Mass measurements

Mass spectra were obtained in positive ion mode using an integrated ESI-Q-TOF_{micro} quadruple time-of-flight mass spectrometer (Micromass, Manchester, UK) equipped with an ESI source. Solutions of the complexes were injected into the mass spectrometer using an integrated syringe pump at a flow rate varying from 5 to 20 μL/min. The capillary voltage was set to 3.2 kV. The cone voltage was optimized for maximum precursor ion abundance within the range of 20–30 V. Elemental compositions were determined by accurate mass measurements with deviations being found to be less than 5ppm from the calculated values. Leucine enkephaline or the ligands itself were used as reference compounds.

Argon was used as the collision gas for the tandem mass spectrometric (MS/MS) measurements. The complex ion was selected and activated in CID mode by increasing the collision energies (3–100 eV) up to the energy where a relative abundance of 30% for the selected complex was found. The MS/MS product ion spectra were averaged over 100 accumulations (1 min) for each collision energy step with high reproducibility. Elemental compositions of the singly charged complexes were confirmed by accurate mass measurements.

RESULTS AND DISCUSSION

Formation of homoleptic complexes with different copper salts

Doubly charged tris-ligand complexes $[M(L)_3]^{2+}$ were detected only in the presence of *dap* and *bis*; these complexes have been described previously.[53]

The ligands studied (cf. Scheme 2) generate in the majority of cases Cu^{II} complexes with $CuCl_2$, $Cu(acac)_2$, $Cu(ac)_2$ and $Cu(OTf)_2$ of the type $[Cu(L)X]^+$ [with the exception of ligands *dipbis*, which form no complexes with $CuCl_2$ and $Cu(OTf)_2$ and *phbis* generating no complexes with $Cu(CH_3COO)_2$ and $Cu(OTf)_2$].

The relative abundances (RAs) of the $CuCl_2$ complexes $[Cu(L)_2]^+$ with *dap*, *dmdap*, and *dedap* vary between 40 and 100% compared with their bis-isoquinoline analogues (*bis*,

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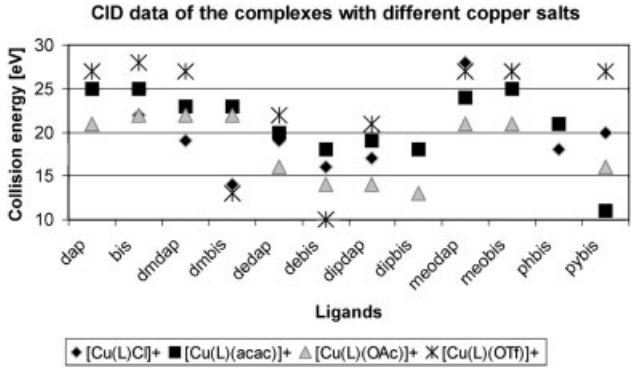

Scheme 2.

dmbis and *debis*) with RAs of only 2 to 5%, indicating the '*large surface effect*' of the diazaperylene ligands. In the mass spectra of ligands *dap* and *bis* with $Cu(BF_4)_2$ only $[1:1]^+$ complexes $[Cu^I(L)]^+$ were observed, with the ligands *dmdap*, *dmbis*, *dedap*, *debis*, *dipdap*, *dipbis* and *phbis*; however, both $[Cu^I(L)]^+$ and $[Cu^I(L)_2]^+$ were detected. Complexes of the type $[Cu(L)F]^+$ containing coordinated F^- as the counter ion were observed for the ligands *meodap*, *meobis* and *pybis*. Thus, in the case of only poorly coordinating anions like tetrafluoroborate, the ionization of the $Cu(BF_4)_2$ complexes resulted in both the loss of the counter ions and reduction from Cu^{II} to Cu^I. It is known that copper-containing complexes show redox reactions (Cu^{2+} reduction to Cu^+) during both the ESI process and the dissociation in a collision cell; here the ESI process and the nature of the ligands play an important role.[60,61]

Cu^I ions prefer the fourfold coordination with tetrahedral geometry while Cu^{II} ions are found preferably in fivefold coordination either with a square pyramidal or a trigonal bipyramidal geometry. In particular, the *pybis* complexes prefer the $[1:1]^+$ forms with the four coordinating nitrogen atoms. Therefore, in the mass spectra of the complexes with *pybis* as ligands the doubly charged species $[Cu(pybis)]^{2+}$ at *m/z* 237 (RA 100%) could be detected. The ion $[(Cu\text{-}pybis)_2]^{2+}$ at *m/z* 473 (RA 30%) for the $[2:2]^{2+}$ complex with *pybis* could also be detected – in agreement with the X-ray solid state structure of this complex. In the case of *meodap* no $[Cu(L)_2]^+$ complex was observed, only $[Cu^{II}(meodap)X)]^+$ for different counter ions, X, with RAs between 50 and 100%.

