Macrocyclic Melamine-Based Ligand Complexes as Building Blocks for the Metal-Directed Synthesis of Heterometallic Di- and Trinuclear Compounds

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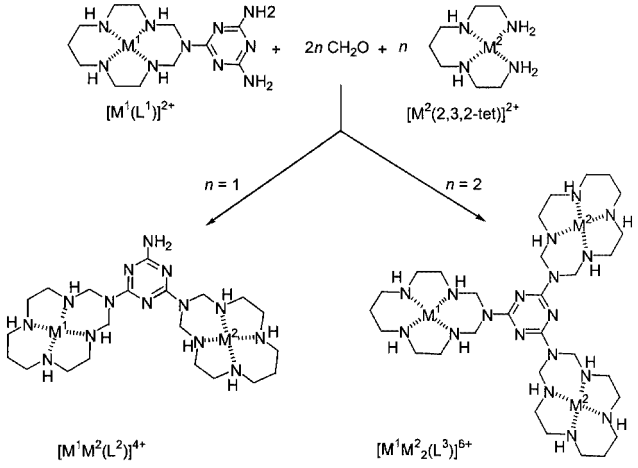
Heterodi- and heterotrimetallic Ni^{II}/Cu^{II}, Ni^{II}_2/Cu^{II} and Ni^{II}/Cu^{II}_2 complexes of bis- and tris-macrocyclic ligands, linked by a 1,3,5-triazine spacer group, are obtained as products of copper(II)- or nickel(II)-assisted condensations of the open-chain tetraamine complexes $[M^2(2,3,2\text{-tet})]^{2+}$ [2,3,2-tet= bis-*N*,*N*′-(2-aminoethyl)propane-1,3-diamine, $M^2 = Ni^{II}$ or Cu^{II}] with formaldehyde and the monomacrocyclic ligand complexes $[M^1(L^1)]^{2+}$, where L^1 is a cyclam-type macrocycle with a pendent melamine group ($M^1 = Cu^{II}$ or Ni^{II}). The spectroscopic (UV/Vis and EPR) and electrochemical properties of the oligonuclear heterometallic compounds in comparison with those of the homometallic analogues indicate small, but significant, intramolecular metal-metal interactions.

Introduction

A number of metalloproteins have oligonuclear active sites,[1] cooperative effects in dinuclear enzyme mimics have been studied extensively,[2−4] and examples of very active catalysts with more than one metal center involved may indicate that there is some potential in oligonuclear metal catalysts. Generally, the two (or more) metal ions have different functions in enzymatic catalytic processes and, therefore, the two sites in model compounds and active molecular catalysts should be structurally and/or electronically different.[5] The synthesis of ligands with two different coordination sites is not easy,[5,6] and coordination of two different metal ions to symmetrical ligands leads to problems with the separation of the product mixtures, especially with labile metal ions. The sequential synthesis of oligonuclear complexes is therefore an appealing concept,[7] and for oligomacrocylic ligand complexes, consecutive metal-ion-directed processes should be an efficient preparative technique.

There are a few mixed $Ni^{II}Cu^{II}$ complexes of bis-tetraazamacrocyclic ligands[8−10] but no corresponding trinuclear complexes have been described so far. The nickel(II)- and copper(II)-directed reactions of $[M^2(2,3,2\text{-tet})]^{2+}$ [2,3,2-tet = bis *N*,*N*′-(2-aminoethyl)propane-1,3-diamine, $M^2 = Ni^{II}$ or Cu^{II}] with formaldehyde and melamine (melamine = 2,4,6-triamino-1,3,5-triazine) lead to mixtures of homometallic mono-, bis- and tris-macrocyclic ligand complexes.[11−14] The fact that products of different nuclearity are formed in the one-pot reactions suggests that the melamine amino groups of the mono- and bis-macrocyclic ligand complexes can serve as locking fragments in the formation of the second and third macrocyclic subunit. Here we report the use of the recovered mono-macrocyclic ligand complexes as starting materials for the di- and trinuclear mixed-metal complexes (see Scheme 1).



