10. Chiral Tetraamines Based on (*S*)-2-(Aminomethyl)pyrrolidine: Template Synthesis and Properties of Copper(II) Complexes

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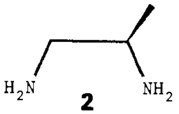
The template reaction of {bis[(*S*)-2-(aminomethyl)pyrrolidine]}copper(II) with formaldehyde, nitroethane, and base in MeOH yields optically pure {1,7-bis[(*S*)-pyrrolidin-2-yl]-4-methyl-4-nitro-2,6-diazaheptane}-copper(II) ([Cu((*S*,*S*)-mnppm)]$^{2+}$) in high yield. The same reaction with *rac*-2-(aminomethyl)pyrrolidine is also described. Preparative details and spectroscopic and electrochemical properties of the Cu^{II} complexes and of the free ligands are reported and compared with structural, spectroscopic, and electrochemical data of the Cu^{II} complex of the unsubstituted parent ligand 1,7-bis[(*S*)-pyrrolidin-2-yl]-2,6-diazaheptane (ppm). The crystal structure of [Cu(ppm)]Cl · ClO$_4$ has been determined by X-ray diffraction methods.

Introduction. – The coordination of optically active multidentates to transition-metal ions may, under certain conditions, produce chiral matrices that can exchange racemic substrates stereoselectively. Such a procedure may then be applied to separation of racemic ligands, if the chiral matrix complex can readily be separated from the two (partly) resolved enantiomers of the substrate. This has been practised extensively in the past, mainly using chromatographic techniques (ligand-exchange chromatography, LEC) [1] [2]. The enantioselectivity of a stereoselective ligand-exchange reaction can be predicted with some accuracy with force-field calculations, and this allows one to design efficient chiral matrix ligands for specific racemate-separation processes [3].



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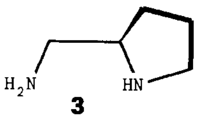

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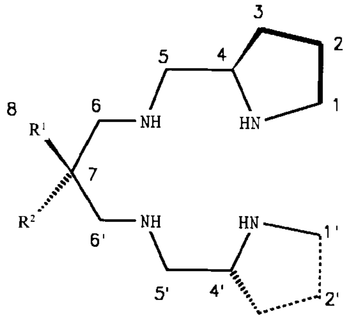
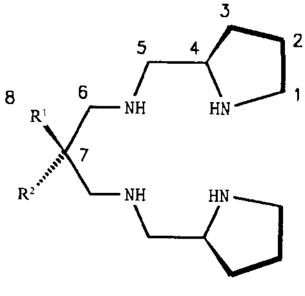


(*R*),(*R*)

1 R^1 = R^2 = H

4 R^1 = CH$_3$
R^2 = NO$_2$

5 R^1 = CH$_3$
R^2 = NH$_2$



(*R*),(*S*)

The quadridentate ligand 1,7-bis[(2*S*)-pyrrolidin-2-yl]-2,6-diazaheptane (ppm, **1**) has been shown to form rather efficient chiral matrices with Co^{III} and Ni^{II} for separation of simple racemic diamines such as 1,2 propane diamine (pn, **2**) and (*S*)-2-(aminomethyl)pyrrolidine (pam, **3**) [4]. The structurally related ligand 1,7-bis[(*S*)-pyrrolidin-2-yl]-4-methyl-4-nitro-2,6-diazaheptane (mnppm, **4**), may be synthesized *via* template condensation of $[Cu(pam)_2]^{2+}$, similar to the one described for bis(amino acid) complexes of Cu^{II} [5]. Its Zn/HCl reduction product 4-amino-1,7-bis[(*S*)-pyrrolidin-2-yl]-4-methyl-2,6-diazaheptane (mappm, **5**) has a side chain that is appropriate for fixation to polymeric supports such as silica gel, and may then form materials suitable for ligand-exchange chromatography.

Here we present details of the synthesis of mappm (**5**), both starting with racemic and optically pure pam (**3**), and structural, spectroscopic, and electrochemical results of $[Cu(ppm)]^{2+}$, $[Cu(mnppm)]^{2+}$, and $[Cu(mappm)]^{2+}$.

