Spontaneous chiral resolution of a coordination polymer with distorted helical structure consisting of achiral building blocks†

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Reaction of achiral 2,5-diphenyl-3,4-di(3-pyridyl)cyclopenta-2,4-dien-1-one (2) with $ZnCl_2$ and $HgBr_2$, respectively, afforded the helically chiral coordination polymers $[(2)ZnCl_2]_\infty$ and $[(2)HgBr_2]_\infty$, which show spontaneous chiral resolution, forming colonies of homochiral crystals.

The formation of helical structures through self-organisation is of fundamental importance for life. This fact has provided an important impetus for the creation of artificial helical structures in Supramolecular Chemistry.[1] In the field of coordination chemistry multidentate chelate ligands have been used with great success for this purpose.[2] In the resulting molecular helicates the organic ligands wind around one or more metal centres which lie on a screw axis. The case of metal centres being an integral part of a helix is less common and may occur when they are coordinated with bidentate bridging ligands, forming a polymer. Metal-containing polymers are of great current interest and their optical, magnetic, electrical and mechanical properties make them promising candidates for new materials.[3] It is only when spontaneous chiral resolution occurs[4] that the chiral information is not lost in the bulk material and can be utilised further.

The simplest case of generating chiral information in this context is the self-organisation of exclusively achiral building blocks to a helical metal-containing polymer. In the absence of chiral auxiliaries, a racemate is formed in such a process. Generally, spontaneous chiral resolution is a rare phenomenon[4] and has only been observed occasionally in the context of coordination polymers.[5] It requires an efficient transfer of stereochemical information between neighbouring homochiral helices. A possibility of paramount importance for biological systems is based on non-covalent, supramolecular interactions (hydrogen bonds, π–π-interactions etc.). To the best of our knowledge, this has been described only twice to date for coordination polymers with purely helical chirality.[6,7]

In the course of our work on redox-active bidentate systems which can act either as bridging or as chelating ligands,[8] we have investigated the cyclopentadienones 1[9] and 2,[10] whose coordination chemistry has remained totally unexplored hitherto.
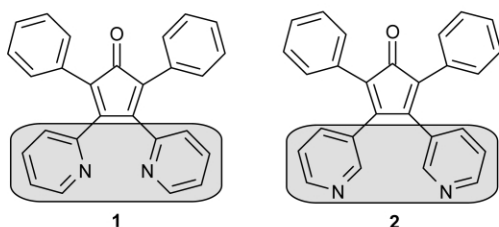
Both compounds are analogues of tetracyclone and differ only by the presence of two 2-pyridyl groups in 1 and two

3-pyridyl groups in 2. This has almost no effect on their electrochemical behaviour (1 $E°'_{0/-}$ = −1.37 V, 2 $E°'_{0/-}$ = −1.29 V). Their organometallic chemistries are rather similar to each other,[11] whereas their "Werner type" coordination chemistry turns out to be completely different. While 1 easily forms chelates, whose structures have been determined in the case of [(1)MCl₂] (M = Zn, Cd, Hg, Pt),[11] 2 acts as a bridging ligand, affording polymers, which are soluble only under depolymerisation in donor solvents such as pyridine. Two such compounds are $[(2)ZnCl_2]_\infty$ and $[(2)HgBr_2]_\infty$,‡ whose solid-state structures of have been determined by X-ray diffraction.§ Since the structures are very similar, only that of the zinc complex will be discussed.
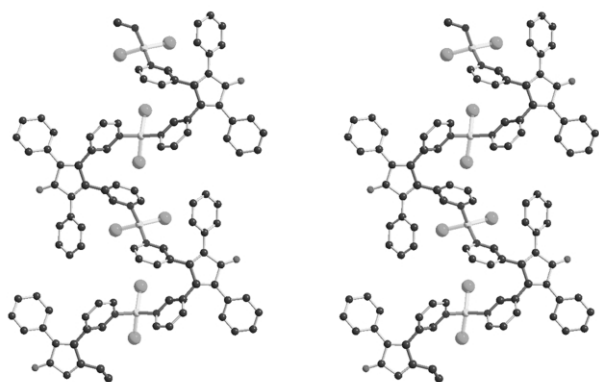
The compound crystallises in the chiral space group C2. The asymmetric unit (Fig. 1) contains two zinc atoms, which are bridged by ligand 2. The polymer chain forms a distorted helix (Fig. 2). The winding axis corresponds to the c-axis and the pitch to the length of c (13.017 Å). The direction of rotation is that of a left-handed screw (M-helix). The helix has C_2-symmetry. Both zinc atoms of the asymmetric unit lie on the crystallographic two-fold axes 0,y,0 und 0,y,0.5 of the space group C2. The winding axis of the helix therefore does not correspond to a crystallographic screw axis parallel to b of the space group C2, but is perpendicular to this, running parallel to c.