Scheme 1

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Results and Discussion

The nickel(II)- or copper(II)-assisted reaction of the open-chain tetraamine 2,3,2-tet with the melamine-substituted macrocyclic ligand compounds $[M^1(L^1)]^{2+}$ results in the formation of the desired di- and trinuclear heterometallic species $[M^1M^2(L^2)]^{4+}$, $[M^1_2M^2(L^3)]^{6+}$ and $[M^1M^2_2(L^3)]^{6+}$ ($M^1 = Cu^{II}$, $M^2 = Ni^{II}$; see Scheme 1). Similar to the analogous reactions leading to the corresponding homo-oligonuclear complexes[13,14] the yields of the one-pot template reactions are low (5−10%) and higher for the copper(II)- than for the nickel(II)-directed reactions. The yields are solvent dependent and the highest were obtained in ethanol/acetonitrile mixtures. As a side-product the modified bis-macrocyclic ligand complex $[NiCu(L^{2a})]^{4+}$, in which the melamine NH_2 protons of L^2 are substituted by CH_2OH groups, is formed in appreciable yield. This complex was fully characterized by MS and elemental analysis (see Exp. Sect.).

The mass spectra of the three new hetero-oligonuclear complexes are clear evidence for the successful syntheses. Peaks for the molecular ions, with expected intensity distributions, were observed in all cases (see Figure 1 for an example). As expected, due to the inertness of the oligo-macrocyclic ligand complexes, no peaks of homo-oligonuclear species were observed; i.e., there are no transmetallation reactions. Characteristic peaks in the IR spectra of the complexes {1630 cm^{-1} (δ_{NH2}) and 1560 cm^{-1} (ν_{CN}) for $[NiCu(L^2)]^{4+}$ and 1550 cm^{-1} (ν_{CN}) for $[NiCu_2(L^3)]^{6+}$ and $[Ni_2Cu(L^3)]^{6+}$} are in good agreement with those of the corresponding homo-oligonuclear compounds.[13,14] The electronic spectra of the homo- and heteronuclear complexes are similar (Table 1). The absorption in the UV region is due to the superposition of the MLCT transition {ν_{max} = 39500 cm^{-1} (ε = 8500 $M^{-1}\cdot cm^{-1}$) and 45500 cm^{-1} (ε = 12000) for $[Cu(cyclam)]^{2+}$ and $[Ni(cyclam)]^{2+}$, respectively, cyclam = 1,4,8,11-tetraazacylotetradecane}[13,14] and a melamine-based π-π transition [ν_{max} = 49100 cm^{-1} (ε = 52000)].[13,14] The intensity of the MLCT bands are approximately proportional to the number of copper(II) and nickel(II) sites in the oligonuclear complexes.

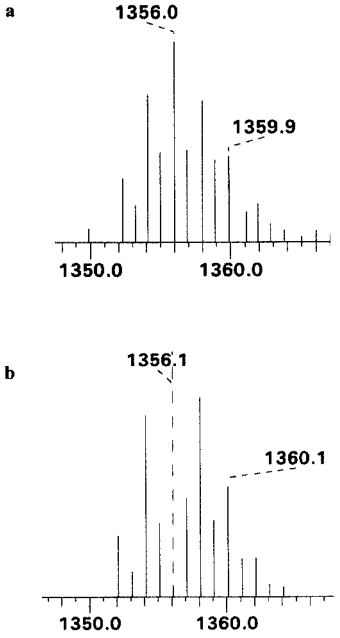

Figure 1. Experimental (a) and calculated (b) distribution of peak intensities for $\{[Ni_2Cu(L^3)](ClO_4)_5\}^+$ in the FAB mass spectrum of the trinuclear mixed-metal complex

