Structural diversity in the assembly of helicate-type nickel(II) complexes with enantiopure bis(β-diketonate) ligands†

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The tartaric acid derived bis(β-diketonate) ligand L affords either 2:3 or 3:2 ligand:metal complexes with nickel(II) ions depending on the stoichiometry of the components; the two complexes posses different electronic and geometric properties.

The chemistry of the helicates developed during the last 15 years to an important topic of metallosupramolecular chemistry.[1] Although helicates were found which possess special properties (*e.g.* luminescence,[2] mesophase behaviour,[3] or interaction with DNA[4]), this was not the motivation to study them in the first place. The simplicity of helicates allows the investigation of fundamental principles of supramolecular chemistry, such as the mechanisms of the self-assembly process or stereochemistry. The latter was already an important task in early investigations. The diastereoselectivity of the helicate formation can be controlled[5] and enantiomerically pure helicates are necessarily obtained by introduction of chiral substituents either in the spacers or at the termini of the ligands, although mixtures of diastereomers of the helicates might be observed.[6]

Recently we introduced the chiral bis(β-diketonate) ligand **L**-H_2 (Scheme 1), which is easily obtained from tartaric acid by ketalization with acetone, ester formation and Claisen-type condensation of the diester with 4-bromoacetophenone. In an earlier study we showed, that **L** forms enantiomerically pure neutral triple-stranded helicates with iron(III) or gallium(III) ions. In contrast to most other helicates, the obtained complexes are readily soluble in non-polar solvents (even hexane) and they can specifically take up lithium perchlorate into chloroform solution.[7] However, up to now we were not able to use the chiral cryptand-type complexes as phase-transfer catalysts (which should be an entry into stereoselective catalytic reactions).

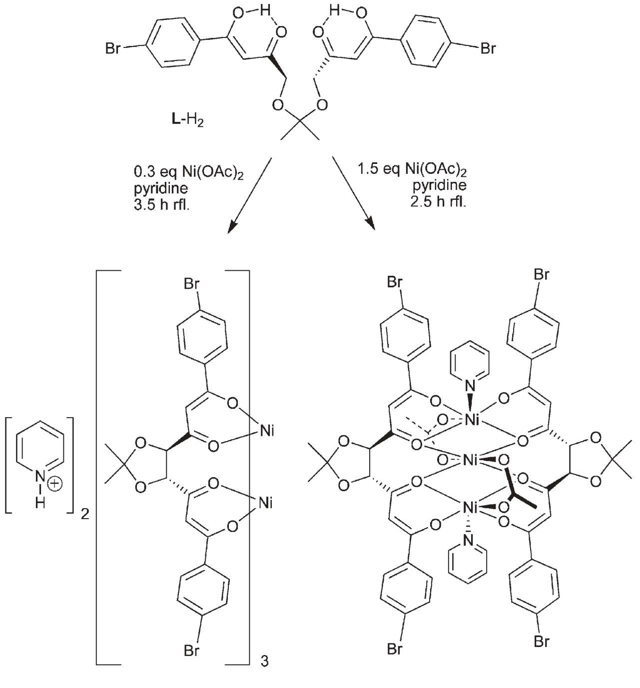
Now we present the complexation studies of **L**-H_2 with nickel(II) acetate which leads to two different coordination compounds with different metal:ligand stoichiometries depending on the reaction conditions.

If the complexation of **L**-H_2 with 0.3 equivalents nickel(II) acetate tetrahydrate is performed in py (3.5 h reflux), a yellow green solid is obtained in 44% yield after work up (Scheme 1). Negative FAB MS shows at high masses ($m/z > 600$) only one dominating peak at m/z 1791 which corresponds to $[NaNi_2(\mathbf{L})_3]^-$ and possesses the correct isotopic pattern.