Experimental. – *Materials.* All reagents were of analytical purity. Racemic and optically pure *2-(aminomethyl)pyrrolidine* (pam, **3**) was prepared according to a procedure modified [6] from that described in [7]. *1,7-Bis[(2*S*)-pyrrolidin-2-yl]-2,6-diazaheptane* (ppm, **1**) was prepared *via* published procedures [8]. α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPA·Cl) ($[\alpha]_D^{20} = -135.5$ (*R*), +135.5 (*S*); 5.2M, CCl_4) was obtained from *JPS Chimie*, Bevaix, Switzerland.

Syntheses. Bis[(S)-2-(aminomethyl)pyrrolidine]copper(II) diperchlorate ($[Cu((S)\text{-pam})_2](ClO_4)_2$) was isolated from a soln. (MeOH) containing 1 equiv. of $Cu(NO_3)_2 \cdot 3H_2O$, 2 equiv. of pam·2HCl, 4 equiv. of NaOH, and $NaClO_4$ in excess. Evaporation at r.t. to near dryness produced a purple precipitate which was separated from $NaClO_4$ by extraction into CH_2Cl_2 and subsequent evaporation at r.t. to near dryness, and recrystallized from MeOH/EtOH. Anal. calc. for $C_{10}H_{24}Cl_2CuN_4O_8$: C 25.95, H 5.23, N 12.11, Cl 15.32; found: C 26.07, H 5.25, N 12.17, Cl 15.47.

{1,7-Bis[(S)-pyrrolidin-2-yl]-4-methyl-4-nitro-2,6-diazaheptane}copper(II) Diperchlorate ($[Cu((S), (S)\text{-mnppm})](ClO_4)_2$). A soln. of (*S*)-pam·2HCl (5.93 g, 34.3 mmol) and NaOH (2.7 g, 67.5 mmol) in MeOH (400 ml) was added to a soln. of $Cu(NO_3)_2 \cdot 3H_2O$ (4.14 g, 17.1 mmol). Et_3N (5.2 g, 51.4 mmol) and nitroethane (2.57 g, 34.3 mmol) were added to the purple soln., and then formaldehyde (37%; 2.61 ml; 34.3 mmol) was added dropwise. The dark purple soln. was heated (60°) for 4 h before diluting it with H_2O (5 l). MPLC (H_2O, then $NaClO_4$ (0.2M); *SP Sephadex C25*) separated a dark green side-product from a major purple fraction. This was evaporated at r.t. to near dryness and the purple precipitate extracted three times into CH_2Cl_2 to separate it from $NaClO_4$. Removal of CH_2Cl_2 under reduced pressure at r.t. yielded 7.85 g (14.0 mmol, 82%) of the purple product. Anal. calc. for $C_{14}H_{29}Cl_2CuN_5O_{10}$: C 29.93, H 5.20, N 12.46, Cl 12.62; found: C 29.67, H 5.57, N 11.98, Cl 12.92.

Bis[(R),(S)-2-(aminomethyl)pyrrolidine]copper(II) Diperchlorate ($[Cu((R),(S)\text{-pam})_2](ClO_4)_2$) and *{1,7-bis[(R),(S)-pyrrolidin-2-yl]-4-methyl-4-nitro-2,6-diazanonane}copper(II) diperchlorate* ($[Cu((R),(S)\text{-mnppm})](ClO_4)_2$) were prepared as described for the complexes $[Cu((S)\text{-pam})_2](ClO_4)_2$ and $[Cu((S),(S)\text{-mnppm})](ClO_4)_2$, resp., except *rac*-pam was substituted for (*S*)-pam.

[4-Ammonio-1(S),7(S)-bis(pyrrolidin-2-yl)-4-methyl-2,6-diazanonane]copper(II) Triperchlorate Hydrate ($[Cu((S),(S)\text{-Hmappm})](ClO_4)_3 \cdot H_2O$). To a soln. of $[Cu((S),(S)\text{-mnppm})](ClO_4)_2$ (1.72 g, 3.07 mmol) in H_2O (250 ml, 50°) was added 10 g of granulated Zn and 80 ml of 1M HCl. After ½ h, the soln. was filtered, excess Cu^{2+} was added to the filtrate, the pH raised (1M, NaOH) to 8.2, and $Cu(OH)_2$ and $Zn(OH)_2$ were removed by filtration. Then, the pH was adjusted to 3.8 (1M, HCl) and the soln. sorbed onto *SP Sephadex C25*. Elution with 0.2M $NaClO_4$ produced two bands, and the second, containing the desired product, was evaporated to *ca.* 50 ml and left to slowly crystallize. Yield: 0.17 g (10%). Anal. calc. for $C_{14}H_{34}Cl_3CuN_5O_{13}$: C 25.94, H 5.31, N 10.82, Cl 16.43; found: C 26.38, H 4.86, N 10.28, Cl 15.67.