The intensities of the d-d electronic transitions are also very similar to the sum of the spectra of the corresponding mononuclear nickel(II) and copper(II) sites (see Table 1). Nickel(II) complexes of melamine-based ligands exist in aqueous solution as equilibrium mixtures of diamagnetic four-coordinate $[NiN_4]$ and paramagnetic six-coordinate $[NiN_4(OH_2)_2]$ species.[14] Because of the larger intensity of the copper(II) d-d transitions those due to nickel(II) appear only as ill-resolved shoulders at the high energy tail of the copper(II) band. This is more pronounced at higher temperatures and in the noncoordinating solvent nitromethane,

Table 1. Spectroscopic[a] and electrochemical[b] data of the di- and trinuclear complexes

Compound	Absorption bands			Cyclic voltammograms	
	d-d	MLCT[c]	π-π[c]	0.1 M $NaNO_3$	3.33×10^{-2} M Na_2SO_4
$[Cu(L^1)]^{2+}$	19400(87)[d]	39500 (8500)	47900 (51000)		
$[Ni(L^1)]^{2+}$	22000(20)[d] 22000(64)[e]		47800 (52000)	883(65)	643(75)
$[Cu_2(L^2)]^{4+}$	19400(176)[d] 20200(157)[e]	39500 (16500)	47000 (57600)		
$[Ni_2(L^2)]^{4+}$	22000(42)[d] 22000(128)[e]		46800 (62000)	865 (70)	593(70), 703(75)
$[NiCu(L^2)]^{4+}$	19400(92)[d] 21100(120)[e]	39500 (9700)	46400 (51700)	865 (80)	600(100)
$[Cu_3(L^3)]^{6+}$	19400(260)[d]	39500 (24400)	46700 (87000)		
$[NiCu_2(L^3)]^{6+}$	19400(184)[d] 20700(201)[e]	39500 (18100)	46100 (75200)	865 (120)	620(120)
$[Ni_2Cu(L^3)]^{6+}$	19900(117)[d] 21300(193)[e]	39500 (11000)	45900 (73700)	865 (120)	605(85)

[a] ν_{max} in cm^{-1} (ε in $L\cdot mol^{-1}\cdot cm^{-1}$). [b] Aqueous solution, $E_{1/2}$ in mV vs. sat.Ag/AgCl (peak separation, ΔE, in mV). [c] Aqueous solution. [d] 0.1 M $NaNO_3$, aqueous solution. [e] Nitromethane solution.

where the amount of the diamagnetic form of nickel(II) is dominant (see Table 1).

EPR spectra of the complexes are indicative of the number of copper(II) sites in the oligomacrocyclic ligand complexes. For $[NiCu(L^2)]^{4+}$ and $[Ni_2Cu(L^3)]^{6+}$ the spectra are, as expected, almost identical (Figure 2), and similar to that of $[Cu(L^1)]^{2+}$.[11,13] The spectrum of $[NiCu_2(L^3)]^{6+}$ is similar to that of $[Cu_2(L^2)]^{4+}$ and typical for a dipole-dipole coupled bis(spin 1/2) system. The rather broad features of the two dicopper(II) compounds (spectra d and e) do not allow us to exclude small amounts of $CuNi_2$ or Cu_3 impurities in the samples. However, the spectra are compatible with pure Cu_2 and $NiCu_2$ samples and transmetallation is unexpected for this type of cyclam-based copper(II) and nickel(II) complexes under the conditions employed, and proven by the mass spectroscopic data and elemental analyses. A detailed interpretation of the EPR spectra with the aim of analyzing the solution structural properties, based on MM-EPR,[15] is in process and will be published elsewhere.[16]

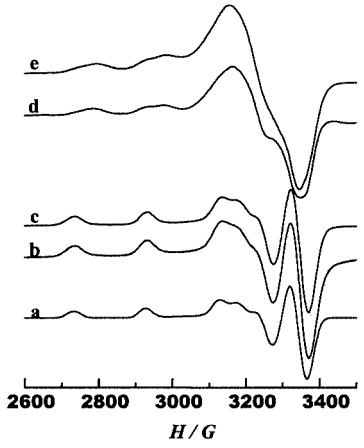

Figure 2. EPR spectra of frozen solutions [DMF/H_2O, (2:1), approx. 10^{-3} M] of: (a) $[Cu(L^1)]^{2+}$, (b) $[NiCu(L^2)]^{4+}$, (c) $[Ni_2Cu(L^3)]^{6+}$, (d) $[Cu_2(L^2)]^{4+}$ and (e) $[NiCu_2(L^3)]^{6+}$