We propose that the dianion $[Ni_2(\mathbf{L})_3]^{2-}$ adopts the structure of a right-handed (ΔΔ) triple-stranded dinuclear helicate as was observed for the corresponding neutral complexes $[M_2(\mathbf{L})_3]$ (M = Ga, Fe) by X-ray structural analyses.[7,8]

If a similar reaction is performed in py with ligand **L**-H_2 and 1.5 eq. of nickel(II) acetate tetrahydrate (Scheme 1), again a yellow green solid is obtained, which did not show a peak of a triple-stranded dinuclear compound by ESI MS but signals in the positive detection mode at m/z 1488 and 1277 correspond to the species $[Ni_3(\mathbf{L})_2(CH_3CO_2)(py)(H_2O)_4]^+$ and $[Ni_3(\mathbf{L})_2H]^+$, respectively.‡ Fortunately we obtained single crystals from dichloromethane and could determine the structure using X-ray crystallography.§

The compound contains two ligands **L**, three nickel(II) atoms, two acetate anions and two pys (Fig. 1). The nickel atoms possess an distorted octahedral coordination geometry with the ligands **L** occupying the equatorial positions. Hereby two metals are coordinating to the β-diketonate units of the ligand,[9] while the third one is included in the centre of the molecule binding to the internal carbonyl oxygens of the β-diketonate which thus act as bridging atoms between the central and the terminal nickel



Scheme 1 Formation of the complexes $[py\text{-}H]_2[Ni_2(\mathbf{L})_3]$ (left) and $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ (right) depending on the stoichiometry in the reaction.

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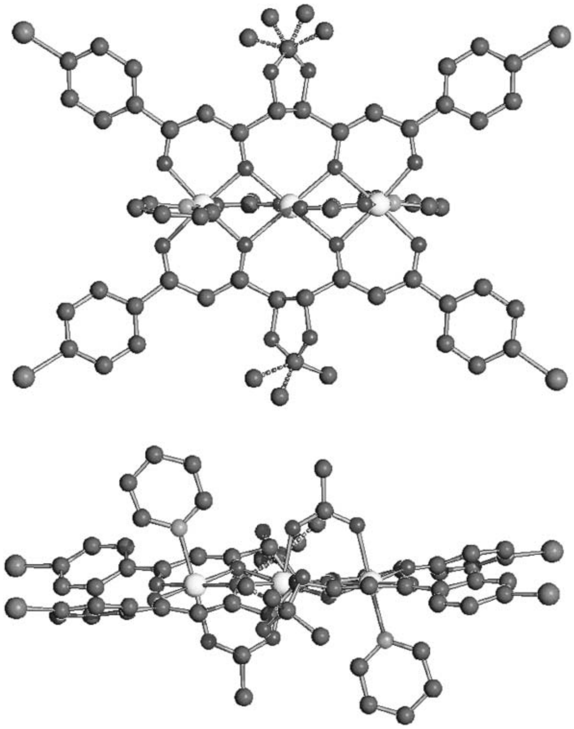

Fig. 1 Two different views of the trinuclear nickel(II) complex $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$. Hydrogen atoms are omitted and disorder of the methyl groups at the dioxolane can be observed.

atoms.[10] The $[Ni_3(\mathbf{L})_2]$ unit is nearly planar with a slight twisting distortion due to the chirality in the ligand backbone. Each of the terminal nickel atoms coordinate (from different faces of the main plane of the complex) an acetate anion. The latter act as bridging ligands and additionally bind to the central metal. The terminal metal centres are electronically and geometrically saturated by coordination of a py each. In this arrangement separations of 3.060 and 3.065 Å are observed between the central and the terminal nickel ions and the Ni–Ni–Ni axis is close to linear with an angle of 178° at the central metal.

The UV-vis spectra of the ligand $\mathbf{L}$-H_2 and the complexes $[py\text{-}H]_2[Ni_2(\mathbf{L})_3]$ and $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ in dichloromethane are very similar.¶ The bands at 265 and 330–350 nm represent π–π^* transitions. In case of the nickel(II) complexes the latter is red shifted compared to the free ligand, in which the β-diketonate is fixed in a cyclic structure by intramolecular H-bonding (see Scheme 1). Only a very weak shoulder can be detected for the nickel d-d transitions at about 390 nm.[11]