4-Amino-1,7-bis[(S)-pyrrolidin-2-yl]-4-methyl-2,6-diazanonane Pentahydrochloride ([(*S*),(*S*)-mappm]·5HCl, **5**). A soln. of $[Cu((S),(S)\text{-Hmappm})]^{3+}$ obtained from ion-exchange chromatography as described above was diluted with H_2O to *ca.* 500 ml. After addition of granulated Zn (5 g), the soln. was heated to 50° under continuous stirring. Excess Zn was removed by filtration, and the pH of the colourless soln. was adjusted to 3 (1M HCl). This soln. was sorbed onto *SP Sephadex C25*. After elution of Zn^{2+} with 0.2M NaCl (pH 3, HCl), the ligand was recovered with 0.5M NaCl (pH 3). This eluate was evaporated to dryness and the ligand extracted from the resulting solid with MeOH. Addition of Et_2O produced the hydrochloride of the free ligand as white powder. Yield: 0.28 g. The hydrochloride of the free ligand was analyzed by its ^1H- and ^{13}C-NMR spectra (see *Results and Discussion*).

[4-Ammonio-1-(R),7(S)-bis(pyrrolidin-2-yl)-4-methyl-2,6-diazanonane]copper(II) triperchlorate ([Cu((*R*),(*S*)-Hmappm)]$(ClO_4)_3$ and *4-amino-1(R),7(S)-bis(pyrrolidin-2-yl)-4-methyl-2,6-diazanonane pentahydrochloride* ((*R*),(*S*)-mappm)·5HCl were obtained as described for [Cu((*S*),(*S*)-Hmappm)]$(ClO_4)_3 \cdot H_2O$ and **5**, respectively, but starting with racemic pam.

{1,7-Bis[(S)-pyrrolidin-2-yl]-2,6-diazanonane}copper(II) chloride perchlorate ([Cu(ppm)]Cl·ClO_4) was obtained by crystallization from a neutral aq. soln. of the product of stoichiometric amounts of the corresponding metal perchlorate and the hydrochloride of ppm [8]. Anal. calc. for $C_{13}H_{28}Cl_2CuN_4O_4$: C 35.58, H 6.43, N 12.77, Cl 16.16; found: C 34.97, H 6.42, N 12.65, Cl 16.33.

Physical Methods. Electronic spectra were recorded on a *Cary 2300* or a *Hewlett-Packard 8450A* spectrophotometer. IR spectra (KBr pellets) were measured witb a *Philips SP3* or a *Perkin Elmer FTIR 1600* instrument. EPR spectra were recorded on a *Varian E9* spectrometer fitted with a *Varian E101* microwave bridge, a *Varian* variable temp. control unit, a *Bruker ER035* NMR *Gauss*meter, and a *Marconi Instruments 2440* microwave counter. NMR spectra were measured on a *Varian GEMINI 300* instrument at 75 MHz (^{13}C-NMR) or 300 MHz (^{1}H-NMR) with 1,4-dioxane or sodium (trimethylsilyl)propionate (TSP), respectively, as internal standards. Electrochemical measurements were performed with a *Metrohm E612* potentiostat in conjunction with a *Metrohm E611* detector. A glassy carbon working electrode, Pt wire counter electrode, and a calomel reference electrode were used in all experiments. For differential pulse polarography, scan rates of 2 mV/s and pulses of 10 mV were adopted in all measurements. In cyclic voltammetry measurements, the scan rate was 100 mV/s. All compounds were measured as *ca.* 1 mM aq. solns. that were 0.1M in $NaClO_4$ and were purged with N_2 prior to measurement. Prep. MPLC separations were done with a system consisting of a *Büchi B-681* pump with 16–160 ml/min pumpheads, *SP Sephadex C25* resin (pressure of up to 3 bars), and a *Perkin Elmer λ2* detector fitted with an *LC Microflowcell.* Microanalyses were done by *Ciba-Geigy AG*, Basel.