The redox potentials of the $Ni^{III/II}$ couple in aqueous solution (0.1 M $NaNO_3$ or 3.3×10^{-2} M Na_2SO_4) were determined by cyclic voltammetry (Table 1). Due to the more positive $E_{1/2}$ values for the $Cu^{III/II}$ transformation[13] these processes were not observed in the potential range studied (0.2−1.0 V). The CV of $[Ni_2(L^2)]^{4+}$ and $[NiCu(L^2)]^{4+}$ in 0.1 M $NaNO_3$ reveal one quasi-reversible $Ni^{III/II}$ transition each, but the current of the mixed-metal species is approximately half that of the homo-dinuclear complex at the same concentration. Under the same conditions the current observed for $[NiCu_2(L^3)]^{6+}$ is smaller than for $[NiCu(L^2)]^{4+}$; this is believed to be due to a smaller diffusion coefficient of the tris(macrocyclic) ligand cationic complex. A similar effect is observed for $[Ni_2(L^2)]^{4+}$ and $[Ni_2Cu(L^3)]^{6+}$. The potentials of the $Ni^{III/II}$ couple for all hetero-oligonuclear complexes are close to that of the corresponding mononuclear compound. This indicates a negligible electrostatic influence of the copper(II) centers on the redox transformation of the nickel ions.

Due to the stabilization of nickel(III) by coordination of sulfate, the $E_{1/2}$ values in sulfate media are less anodic. As expected, $[NiCu(L^2)]^{4+}$ as well as $[NiCu_2(L^3)]^{6+}$ reveal one electrochemical process with potentials similar to the less anodic peaks observed for $[Ni_2(L^2)]^{4+}$ (Figure 3). $[Ni_2(L^2)]^{4+}$ also undergoes a second redox transformation at higher potential. This was interpreted as being due to hydrogen bonding between a water molecule coordinated to one nickel center and sulfate axially coordinated to the adjacent metal ion.[14] It was therefore unexpected that both nickel centers of $[Ni_2Cu(L^3)]^{6+}$ are electrochemically identical in sulfate media. It appears that the formation of the proposed hydrogen-bonded arrangement is less favorable when water is coordinated to copper(II); a possible reason is the differences in M−O (OH_2) bonds {approx. 2.15 and 2.5 Å for tetragonal nickel(II) and copper(II) tetramines[14]}.

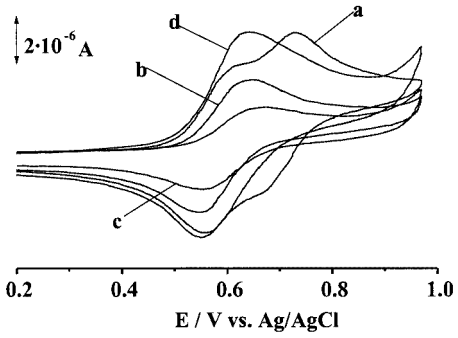

Figure 3. Cyclic voltammograms of 2.5×10^{-3} M solutions of the macrocyclic ligand complexes in 3.33×10^{-2} M Na_2SO_4: (a) $[Ni_2(L^2)]^{4+}$; (b) $[NiCu(L^2)]^{4+}$; (c) $[NiCu_2(L^3)]^{6+}$; (d) $[Ni_2Cu(L^3)]^{6+}$

Conclusion

Based on the available electrochemical and UV/Vis spectroscopic data there is only a weak interaction between the copper(II) and nickel(II) centers. This is supported by the EPR spectra of the systems with two copper centers, which are typical for dipole-dipole coupled dicopper(II) compounds. The electrochemical data indicate that the cooperativity in the binding of sulfate observed for the homometallic dinickel(II) system[14] disappears in the mixed-metal systems. This suggests that axial coordination to the mixed-metal systems is significantly different to that of the homometallic compounds, and this will lead to important differences in the rich host-guest chemistry[13] of the trinuclear systems.