Formation of the heteroleptic complexes with *bpy*, *phen*, and *dmphen*

The ligands *dap*, *bis* and *bpy* form with $CuCl_2$ complexes of the type $[Cu(L)(bpy)]^+$ and $[Cu(L)(bpy)Cl]^+$ (see Table 1). Copper(I) complexes $[Cu(L)(bpy)]^+$ were also observed for the ligands *dedap* and *dipdap*; however, the ligands *dmdap*, *dmbis*, *debis*, *dipbis* and *phbis* preferably form copper(II) compexes $[Cu(L)(bpy)Cl]^+$. In the case of mixtures of $CuCl_2$ with *bpy* and the ligands *meodap*, *meobis* and *pybis*, no heteroleptic metal complexes were obtained.

The mass spectra of the mixtures of $CuCl_2$ with *phen* and the ligands *dedap*, *dipdap*, *pybis* and *meobis* show peaks for the complex $[Cu(L)(phen)]^+$; for the other ligands, the complex type ion $[Cu(L)(phen)Cl]^+$ was detected. From the solution containing *dmphen* and $CuCl_2$, almost all ligands gave peaks for $[Cu(L)(dmphen)]^+$ complexation, except for *dap* and *meodap*. Peaks which can be attributed to the complex $[Cu(L)(dmphen)Cl]^+$ were also seen in the mass spectra of the ligands *dap*, *bis* and *meodap*.

Collision-induced dissociation (CID) studies

Homoleptic complexes

CID measurements can be readily employed to evaluate the relative stabilities of complexes in the gas phase.[53] The corresponding dissociation profile of the complex $[Cu(dmdap)_2]^+$ induced by increasing the collision energy is illustrated in Fig. 1. The CID spectra show the loss of the ligand *dmdap*. As the collision energy was increased the relative abundance of the selected complexes adequately decreased. Each of the two Cu(I) complexes, $[Cu(L)]^+$ and $[Cu(L)_2]^+$, was selected and subjected to CID measurements. The values $E_{1/3}$ (given in Scheme 3), the collision energies at which RA of the precursor ion is found to be 30%, demonstrate the high stability of the [1:1] complexes due to the large collision energy values for complex decomposition of 30–42 eV (except for the $[Cu(L)]^+$ complexes with L = *bis*, *dipbis* and *phbis* where the $E_{1/3}$ values are 10–13 eV only). The corresponding $[Cu(L)_2]^+$ complexes proved to be much less stable with $E_{1/3}$ values of 25–33 eV. It is notable that the complex $[Cu(pybis)]^+$ shows the highest collision energy $E_{1/3}$ of 82 eV.

Table 1. CID data $E_{1/3}$ [eV] of the complexes of all ligands with $CuCl_2$ and *bpy*, *phen*, and *dmphen* in CH_3OH (cone voltage 20–25 V)

Ligand	$[Cu(L)(bpy)Cl]^+$	$[Cu(L)(bpy)]^+$	$[Cu(L)(phen)Cl]^+$	$[Cu(L)(phen)]^+$	$[Cu(L)(dmphen)Cl]^+$	$[Cu(L)(dmphen)]^+$
dap	12	21	17	no	19	no
bis	13	6	13	no	12	23
dmdap	11	no	16	no	no	33
dmbis	12	no	15	no	no	26
dedap	no	18	no	23	no	27
debis	13	no	17	no	no	26
dipdap	no	13	no	23	no	26
dipbis	14	no	15	no	no	27
meodap	no	no	15	no	17	no
meobis	no	no	no	23	no	22
phbis	17	no	18	no	no	30
pybis	no	no	no	19	no	13