Crystal Structure. For diffractometry, a crystal of dimensions 0.25 × 0.30 × 0.32 mm was mounted on a glass fibre with cyanoacrylate resin. Lattice parameters at 21° were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured, and refined on an *Enraf-Nonius CAD4F* four-circle diffractometer employing graphite monochromated Mo$K\alpha$ radiation. Intensity data were collected in the range $1 \leq \theta \leq 25°$ using an ω-scan mode. The scan width and horizontal counter aperture employed were

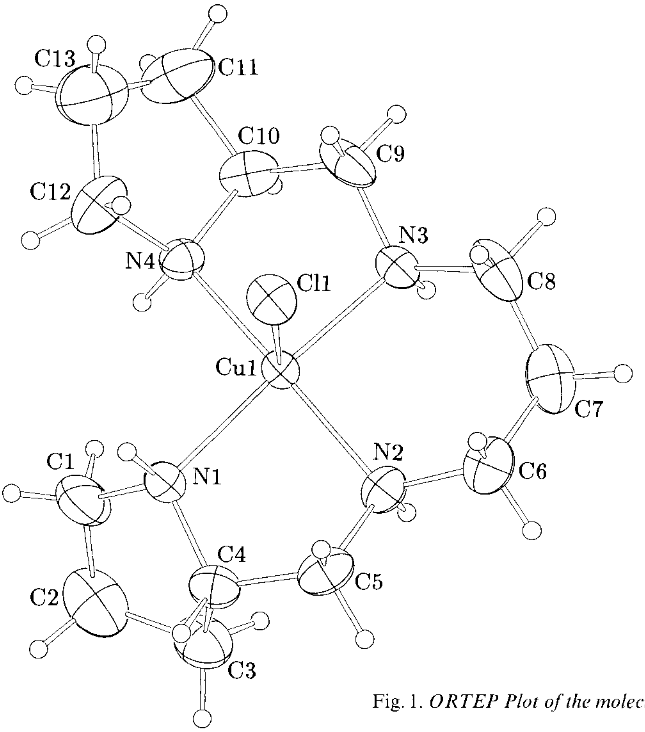


Fig. 1. *ORTEP Plot of the molecular cation [Cu(ppm)Cl]$^+$*

($1.50 + 0.34\tan\theta$)° and ($2.70 + 1.05\tan\theta$) mm, respectively. Data reduction and application of *Lorentz*, polarization, and absorption (max. trans. 0.809, min. trans. 0.568) corrections were carried out using the *Enraf-Nonius Structure Determination Package* [9]. The structure was solved by direct methods using SHELXS-86 [10] and the solution was extended by difference *Fourier* methods. H-Atoms were included at calculated sites with group isotropic thermal parameters, and all other atoms with the exception of minor contributors to disordered species (the ClO_4^- of $[Cu(ppm)]Cl \cdot ClO_4$) were refined anisotropically.

Scattering factors and anomalous dispersion terms used for Cu were taken from International Tables [11] and all others used were those supplied in SHELX-76 [12]. All calculations were carried out using SHELX-76 [12] and plots were drawn using ORTEP [13].

The atom numbering scheme is given in *Fig. 1*. Final atomic coordinates, bond lengths, and bond angles are listed in *Tables 1–3*. Observed and calculated structure factors, H-atom coordinates, and thermal parameters are deposited.