Experimental Section

Physical Methods: Infrared spectra (KBr pellets) were recorded on a Specord 75 IR (Carl Zeiss) spectrometer. Electronic absorption spectra were measured on a Specord M40 (Carl Zeiss) spectrophotometer. EPR spectra were obtained with a Bruker ESP300E spectrometer (9.4635 GHz) as approx. 1×10^{-3} mol·L^{-1} frozen (liquid nitrogen temperature) solutions in DMF/water (2:1). Fast atom bombardment mass-spectra (FAB^+ mode) were obtained

with a MAT8400 mass spectrometer, using *p*-nitrobenzyl alcohol (Nibelol) as the matrix. Cyclic voltammograms were generated using a PI-50−1.1 potentiostat, equipped with a PR-8 function generator (Izmeritel, Gomel) and an N-307 X-Y recorder (ZIP, Krasnodar). A standard three-electrode scheme was used, consisting of a glassy carbon working, a Ag/AgCl reference and a Pt wire auxiliary electrode. All solutions for electrochemistry were purged with nitrogen before measurement. Analytical data were obtained from the microanalytical laboratory of the chemical institutes of the University of Heidelberg.

Materials: AR grade chemicals and solvents were used as supplied for all reactions. Open-chain amine metal complexes $[M(2,3,2\text{-tet})](ClO_4)_2$ [M = Ni or Cu; 2,3,2-tet= bis-*N*,*N*′-(2-aminoethyl)-propane-1,3-diamine] and macrocyclic ligand mononuclear $\{[Ni(L^1)](ClO_4)_2{\cdot}H_2O$ and $[Cu(L^1H)](ClO_4)_3{\cdot}H_2O\}$ and homodinuclear $\{[Ni_2(L^2)](ClO_4)_4{\cdot}2H_2O$ and $[Cu_2(L^2)](ClO_4)_4{\cdot}2.5H_2O\}$ complexes were prepared as described previously.[13,14]

Syntheses: ***Caution! Perchlorate salts of metal complexes are potentially explosive. Although we did not experience any problems, such complexes should be handled very carefully.***

In a typical procedure 4.0 mmol of $[Ni(L^1)](ClO_4)_2{\cdot}H_2O$ {or $[Cu(L^1H)](ClO_4)_3{\cdot}H_2O\}$ and 9.1 mmol of $[Cu(2,3,2\text{-tet})](ClO_4)_2$ {or $[Ni(2,3,2\text{-tet})](ClO_4)_2\}$ were dissolved in a mixture of acetonitrile (25 mL), ethanol (35 mL) and triethylamine (3 mL), and the resulting solution was brought to reflux. A solution of 37% aqueous formaldehyde (23.0 mmol) in ethanol (15 mL) was added dropwise during one hour. The reaction mixture was refluxed for an additional 48 h, then cooled to ambient temperature and filtered. The solution was diluted to 2 L and absorbed onto a Sephadex C-25 (Na^+ form) ion exchange column, which was first washed with water (0.5 L). The first band eluted with 0.25 M $NaClO_4$ contained unchanged starting materials and was discarded.

Two bands eluted from the column with 0.4 M $NaClO_4$. The first band was collected, the solvents evaporated under low pressure to a small volume and left to dry at ambient temperature. The solid red-yellow residue was treated with 30 mL of acetonitrile to extract the macrocyclic complex. This was precipitated from the purple acetonitrile solution by slow diffusion of diethyl ether, and the solid was carefully triturated in 10 mL of 1 M aqueous $NaClO_4$. The precipitate, **$[NiCu(L^{2a})](ClO_4)_4\ 3H_2O$**, was collected by filtration, washed with ethanol and dried in air. Yield 0.22 g, 5%. $C_{23}H_{55}Cl_4CuN_{14}NiO_{21}$ (1127.8): calcd. C 24.49, H 4.92, N 17.39; found C 24.28, H 4.84, N 17.62. MS: *m*/*z* = 972 ($[CuNi(L^{2a}\text{-}2H)](ClO_4)_3^+$), 944 ($[CuNi(L^{2a}\text{-}CH_2OH)](ClO_4)_3^+$), 914 ($[CuNi(L^{2a}\text{-}2CH_2OH)](ClO_4)_3^+$).