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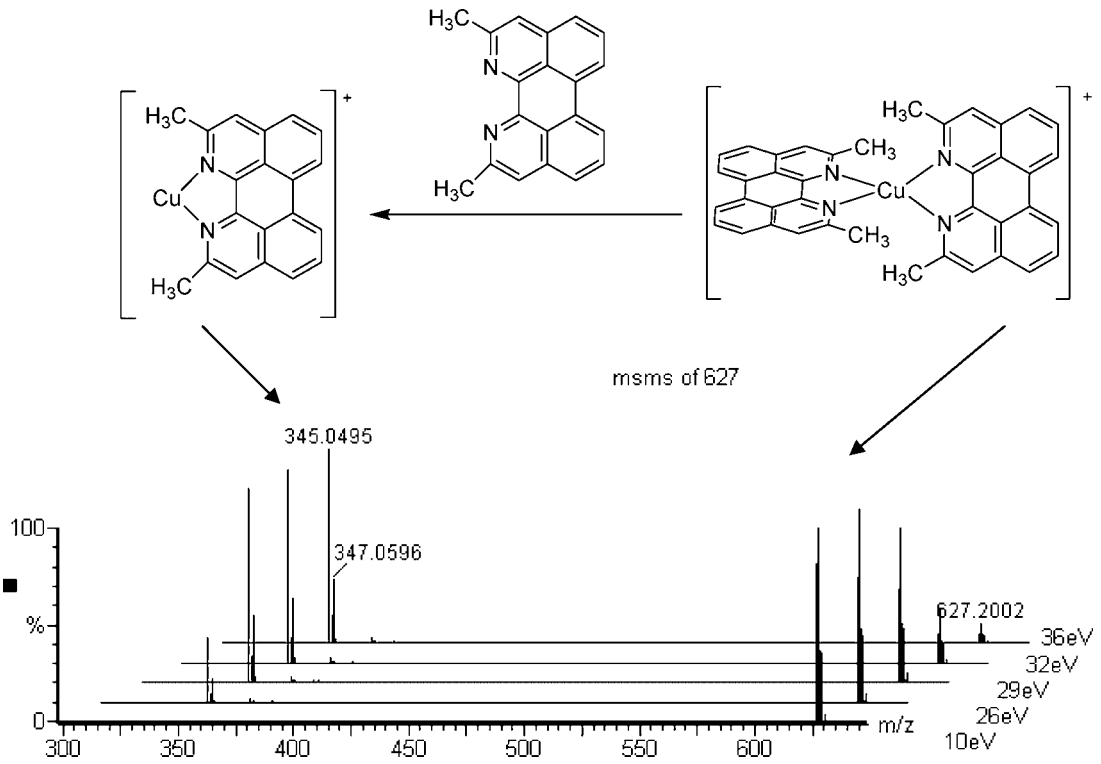
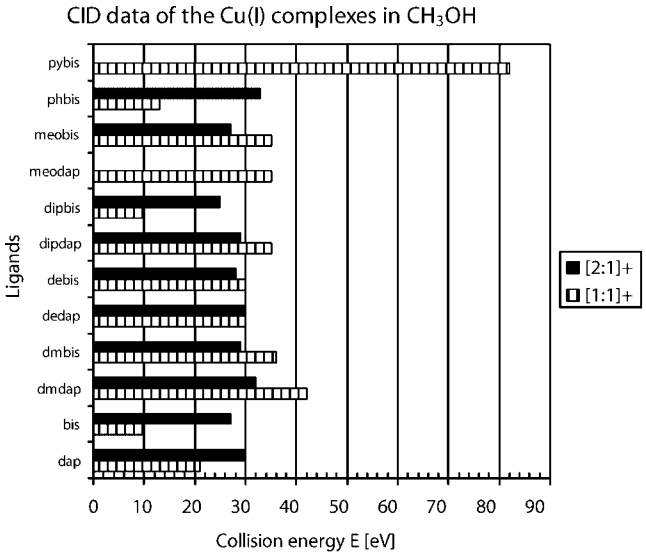


Figure 1. The dissociation profiles (product ion scans) of the complex $[Cu(dmdap)_2]^+$ *m/z* 627 induced by increasing the collision energy from 10 to 36 eV.