Circular dichroism (CD) spectroscopy of the ligand $\mathbf{L}$-H_2 as well as of the complexes lead to surprisingly different results (Fig. 2). The free ligand $\mathbf{L}$-H_2 shows in dichloromethane a signal with a positive Cotton effect at 300 nm and one with a negative effect at 340 nm. Similar signals are observed for the triple-stranded complex $[Ni_2(\mathbf{L})_3]^{2-}$ at 330 (+) and 380 (−) nm which apparently show exciton coupling due to the coupling of the low energy π–π^* transitions. Additional long-range exciton coupling interactions can not be ruled out.[12] The dissymmetry of the signal at 380 nm should be due to a strong partitioning of the Ni d–d transition at 390 nm.[11] The π–π^* transitions of $[Ni_2(\mathbf{L})_3]^{2-}$ correspond to those found for $[Ga_2(\mathbf{L})_3]$ (320 (+) nm, 360 (−) nm). It can be expected that $\mathbf{L}$ adopts a similar conformation in the complexes. Therefore a ΔΔ conformation should be present at the metal complex units of $[Ni_2(\mathbf{L})_3]^{2-}$ as was observed for $[Ga_2(\mathbf{L})_3]$. CD spectroscopy does not rule out that the ΔΛ or ΛΛ isomers are formed as minor species. However, for $[Ga_2(\mathbf{L})_3]$ only one enantiomerically pure diastereomer was detected by NMR.[7]

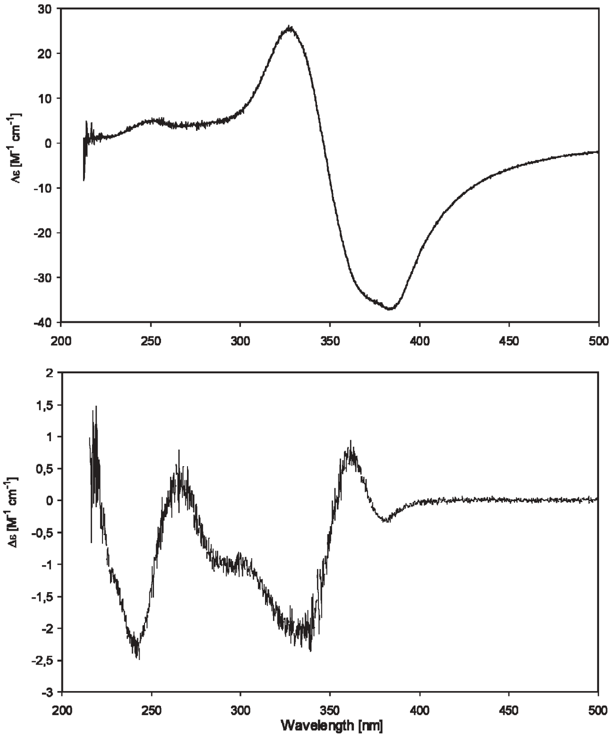

Fig. 2 CD spectra of $[Ni_2(\mathbf{L})_3]^{2-}$ (top) and $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ (bottom) in dichloromethane at 296 K.

For $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ a more complex spectrum is observed. Low intensity bands with negative Cotton effects are detected at 238 and 338 nm, while even weaker ones are found at 290 (shoulder) and 383 nm. Bands with positive Cotton effects appear at 265 (weak) and 361 nm. $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ does not adopt a conformation with "pronounced chirality", most likely leading to an arrangement of the chromophores that results in a weak exciton coupling and thus in low intensity of the spectrum. This is in contrast to the triple-stranded species. However, although the central bis-β-diketonate NiO_4 units of the distorted octahedra of $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ are planar, the organic substituents at the chelating units of $\mathbf{L}$ adopt a right handed helical twist. The twist induces a chiral environment at the central nickel atom due to the *trans*-substituted dioxolane ring in the spacer. The spectrum of $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ is even more complicated compared to $[Ni_2(\mathbf{L})_3]^{2-}$ which is probably due to the lower symmetry of the trinuclear complex as well as to the presence of py ligands as additional chromophores.

Ligand $\mathbf{L}$-H_2 shows fluorescence in the solid phase but not in dichloromethane solution at room temperature (c = 5.07 mM). Moreover, $[Ni_2(\mathbf{L})_3]^{2-}$ does not fluoresce in solution, while $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ leads to the fluorescence spectrum which is shown in Fig. 3. Excitation at 345 nm leads to a broad ligand centred fluorescence band at 454 nm. The excitation spectrum, which corresponds to the emission at 454 nm is also shown in Fig. 3.