Table 1. *Positional Parameters for* $[Cu(C_{13}H_{28}N_4)Cl]ClO_4$

	x (× 10^4)	y (× 10^4)	z (× 10^4)		x (× 10^4)	y (× 10^4)	z (× 10^4)
Cu(1)	67(1)	2132(1)	2311(1)	C(10)	2454(8)	1710(7)	3136(6)
Cl(1)	−162(2)	4400(1)	2502(1)	C(11)	3754(9)	2272(13)	3170(9)
N(1)	−198(4)	2257(5)	1045(3)	C(12)	2702(7)	3088(8)	2004(7)
N(2)	−1787(5)	1801(4)	2346(4)	C(13)	3852(13)	3115(14)	2513(8)
N(3)	282(5)	1836(4)	3551(3)	Cl(2)	4319(2)	195(2)	603(1)
N(4)	1978(4)	2035(5)	2272(4)	O(1)	873(17)	999(10)	5790(7)
C(1)	589(8)	1475(11)	482(6)	O(2)	−112(22)	−380(12)	4922(11)
C(2)	−184(13)	652(8)	62(7)	O(3)	1130(26)	−1157(19)	5971(11)
C(3)	−1442(9)	718(7)	522(6)	O(4)	1243(37)	−211(14)	4774(10)
C(4)	−1513(6)	1984(6)	828(4)	O(5)	−257(32)	−351(32)	6337(25)
C(5)	−2332(6)	2266(7)	1567(5)	O(6)	1509(32)	35(36)	6223(22)
C(6)	−2503(7)	2169(9)	3079(5)	O(7)	−376(26)	319(27)	5661(22)
C(7)	−1956(10)	1738(8)	3908(6)	O(8)	244(37)	−1393(37)	5774(28)
C(8)	−706(9)	2285(7)	4103(4)	O(9)	1828(40)	−413(37)	5373(33)
C(9)	1554(8)	2221(7)	3762(4)				

Table 2. *Bonds Lengths* [Å] *for* $[Cu(C_{13}H_{28}N_4)Cl]ClO_4$

Cl(1)–Cu(1)	2.621(1)	C(5)–C(4)	1.498(9)	C(8)–N(3)	1.463(8)
N(2)–Cu(1)	2.010(4)	C(8)–C(7)	1.502(11)	C(10)–N(4)	1.510(9)
N(4)–Cu(1)	2.038(4)	C(11)–C(10)	1.526(10)	C(2)–C(1)	1.417(12)
C(4)–N(1)	1.475(7)	C(13)–C(12)	1.468(13)	C(4)–C(3)	1.529(9)
C(6)–N(2)	1.453(8)	N(1)–Cu(1)	2.037(4)	C(7)–C(6)	1.523(10)
C(9)–N(3)	1.463(8)	N(3)–Cu(1)	2.012(4)	C(10)–C(9)	1.499(10)
C(12)–N(4)	1.491(8)	C(1)–N(1)	1.518(8)	C(13)–C(11)	1.424(14)
C(3)–C(2)	1.527(14)	C(5)–N(2)	1.467(7)		

Table 3. *Bonds Angles* [°] $[Cu(C_{13}H_{28}N_4)Cl]ClO_4$

N(1)–Cu(1)–Cl(1)	91.8(1)	C(5)–C(4)–N(1)	108.9(5)	C(5)–N(2)–Cu(1)	107.3(3)
N(2)–Cu(1)–N(1)	84.5(2)	C(4)–C(5)–N(2)	110.7(5)	C(6)–N(2)–C(5)	111.3(5)
N(3)–Cu(1)–N(1)	174.2(2)	C(8)–C(7)–C(6)	112.5(6)	C(9)–N(3)–Cu(1)	106.2(3)
N(4)–Cu(1)–Cl(1)	98.7(1)	C(10)–C(9)–N(3)	108.8(5)	C(10)–N(4)–Cu(1)	108.7(4)
N(4)–Cu(1)–N(2)	166.1(2)	C(11)–C(10)–N(4)	103.5(7)	C(12)–N(4)–C(10)	106.6(5)
C(1)–N(1)–Cu(1)	117.7(4)	C(13)–C(11)–C(10)	109.0(8)	C(3)–C(2)–C(1)	104.6(7)
C(4)–N(1)–C(1)	105.1(5)	C(12)–C(13)–C(11)	109.2(8)	C(3)–C(4)–N(1)	103.2(5)
C(6)–N(2)–Cu(1)	118.8(4)	N(2)–Cu(1)–Cl(1)	95.2(1)	C(5)–C(4)–C(3)	118.8(6)
C(8)–N(3)–Cu(1)	116.5(4)	N(3)–Cu(1)–Cl(1)	93.7(1)	C(7)–C(6)–N(2)	113.5(6)
C(9)–N(3)–C(8)	115.0(5)	N(3)–Cu(1)–N(2)	93.0(2)	C(7)–C(8)–N(3)	111.5(5)
C(12)–N(4)–Cu(1)	118.7(4)	N(4)–Cu(1)–N(1)	96.4(2)	C(9)–C(10)–N(4)	107.1(5)
C(2)–C(1)–N(1)	110.4(7)	N(4)–Cu(1)–N(3)	84.7(2)	C(11)–C(10)–C(9)	113.1(7)
C(4)–C(3)–C(2)	104.0(6)	C(4)–N(1)–Cu(1)	110.4(3)	C(13)–C(12)–N(4)	106.8(7)