In addition, complexes $[Cu(L)X]^+$ containing different counter ions (X = Cl, *acac*, OAc and OTf) were studied employing the ESI spectra; CID measurements were conducted to compare also the relative stabilities of these complexes (see Scheme 2). These $[Cu(L)X]^+$ complexes fragmented upon CID by loss of the respective anion.

The collision energies for the complexes with triflate as ligand are generally higher than in the corresponding complexes with Cl, *acac*, and OAc. The $E_{1/3}$ values of the complexes $[Cu(L)X]^+$ with *dap*, *bis*, *dmdap*, *meodap* and *meobis* were larger (20–28 eV) than those with *dmbis*, *dedap*, *debis*, *dipdap*, *dipbis* and *phbis* (10–22 eV). The influence of the counter ion on the stability of the complexes with *pybis* is remarkable: the energy values for these complexes vary between 10 eV for $[Cu(pybis)acac]^+$ and 27 eV for $[Cu(pybis)OTf]^+$.



Scheme 3.

Heteroleptic complexes with bpy, phen and dmphen

The collision energies for the heteroleptic complexes with *bpy* {$[Cu(L)(bpy)Cl]^+$ and $[Cu(L)(bpy)]^+$} range within 12–17 eV and 13–21 eV, respectively (see Table 1). The analogous heteroleptic complexes with *phen* {$[Cu(L)(phen)Cl]^+$ and $[Cu(L)(phen)]^+$} exhibit slightly higher dissociation energies (13–18 eV and 19–23 eV, respectively), because the rigidity of the phenanthroline structure introduces a considerable degree of preorganization.

In general, all mixed complexes with *bpy* dissociated preferably via the loss of *bpy* and not via the loss of the diazaperylene or bisisioquinoline ligands. In the case of the Cu(I) complexes $[Cu(L)(phen)]^+$ with L = *dedap*, *didap*, *pybis* the dissociation occurs via the loss of *phen*, but in the CID mass spectra of the copper(II) complexes $[Cu(L)(phen)Cl]^+$ (with L = *bis*, *dmbis*, *debis*, *dipbis*, *meodap*, *phbis*), the $[M–L]^+$ ions only were observed. The complex $[Cu(dmdap)(phen)Cl]^+$, however, dissociates via the loss of *phen*, indicating that the dimethyl-substituted *dmdap* binds the copper cation much more strongly than phenanthroline.

It can be seen in Table 1 that the dissociation energies $E_{1/3}$ for the complexes with *dmphen* $[Cu(L)(dmpen)Cl]^+$ and $[Cu(L)(dmphen)]^+$ are between 12 and 19 eV, and 22 and 33 eV, respectively, and are consistently greater than those for the analogous complexes with *bpy* and *phen* – a result attributed to the effect of the *electron-releasing* methyl groups in the *ortho* position to the coordinating nitrogen donor atoms

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and the fixed planar structure of the phenanthroline ring of *dmphen*.

Heteroleptic complexes with the new ligands

To investigate the effect of preorganization of ligands and the influence of the different substituents at the ligands as important factors for formation of the complexes, mixtures of $CuCl_2$ with two different, recently synthesized new ligands were subjected to CID measurements. For the $CuCl_2$/ligand mixtures studied, the mass spectra were recorded at the cone voltages at which the relative abundances of the mixed complex types $[Cu(L_A)(L_B)]^+$ are the best to determine the collision energies $E_{1/3}$ for the decomposition occurring via loss of one neutral ligand. It can be seen in Table 2 that only the 2,11′-dimethyl-substituted ligand *dmdap* forms stable complexes {$E_{1/3}$ ranges from 29 to 36 eV; except for the complex $[Cu(dmdap)(bis)]^+$ with $E_{1/3}$ 15 eV} with almost all other ligands (with the exception of *meobis* and *pybis*).

The 3,3′-dimethyl-substituted bis(isoquinoline) analogue *dmbis* shows a comparable complexational behaviour toward the ethyl- and isopropyl-substituted ligands; in addition, the complex ion $[Cu(dmbis)(meobis)]^+$ could be detected.

Obviously, the most stable complex is formed when employing the mixture of the two dimethyl-substituted ligands *dmdap* and *dmbis* $[Cu(dmdap)(dmbis)]^+$ ($E_{1/3}$ 36 eV). This complex seems to be more stable than the $[2:1]^+$ complexes which consist of the same ligands $[Cu(dmdap)_2]^+$ and $[Cu(dmbis)_2]^+$ ($E_{1/3} = 32$ eV and 29 eV, respectively).