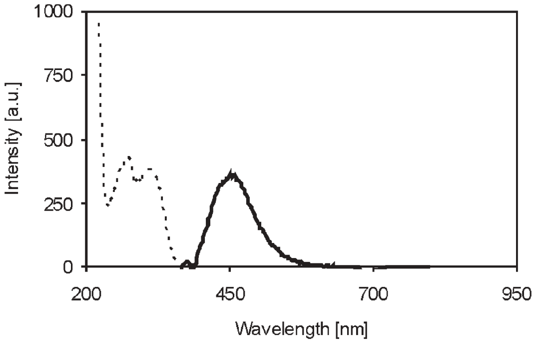

Fig. 3 Excitation/emission spectrum of $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ at 0.0048 M in dichloromethane (296 K). (···) Excitation spectrum corresponding to the emission at 445 nm; (—) emission upon excitation at 345 nm.

As was already described for the CD spectroscopy, the conformation of the ligand in the two nickel(II) complexes seems to be significantly different. This is also reflected in the fluorescence spectra, which leads in case of the high symmetry $[Ni_2(\mathbf{L})_3]^{2-}$ to inactivity in dichloromethane at room temperature while for the less symmetric $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ a broad ligand centred fluorescence band is detected.

Several achiral bis(β-diketonate) ligands have been described in the literature and were used to prepare complexes which are structurally similar to the complex $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$. Dinuclear nickel(II) complexes of the composition $[Ni_2(py)_4$(bis-β-diketonate)$_2]$ without a central metal atom have been reported.[9,13] Similar ligands also form dinuclear triple-stranded helicate-type coordination compounds with d-metals or lanthanoids.[8,14] Additionally, a dinuclear uranyl complex with a central nickel(II) ion possesses a coordination environment at the transition metal similar to the one found in our trinuclear complex.[10]

In this paper we presented the coordination chemistry of our chiral bis(β-diketonate) ligand **L** with nickel(II) which either leads to a "classical" dinuclear triple-stranded helicate $[Ni_2(\mathbf{L})_3]^{2-}$ or a trinuclear double-stranded complex $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$. The outcome of the reaction can be simply controlled by the stoichiometry of the ligand and the metal. Preliminary investigations of the CD spectra in solution show significant differences in the geometry of the coordinated ligands. As a remarkable difference in the behavior of the compounds, fluorescence of $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$ was observed in dichloromethane at room temperature, while the triple-stranded complex is non-emissive under similar conditions. This behavior is attributed to conformational differences of the ligand in the two different coordination compounds. In further studies we will focus on the coordination chemistry of our ligand with other metals in order to obtain homo- as well as heteronuclear complexes. Chirality transfer from the ligands to the metal will be a major aspect in those investigations.[15]

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Notes and references

‡ Elemental analysis for $[py\text{-}H]_2[Ni_2(\mathbf{L})_3]\cdot 3H_2O$. Calc.: C 47.87, H 3.66, N 1.41; found: C 47.58, H 3.68, N 1.32%. $[Ni_3(\mathbf{L})_2(CH_3CO_2)_2]\cdot 5py\cdot 3H_2O$. Calc.: C 48.85, H 3.99, N 3.80; found: C 49.45, H 4.08, N 3.77%.

§ *Crystal data* for $(C_{23}H_{18}O_6Br_2)_2Ni_3\cdot 2C_5H_5N\cdot 2C_2H_3O_2\cdot CH_2Cl_2$, M = 1637.73, monoclinic, space group $P2_1$ (no. 4), a = 14.030(2), b = 19.345(2), c = 14.077(2) Å, β = 118.43(1) Å, V = 3359.9(8) Å^3, D_c = 1.619 g cm^{-3}, μ = 3.355 mm^{-1}, Z = 2, λ = 0.71073 Å, T = 198 K, 32419 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.62 Å^{-1}, 12426 independent (R_{int} = 0.074) and 8619 observed reflections [$I \geqslant 2\sigma(I)$], 831 refined parameters, R = 0.064, wR_2 = 0.159. CCDC 277819. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509147k

¶ UV-vis spectra (CH_2Cl_2) λ_{max}/nm (ε/M^{-1} cm^{-1}): **L**-H$_2$: 265 (53 000), 328 (152 000); $[py\text{-}H]_2[Ni_2(\mathbf{L})_3]$: 265 (69 000), 350 (83 000); $[Ni_3(py)_2(CH_3CO_2)_2(\mathbf{L})_2]$: 265 (56 000), 345 (78 000).

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