Crystal Data of [Cu(ppm)]Cl·ClO$_4$. $C_{13}H_{28}Cl_2CuN_4O_4$, $M = 438.85$, orthorhombic space group $P2_12_12_1$, $a = 10.641(2)$, $b = 11.429(3)$, $c = 14.895(3)$ Å, $V = 1933.2(7)$ Å^3, $D_c(Z = 4) = 1.608$ g·cm^{-3}, $\mu(\mathrm{Mo}K\alpha) = 13.88$ cm^{-1}, $\lambda(\mathrm{Mo}K_\alpha) = 0.7107$ Å, $F(000) = 916$ electrons. Specimen: blue prisms, $N = 1843$, $N_0 = 1628$, ranges of *hkl* 0–32, 0–13, 0–18, $R = 0.035$, $R_w = 0.041$, $w = 0.96/[\sigma^2(F_0 + 0.0013\, F_0^2)]$, residual extrema $+0.3$ eÅ^{-3} and -0.2 eÅ^{-3}.

Results and Discussion. – Multidentate ligands based on L-proline are of interest for stereospecific reactions, because of the stereochemical fixation of the α-substituent through five-ring formation with the amine in addition to the relative bulkiness of the substituent. A number of such ligands have been reported [8] [14–23]. The ligands mnppm (**4**) and mappm (**5**) are very similar to ppm (**1**); however, the ligands based on the template condensation described here have an additional NO_2 or NH_2 substituent, and this is an important aspect in view of the fixation to supports for the preparation of chiral devices for stereoselective reactions (*e.g.* racemate separation). In particular, the pendant amine of $[Cu(mappm)]^{2+}$ is ideal for fixation to supports *via* well-established methods [24]. Therefore, the isolation of the nitro reduction product described here is of some importance, especially in the context of the template condensation reactions with the readily available amino-acid derivatives [5].

Template condensation of $[Cu((S)\text{-pam})_2]^{2+}$ and $[Cu((R),(S)\text{-pam})_2]^{2+}$ is only possible with *cis*-coordination of the two ligands. With labile Cu^{II} complexes, this does not seem to be a problem, as long as some *cis*-complex is present in the equilibrated solution [5]. Successful condensation was indicated by strong absorptions in the IR spectra at ~ 1550 and ~ 1350 cm^{-1} ($\nu_{as}(RNO_2)$ and $\nu_s(RNO_2)$, respectively), $E_{1/2}(RNO_2) \approx -0.6$ V *vs.* SHE (see *Table 4*, below) and the microanalytical data. The structure of the coordinated ligands is supported by the spectral changes resulting from the Zn/acid reduction of the pendant NO_2 group and the analysis of the NMR spectra of the isolated free ligands. The solution structure of $[Cu((S),(S)\text{-mnppm})]^{2+}$, $[Cu((R),(S)\text{-mnppm})]^{2+}$, $[Cu((S),(S)\text{-Hmappm})]^{3+}$, and $[Cu((R),(S)\text{-Hmappm})]^{3+}$ are, according to their physical properties, very similar to the parent $[Cu(ppm)]^{2+}$ complex, whose solid-state structure has been determined.