The ligands *dap*, *bis*, and *meobis* which are unsubstituted in the *ortho* positions to the coordinating nitrogen atoms build complexes only with each other {*meobis* also forms complexes $[Cu(meobis)(dmbis)]^+$ and $[Cu(meobis)(dedap)]^+$ with $E_{1/3}$ values of 27 eV and 24 eV, respectively}.

The ligand *meodap* forms with *dmdap* exceptionally one $[2:1]^+$ complex which is fairly stable with $E_{1/3} = 32$ eV. The values for the dissociation energies of the complexes resulting from mixtures between the 2,11′-diethyl- and –diisopropyl-substituted ligands {$[Cu(dedap)(debis)]^+$, $[Cu(dedap)(dipdap)]^+$, $[Cu(dedap)(dipbis)]^+$, $[Cu(debis)(dipdap)]^+$ $[Cu(debis)(dipbis)]^+$ and $[Cu(dipbis)(dipdap)]^+$} are similar and range from 21 to 27 eV.

In the case of the mixed complexes with *phbis*, the most stable ones are combinations with *dmdap* {$[Cu(phbis)(dmdap)]^+$ 34 eV}. The complexes $[Cu(phbis)(dedap)]^+$ (25 eV) and $[Cu(phbis)(dipdap)]^+$ (23 eV) prove to be less stable than the corresponding complexes with *phbis* of their bis(isoquinoline) analogues {$[Cu(phbis)(debis)]^+$ (31 eV) and $[Cu(phbis)(dipbis)]^+$ (29 eV)}.

The alkyl-substituted diazaperylene ligands are sterically hindered proximate to the nitrogen donor atoms. The ligands *debis* and *dipbis*, in contrast to *dedap* and *dipdap*, together with *phbis*, are able to twist from the common plane of resonance but, still, can successfully complex the copper cation. Surprisingly, the complexes $[Cu(pybis)(dedap)]^+$ and $[Cu(pybis)(dipdap)]^+$ could be also observed, but the energy values ($E_{1/3} = 18$ eV and 16 eV, respectively) are very low.

As depicted in Table 2 the collision energy values for the homoleptic $[Cu(L)_2]^+$ complexes show very clearly three important factors for influencing the stability of the complexes:

(i) The preorganization of the ligands (*dap* > *bis*, *dmdap* > *dmbis*, *dedap* > *debis* and *dipdap* > *dipbis*).
(ii) The substituent effect of electron-releasing methyl groups when positioned in the *ortho* positions to the coordinating nitrogen atoms: $[Cu(dmdap)_2]^+ - 32$ eV > $[Cu(dap)_2]^+ - 30$ eV; $[Cu(dmbis)_2]^+ - 29$ eV > $[Cu(bis)_2]^+ - 27$ eV.
(iii) The influence of steric hindrance due to bulky substituents: *dmdap*, *dmbis* (32 eV, 29 eV) > *dedap*, *debis* (30 eV, 28 eV) > *dipdap*, *dipbis* (29 eV, 25 eV).

The σ-donor and π-acceptor properties of the ligands *bpy* and *phen* are well known and are responsible for octahedral transition metal complexation with strong ligand field splitting and high complex stability.[45] Methoxy substituents, however, are known to be of π-donor character, leading to a decrease in the π-acceptor properties of the aromatic ligand and reducing the ligand field splitting, as shown for the ligands *meodap* and *meobis* by means of their low tendencies to build stable octahedral complexes.[62]

In order to evaluate the results of the CID experiments in terms of complex stability, the $[1:1]^+$ and $[2:1]^+$ complexes with $CuCl_2$ with *bpy*, *phen* and *dmphen* were generated and comprehensively studied in solution. It is known that, in solution, the binding constants of the phenanthroline ligands are typically larger than those of the 2,2′-bipyridine analogues because the rigidity of the phenanthroline mediates a greater degree of preorganization. The methyl groups in positions 2 and 9 increase steric hindrance in *dmphen* as a ligand for copper(I) compared with the non-substituted 1,10-phenanthroline. With regard to the stability