$[NiCu(L^2)](ClO_4)_4{\cdot}3H_2O$ eluted as the second band with 0.4 M $NaClO_4$. The eluate was evaporated to 40 mL under reduced pressure and cooled in a refrigerator. The red-orange precipitate was filtered, washed with ethanol and dried in air. Yield 0.47 g, 11%. The product was purified by reprecipitation from an aqueous solution by addition of $NaClO_4$. IR (KBr): $\tilde{\nu}$ = 3210m cm^{-1} [ν(NH), macrocycle], 1630m [δ(NH_2), melamine], 1560s [ν(CN), melamine], ca. 1100vs, 626m [ν(ClO_4)]. $C_{12}H_{52}Cl_4CuN_{14}NiO_{19}$ (960.7): calcd. C 23.60, H 4.90, N 18.35; found C 23.79, H 4.95, N 18.12. MS: *m*/*z* = 914 ($[CuNi(L^2)](ClO_4)_3^+$).

The tris-macrocyclic ligand complexes were eluted as the third band with 0.8 M $NaNO_3$. The eluate was reduced to a volume of 40 mL. After cooling, the precipitate of $NaNO_3$ was removed by filtration. After addition of 2 g of $NaClO_4$ the solution was left at room temperature for a few days to allow crystals to form. The product was filtered, washed with ice-cold water and ethanol and dried in air.

$[NiCu_2(L^3)](ClO_4)_3(NO_3)_3{\cdot}3H_2O$. Yield 0.36 g, 7%. IR (KBr): $\tilde{\nu}$ = 3190m cm^{-1} [ν(NH), macrocycle], 1550s [ν(CN), melamine], 1370s [ν(NO_3)], ca. 1100vs, 626m [ν(ClO_4)]. $C_{30}H_{72}Cl_3Cu_2N_{21}NiO_{24}$ (1403.2): calcd. C 25.68; H 5.17; N 20.96; found C 25.77; H 5.36; N 21.32. MS: *m*/*z* = 1248 ($[NiCu_2(L^3)](ClO_4)_2(NO_3)_3^+$).

$[NiCu_2(L^3)](ClO_4)_6{\cdot}4H_2O$: This product was obtained by addition of $NaClO_4$ to an aqueous solution of $[NiCu_2(L^3)](ClO_4)_3(NO_3)_3{\cdot}3H_2O$. Yield: nearly quantitative. IR (KBr): $\tilde{\nu}$ = 3226 cm^{-1} [ν(NH), macrocycle], 1550s [ν(CN), melamine], ca. 1100vs, 626m [ν(ClO_4)]. $C_{30}H_{74}Cl_6Cu_2N_{18}NiO_{28}$ (1533.5): calcd. C 23.50, H 4.86, N 16.44; found C 23.62, H 5.02, N 16.42.

$[Ni_2Cu(L^3)](ClO_4)_6{\cdot}5H_2O$: Yield 0.21 g, 3%. IR (KBr): $\tilde{\nu}$ = 3200m cm^{-1} [ν(NH), macrocycle], 1550s [ν(CN), melamine], ca. 1100vs, 626m [ν(ClO_4)]. $C_{30}H_{76}Cl_6CuN_{18}Ni_2O_{29}$:calcd. C 22.00, H 4.48, N 17.11; found C 22.06, H 4.65, N 16.78. MS: *m*/*z* = 1356 ($[CuNi_2(L^3)](ClO_4)_5^+$).

Acknowledgments

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