The structure of [Cu(ppm)]Cl·ClO$_4$ consists of a quadridentate ligand, with four secondary amine donor groups, and a Cl ligand coordinated to a Cu^{II} ion. A disordered ClO_4^- anion balances the charge. The two amine groups N(1) and N(4) adjacent to the chiral centres have the same chiralities, presumably imposed by the configuration of C(4) and C(10). The other two amine groups have opposite chiralities. The same geometry occurs in a number of Cu^{II} complexes with similar ligand systems [5], and it is likely to be the result of the fact that this enables the six-membered chelate ring to adopt an energetically favourable chair conformation. The Cu—N bond lengths to the amine groups at each end of the quadridentate are longer than those to the remaining amine groups, and the average Cu—N distances are typical of Cu^{II} tetraamines. The Cu—Cl bond length is longer than expected for a Cu^{II} 4 + 1 geometry [25]. However, there is also a weak intermolecular Cu—Cl interaction (3.138 Å), and the geometry is, therefore, best described as tetragonally distorted octahedral (4 + 2) with bridging Cl ligands occupying the axial sites. The origin of the distortion along the tetragonal axis has not been analyzed in detail but probably has steric reasons. The square base defined by the amine N-atoms is tetrahedrally distorted, and the Cu-atom lies above the best plane defined by these four atoms.

Condensation of bis(amino acid)copper(II) complexes with formaldehyde and nitroethane leads to ligands that are structurally related to mnppm (**4**) [5]. Since α-amino acids

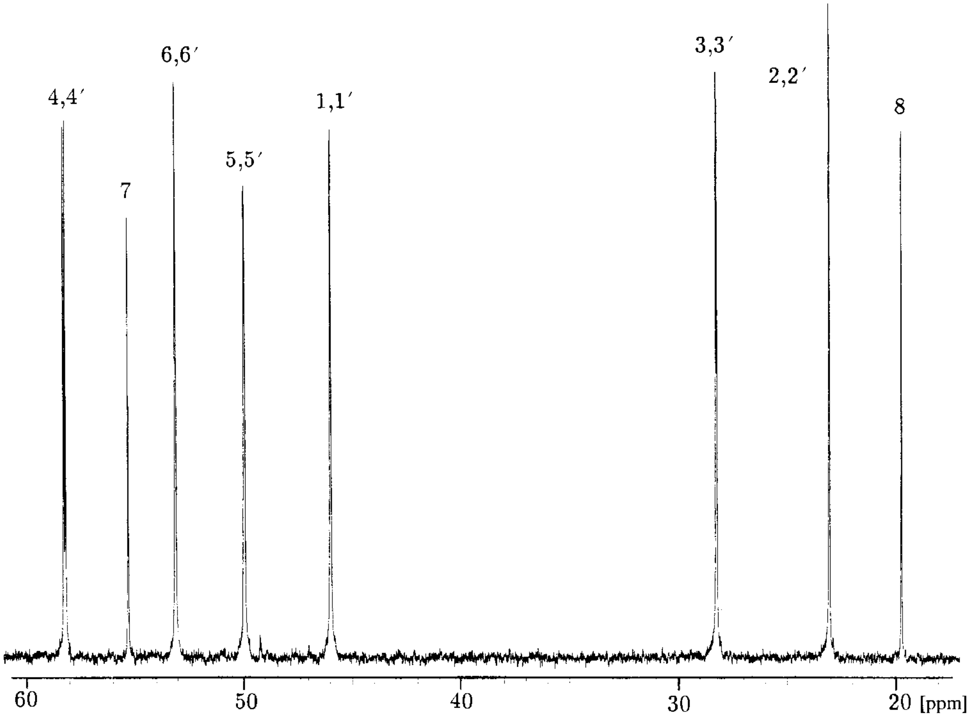


Fig. 2. *^{13}C-NMR* (101 MHz, D_2O, pD ~ 3) *spectrum of mappm* (**5**)

are purportedly more susceptable to racemization in presence of metal ions [5] [26] than diamines such as pam (**3**), racemization during the rather mild template reaction was not a problem. Optical purity of mappm (**5**) was established by ^{1}H-NMR spectroscopy of the *Mosher*-acid derivative of (*S*),(*S*)-mappm (experimental details are similar to published procedures [27]). Also, the ^{13}C-NMR spectrum of the free ligand mappm (**5**), presented in *Fig. 2*, indicates that the ligand is asymmetric[1]), *viz.* the configuration at C(4) and C(4′) is (*S*), and one pyrrolidinyl ring is *syn*, while the other is *anti* with respect to the amine-substituent (note that only in the mixed (*R*),(*S*)-form (racemate) C(7) is stereogenic). The condensation of coordinated amino acids, with formaldehyde and nitroethane, is fully stereospecifc, *viz.* only one out of three possible products is found [5] [28]. It was not possible to prove stereospecificity in the case of the template condensation of pam (**3**), as the two possible (*R*),(*S*)-isomers possess the same symmetry. However, one would intuitively believe that the amino group lies on the opposite side to the inward facing pyrrolidinyl rings by analogy with similar studies of sterically crowded systems where coordination of the NO_2 groups during the condensation reaction have been suggested.

