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Spontaneous Resolution of a Triple-Stranded Dinickel(II) Helicate Generated via Intermolecular Transamination Reaction of *S*-Methylisothiocarbohydrazide in the Presence of Ni^{2+}

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Dedicated to Professor M. T. Reetz on the occasion of his 65th birthday

Keywords: Triple-stranded helicates / Nickel(II) / Spontaneous resolution / Chiroptical properties / Magnetic properties

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The reaction of *S*-methylisothiocarbohydrazide hydroiodide $[H_2NNHC(SCH_3)NNH_2{\cdot}HI]$ with $NiCl_2{\cdot}6H_2O$ in water at room temperature yielded a triple-stranded dinickel(II) helicate $[Ni^{II}(L^1–L^1)_3Ni^{II}]I_4{\cdot}4H_2O$ ($\mathbf{1}^{4+}{\cdot}4I^-{\cdot}4H_2O$), where $L^1–L^1$ = $H_2NNHC(SCH_3)NNC(SCH_3)NHNH_2$, in 35 % yield, which spontaneously separates in enantiomers upon crystallization. The enantiomers do not racemize at room temperature, even not after 15 h of heating at 90 °C. X-ray diffraction structures of both enantiomers, chiroptical and magnetic properties of $\mathbf{1}^{4+}{\cdot}4I^-{\cdot}4H_2O$ are reported. Demetallation of the complex by treatment with S^{2-} resulted in 3,6-bis(methylthio)-1,4-dihydro-1,2,4,5-tetrazine (**2**). Compound **2** undergoes 2-e^- oxidation in air to give the known 3,6-bis(methylthio)-1,2,4,5-tetrazine (**3**).

Introduction

Transition metal polynuclear double- and triple-stranded helicates have been the object of interest and intensive studies for more than 20 years.[1–3] Numerous examples of metal helicates are now documented in the literature.[4–7] Their building up in most cases is based on self-organization of presynthesized one-stranded ligands in the presence of metal ions with definite stereochemical preferences. The helicates are usually formed as a racemic mixture of the two enantiomers, which sometimes can be separated by chiral chromatographic methods.[8] Separation of enantiomers can be also achieved by exploring specific interactions between the helicate and a chiral counterion.[9] In addition, stereoselective synthesis of metal helicates can be realized through enantiopure chiral ligands[5,10] or auxiliary organic chiral templates that predetermine the stereochemistry of the reaction and can be removed after its termination without system racemization.[11] In very rare cases the pure enantiomers can be obtained by spontaneous separation during crystallization.[12] It should be noted that for the self-assembly labile metal ions are normally employed. As a consequence the enantiomerically pure compounds easily undergo racemization precluding investigation of their chiroptical properties. Only a few examples of resolved transition metal helicates have been reported in the literature. In these particular cases stabilization to racemization was achieved either by oxidation of the readily assembled cobalt(II) complex $[Co_2L_3]^{4+}$ to the inert cobalt(III) species $[Co_2L_3]^{6+}$,[13] or by increasing the nuclearity of the triply stranded metal helicate.[14]

Herein we report the synthesis, X-ray diffraction structure, chiroptical and magnetic properties of an unprecedented triple-stranded dinickel(II) helicate $[Ni^{II}(L^1–L^1)_3Ni^{II}]^{4+}$ (Scheme 1), which spontaneously separates in enantiomers upon crystallization.

Results and Discussion

We discovered that the reaction of *S*-methylisothiocarbohydrazide hydroiodide $[H_2NNHC(SCH_3)NNH_2{\cdot}HI]$ with $NiCl_2{\cdot}6H_2O$ in water at room temperature yielded lilac crystals of $[Ni^{II}(L^1–L^1)_3Ni^{II}]I_4{\cdot}4H_2O$ in 35% yield (Scheme 1). Recrystallization from water enabled the growth of large crystals of good quality (see Figure S1, Supporting Information) with spontaneous resolution of the enantiomers. Alternatively the separation of enantiomers of $[Ni^{II}(L^1–L^1)_3$-