The single crystal consists of homochiral polymer chains only. Neighbouring chains are united by π–π-interactions[12] between phenyl groups and cyclopentadienone units (Fig. 3). The distances between the two rings range from 306 to 361 pm and their best planes form a dihedral angle of 11.5°.

Upon crystallisation bunches of needles are formed, which show pronounced (and partially opposite) Cotton effects in their
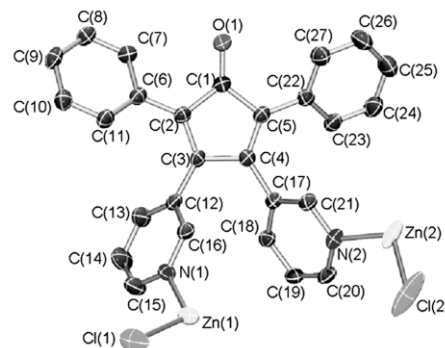
Fig. 1 Asymmetric unit of $[(2)ZnCl_2]_\infty$. Selected bond lengths [pm] and angles [°]: Zn(1)–N(1) 205.3(3), Zn(1)–Cl(1) 221.80(12), Zn(2)–N(2) 207.2(3), Zn(2)–Cl(2) 219.85(16), N(1)–C(15) 135.2(6), N(1)–C(16) 133.4(5), N(2)–C(20) 134.9(5), N(2)–C(21) 133.2(5), C(1)–O(1) 121.4(4), C(1)–C(2) 151.8(5), C(1)–C(5) 150.8(5), C(2)–C(3) 134.8(5), C(3)–C(4) 151.1(5), C(4)–C(5) 134.0(5); N(1)–Zn(1)–N(1a) 95.36(19), Cl(1)–Zn(1)–Cl(1a) 120.64(8), N(2)–Zn(2)–N(2a) 91.74(19), Cl(2)–Zn(2)–Cl(2a) 117.74(12).

† Dedicated to Professor Peter Jutzi on the occasion of his 65th birthday.

Fig. 2 Stereo view of a section of the helical polymer chain of (*M*)-$[(2)ZnCl_2]_\infty$. The polymer backbone (shortest atom chain) is shown in bold.
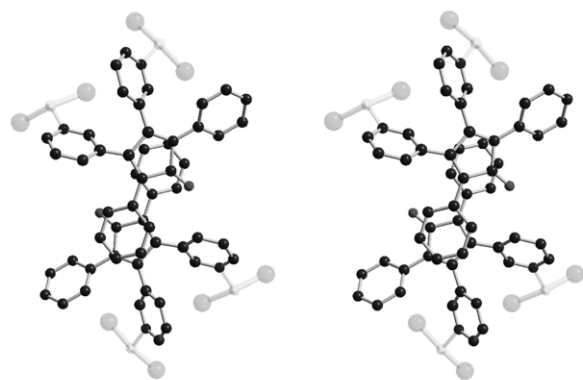
Fig. 3 Interaction of the polymer chains of $[(2)ZnCl_2]_\infty$. View along *b*.

CD spectra.¶ This behaviour reveals that locally one enantiomer is formed in excess, probably even exclusively, and furthermore suggests that radial growth of single colonies of homochiral crystals starting from single nucleation points occurs.[6a,7b] The CD spectrum of all crystals of a single batch proves that overall the expected racemic conglomerate is formed.

In the present case a single molecular parameter decides whether chelate complexes or coordination polymers are formed. Supramolecular interactions in the strict sense of the word, especially π–π-interactions, are responsible for the fact that the coordination polymers $[(2)ZnCl_2]_\infty$ and $[(2)HgBr_2]_\infty$, which consist of exclusively achiral building blocks, show helical chirality with spontaneous chiral resolution. The redox chemistry of the coordination polymers based on **2** will be of special future interest. We have already been able to show for $[(1)ZnCl_2]$ and similar diamagnetic chelates that a ligand-centred reduction leads to even more stable paramagnetic complexes.[11]

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Notes and references

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