Table 2. CID data $E_{1/3}$ [eV] of the complexes of all ligands with $CuCl_2$ in CH_3OH (cone voltage 20–25 V)

	dap	*bis*	*dmdap*	*dmbis*	*dedap*	*debis*	*dipdap*	*dipbis*	*meodap*	*meobis*	*phbis*	*pybis*
dap	30 eV	16 eV	35 eV	no	no	no	no	no	no	24 eV	no	no
bis	16 eV	27 eV	15 eV	no	no	no	no	no	no	24 eV	no	no
dmdap	35 eV	15 eV	32 eV	36 eV	30 eV	29 eV	29 eV	29 eV	32 eV	no	34 eV	no
dmbis	no	10 eV	36 eV	29 eV	22 eV	29 eV	27 eV	21 eV	no	27 eV	31 eV	no
dedap	no	no	30 eV	22 eV	30 eV	23 eV	23 eV	23 eV	no	24 eV	25 eV	18 eV
debis	no	no	29 eV	29 eV	23 eV	28 eV	21 eV	27 eV	no	no	31 eV	no
dipdap	no	no	29 eV	27 eV	23 eV	21 eV	29 ev	22 eV	no	no	23 eV	16 eV
dipbis	no	no	29 eV	21 eV	23 eV	27 eV	22 eV	25 eV	no	no	29 eV	no
meodap	no	no	32 eV	no	no	no	no	no	no	no	no	no
meobis	24 eV	24 eV	no	27 eV	24 eV	no	no	no	no	27 eV	no	no
phbis	no	no	34 eV	31 eV	25 eV	31 eV	23 eV	29 eV	no	no	33 eV	no
pybis	no	no	no	no	18 eV	no	16 eV	no	no	no	no	no

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Table 3. Complex stability constants, log K_1 and log K_2 and log β_2 of the complexes $[Cu(L)]^+$ and $[Cu(L)_2]^+$ with L = *bpy*, *phen*, *dmphen* in solution and the collision voltages $E_{1/3}$ [eV] for the dissociation of these complexes in the gas phase

Ligands	[Cu(L)]		[Cu(L)$_2$]			
	log K_1	$E_{1/3}$[eV]	log K_2	$E_{1/3}$[eV]	logβ_2	$[CuL_2]^+$
dmphen	7.9	36	7.6	25	15.5	1.24[a]
phen	6.3–9.25	34	6.1–6.7	19	15.3	1.17
bpy	6.3–8.39	33	5.6–5.7	14	13.65	1.06

[a] Occurrence potential.[65]

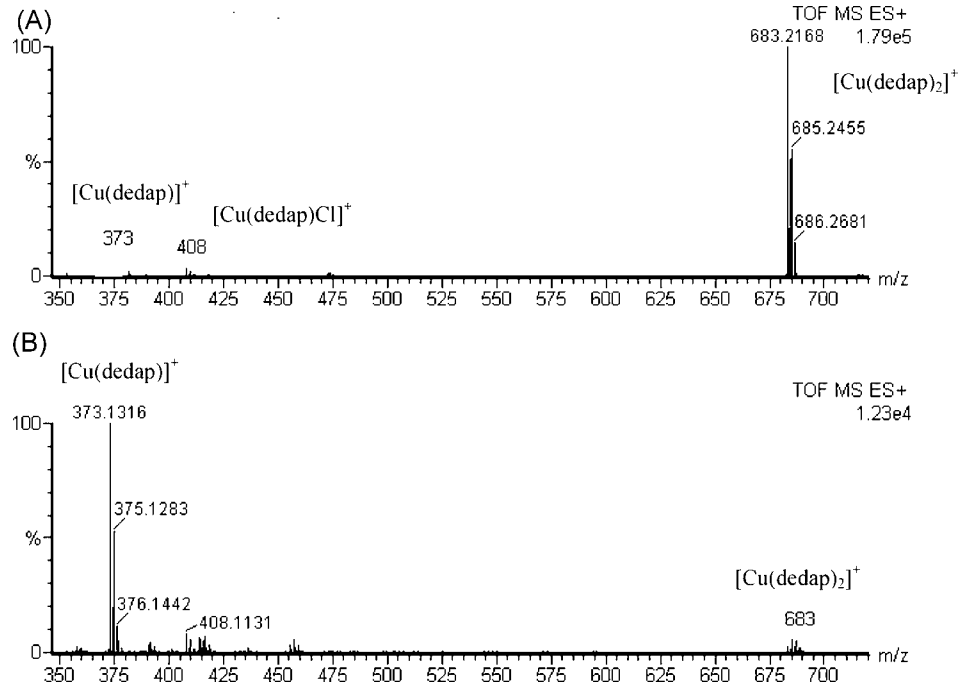

Figure 2. ESI mass spectra of $[Cu(dedap)]^+$ and $[Cu(dedap)_2]^+$ in (A) CH_3OH and (B) CH_3CN.