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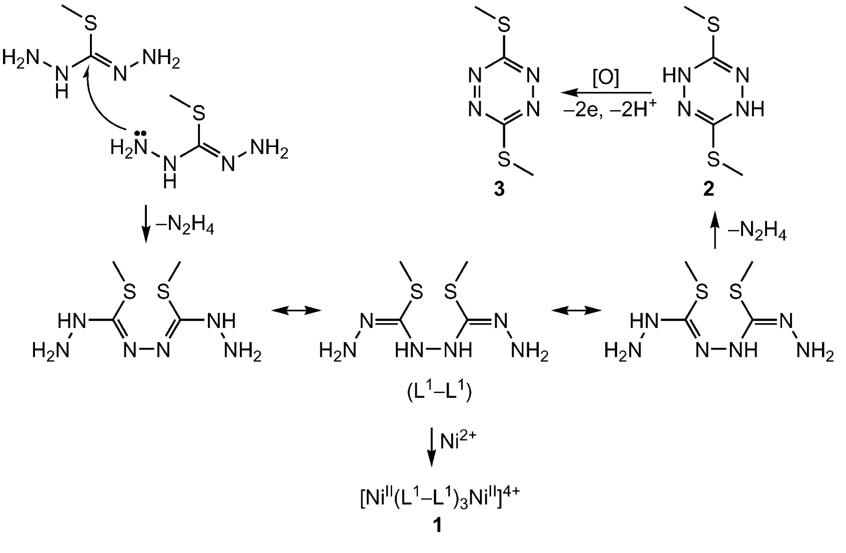

Scheme 1.

$Ni^{II}]I_4$ was realized via *entrainment*.[15] An enantiopure crystal was used as a seed for the growth of new crystals of the same chirality from a racemic solution of $\mathbf{1}^{4+}\cdot 4I^-$. In particular, by using a seed crystal of (*M*)-$\mathbf{1}^{4+}\cdot 4I^-$, 0.9 g of crystals consisting of ca. 90% of (*M*)-$\mathbf{1}^{4+}\cdot 4I^-$ and 10% of (*P*)-$\mathbf{1}^{4+}\cdot 4I^-$ was isolated after 48 h at room temperature from 100 mL of a supersaturate solution containing 3.2 g of racemate. A second entrainment procedure afforded 0.3 g of pure enantiomer (*M*)-$\mathbf{1}^{4+}\cdot 4I^-$ with $[\alpha]_D = -1350$.

Spontaneous resolution is the separation of enantiomers in *conglomerates*,[15] the cheapest and most efficient procedure for separation of enantiomers. The conglomerates were identified via determination of the crystal structure of both enantiomers in combination with CD spectroscopy and polarimetry of their solutions, as these did not racemize under experimental conditions employed (vide infra). It should, however, be noted that conglomerate formation is a rare phenomenon, especially because more than 90% of compounds crystallize in centrosymmetric space groups.

Microanalytical data and thermal analysis support the formulation $[Ni^{II}(L^1–L^1)_3Ni^{II}]I_4\cdot 4H_2O$ ($\mathbf{1}^{4+}\cdot 4I^-\cdot 4H_2O$) for the racemic mixture. The positive mode ESI mass spectrum shows a large number of peaks (see Exp. Sect.) with isotopic distributions, which are in good agreement with those predicted for ions resulting from fragmentation of $[Ni^{II}(L^1–L^1)_3$-$Ni^{II}]I_4$. Unlike numerous examples reported in the literature, the one-stranded ligand with linear "tail-to-tail" arrangement of two identical binding sites linked via an azine bridge is generated in situ via intermolecular "transamination reaction" of *S*-methylisothiocarbohydrazide as shown in Scheme 1. The binding sites are twisted to releave S···S steric interaction clashes. Full rotation around the central azine bond is prevented by this interaction. The noted conformational restrictions are of particular importance for inducing helicity. It should, however, be noted that a similar principle based on exploiting H···H repulsions has been systematically used since two decades for assembly of both binuclear d-block[16] and f-block[17] triple-stranded helicates with diphenylmethane spacers.