Electrochemical and spectroscopic data of the complexes are collected in *Table 4*. The electrochemistry of $[Cu((S),(S)\text{-mnppm})]^{2+}$ and $[Cu((R),(S)\text{-mnppm})]^{2+}$ exhibits, in addition to the irreversible $Cu^{II/I}$ potentials, irreversible waves at $E_{1/2} = -0.57$ and -0.58 V (*vs.*

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[1]) The assignments in *Fig. 2* are in agreement with the spectral properties of a range of similar ligands such as pam (**3**), ppm (**1**), and the products of template condensations with amino acids.

SHE), respectively. These are absent in the precursor, the unsubstituted, and NO_2-group-reduction products $[Cu(ppm)]^{2+}$, $[Cu((S),(S)\text{-Hmappm})]^{3+}$, and $[Cu((R),(S)\text{-Hmappm})]^{3+}$. Together with the distinct vibrational properties of the present NO_2 group ($\nu_{as} \sim 1550$ cm^{-1} and $\nu_s \sim 1350$ cm^{-1} [5] [29] [30]), this usually is an indication of a successful template condensation of the type described here.

Table 4. *Spectroscopic and Electrochemical Data of the Cu^{II} Complexes of pam, ppm, mnppm, and mappm*

Parameter	$[Cu((S)\text{-pam})_2]^{2+}$	$[Cu((R)/(S)\text{-pam})_2]^{2+}$	$[Cu((S)/(S)\text{-mnppm})]^{2+}$	$[Cu((R),(S)\text{-mnppm})]^{2+}$	$[Cu((S),(S)\text{-Hmappm})]^{3+}$	$[Cu((R)/(S)\text{-Hmappm})]^{3+}$	$[Cu((S),(S)\text{-ppm})]^{2+}$
g_{iso}	2.11	2.10	2.10	2.10	2.11	2.10	2.10
$g_\perp$	2.05	2.05	2.04	2.05	2.06	2.05	2.05
$g_\parallel$	2.22	2.21	2.21	2.21	2.21	2.21	2.20
A_{iso} [10^{-4} cm^{-1}]	82	83	88	83	75	84	83
$A_\perp$ [10^{-4} cm^{-1}]	23	25	31	25	17	26	25
$A_\parallel$ [10^{-4} cm^{-1}]	201	200	201	200	191	203	199
$\tilde{\nu}_{VIS}$ [cm^{-1}][a])	18315 (95)	18282 (94)	18484 (98)	18484 (106)	18011 (137)	18011	18760 (109)
ν_{as} (NO_2)		–	1543	1553	–	–	–
$E_{1/2}$[b])	–0.31	–0.31	–0.46 (–0.57)	–0.46 (–0.58)	–0.62	–0.57	–0.58

[a]) ε [M^{-1} cm^{-1}] in parantheses.

[b]) *Vs.* SHE (Cu$^{II/I}$ potential; $E_{1/2}$ ($R-NO_2$) in parentheses).

The spin *Hamiltonian* parameters of the Cu^{II} tetraamines reported in *Table 4* are all virtually invariant and consistent with a $(d_{x^2-y^2})^1$ ground state. The rather large values for $A_\parallel$ indicate planarity of the CuN_4 group [31] [32]. The broad and unresolved transitions in the dd spectra around 18500 cm^{-1} are consistent with weak interactions at apical sites (tetragonal (4 + 2) geometry), comparable with the structure of $[Cu(ppm)]^{2+}$ in the solid state (*Fig. 1*). Coordination of the pendant amine of $[Cu(mappm)]^{2+}$ would be expected to lead to appreciable spectral changes [33]. However, the close spectroscopic similarity between the series of Cu^{II} complexes **1**, **4**, and **5** indicates that the chromophore of all systems is very similar, *i.e.* the pendant amine of $[Cu(mappm)]^{2+}$ is not coordinated. This is not unexpected, but is an important result in view of coupling reactions of the pendant amine to polymeric supports.

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