of *dmphen* and their copper(I) chelates, the methyl groups should increase the stability only slightly due to the inductive *sigma*-donor effect. The collision energies $E_{1/3}$ [eV] for these complexes in the gas phase together with the corresponding literature values of the complex stability constants are given in Table 3.[63,64] It can be seen that the complex stability constants log K_1, log K_2, and log β_2 for the complexes $[Cu(L)]^+$ and $[Cu(L)_2]^+$ in solution are decreased in the same order as the corresponding dissociation energies $E_{1/3}$ obtained from the three CID experiments: *dmphen* > *phen* > *bpy*. Threshold activation voltages, determined by using energy-variable CID in a quadrupole ion trap mass spectrometer, reported for the complexes $[Cu(L)_2]^+$ with *dmphen*, *phen* and *bpy* revealed the same trend with respect to relative stabilities.[65] The linear dependence of the collision energies in the gas phase and the complex stability constants in solution supports the feasibility of comparing relative complex stabilities on the basis of CID measurements.

Solvent effect

The critical comparison of the mass spectra of the copper(I) complexes with e.g. $CuCl_2$ $[Cu(dedap)]^+$ and $[Cu(dedap)_2]^+$ in CH_3OH and CH_3CN as given in Fig. 2 shows that the intensities of the $[Cu(L)_2]^+$ ions in CH_3CN are generally lower than in CH_3OH. Major differences in the mass spectra of Cu(I) complexes $[Cu^I(L)]^+$, subject to the solvent, were obtained with *dedap* and *dipdap*, because the intensities of the ions of the complexes $[Cu(dedap)]^+$ and $[Cu(dipdap)]^+$ were much higher in CH_3CN (RA 100% and 90%, respectively) than those of the ions of the complexes in CH_3OH (RA only 5%; see also Fig. 1; e.g. the *m/z* 373 ion $[Cu(dedap)]^+$ with RA below 5% in CH_3OH and 100% in CH_3CN). The gas-phase interaction of metal cations with ligands in terms of the reduction reaction of Cu^{II} complexes to Cu^I species has been observed earlier – this effect could be attributed to charge transfer from the ligand to the metal ion by electron transfer reaction.[66–69] Upon the addition of CH_3CN the formation of complexes $[Cu(L)CH_3CN]^+$ (with L = *dedap* and *dipdap*) was also observed. However, the energy values for the CID experiments in the different solvents CH_3CN and CH_3OH are similar, proving that the solvation-mediated effects are negligible for the stability of the complexes compared with the intrinsic nature of the binding interactions.

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CONCLUSIONS

Electrospray ionization mass spectrometry allowed the observation of a series of homoleptic and heteroleptic complexes consisting of two different ligands {[Cu(L_A)(L_B)] with different counter ions}. In each case, the collision energies for the complexes $[Cu(L_A)(L_B)]^+$ with *bpy*, *phen* and *dmphen* are higher for the complexes with *dmphen* as an additional ligand than for the corresponding *phen* and *bpy* analogues.

The CID results agreed well with the order of the stability constants of the corresponding complexes in solution. Steric hindrance of the substituents in the *ortho* position to the donor nitrogen atoms and twist from planarity of bis-isoquinoline ligands influence the CID energies of the copper complexes. The $E_{1/3}$ values were larger for complexes with differently substituted diazaperylene ligands as a consequence of both the higher planarity and the improved preorganization for complex formation. The stabilizing effect of the electron-releasing methyl group in the *ortho* position influences the relative binding strength of the complexes with *dmdap*, *dmbis* and *dmphen*.

The most stable complex proves to be $[Cu(pybis)]^+$ with $E_{1/3} = 82$ eV. This is hardly surprising because of the four coordinating donor atoms.

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