Demetallation of complex $\mathbf{1}^{4+}\cdot 4I^-$·by treatment with S^{2-} resulted in 3,6-bis(methylthio)-1,4-dihydro-1,2,4,5-tetrazine **2**[18,19] (Scheme 1 and Figure S1a in the Supporting Information) as confirmed by X-ray diffraction.[20] This species is presumably formed from $L^1–L^1$ by intramolecular transamination with expulsion of N_2H_4 molecule. Compound **2** undergoes 2-e⁻ oxidation in air to give the known 3,6-bis(methylthio)-1,2,4,5-tetrazine (**3**)[18] according to X-ray crystallography (see Scheme 1 and Figure S1b).[20] Non-innocent behavior has also been reported for a number of metal complexes with ligands based on *S*-alkylisothiosemicarbazide.[21,22] The transformations leading to species **2** and **3** seem to be suppressed in the presence of nickel(II) by shifting the equilibrium towards $L^1–L^1$ which is stabilized as dimetal triple-stranded helicate. Both enantiomers with iodide as counteranion were easily converted into tetraphenylborate salt with retention of chirality. Attempts to prepare mononuclear octahedral nickel(II) complexes with *S*-methylisothiosemicarbazide $[H_2NNHC(SCH_3)NH]$, which can be regarded as a half of the molecule $L^1–L^1$ and, therefore, labeled L^1, namely $[Ni(L^1)_3]^{2+}$, yielded a square-planar complex $[Ni(L^1)_2]^{2+}$ (**4**), in which two *S*-methylisothiosemicarbazide ligands according to X-ray analysis[20] are orientated in antiparallel fashion with two SCH_3 groups trans to each other (Figure 1). In addition, ESI mass spectra of the reaction mixture did not show peaks, which may be attributed to $[Ni(L^1)_3]^{2+}$.

A racemate crystallizes in one of three ways as (i) a racemic compound, in which both enantiomers are present in the same crystal; (ii) as a conglomerate, an assemblage of crystals, consisting of molecules of the same chirality; (iii) as a pseudoracemate, in which the crystals contain the two enantiomers in a non-ordered arrangement.[15]

X-ray diffraction studies of $[Ni^{II}(L^1–L^1)_3Ni^{II}]I_4$[23] showed that the (*P*)-enantiomer has the composition

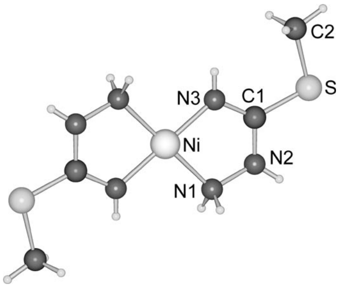

Figure 1. SCHAKAL plot of the structure of the cation in $[Ni^{II}(L^1)]I_2$ (**4**). Selected bond lengths [Å] and angles [°]: Ni–N1 1.9119(16), Ni–N3 1.8624(17), N1–N2 1.427(2), N2–C1 1.350(3), C1–N3 1.300(2), C1–S 1.7441(19), S–C2 1.801(2) Å, N1–Ni–N3 84.24(7), $\Theta_{N1-N2-C1-N3}$ 9.0(2)°.

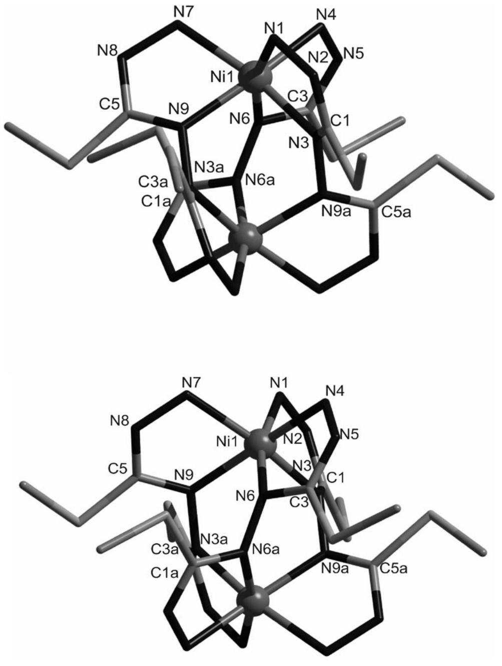

Figure 2. Structures of *P*-enantiomer (top) and of the *M*-enantiomer (bottom); hydrogen atoms were omitted for clarity.

$\mathbf{1}^{4+}\cdot4I^-\cdot2.4H_2O$ and crystallizes in the tetragonal space group $P4_12_12$, while the (*M*)-enantiomer with the formulation $\mathbf{1}^{4+}\cdot4I^-\cdot3.8H_2O$ in $P4_32_12$ space group. The structures of the cations (*P*)-$\mathbf{1}^{4+}$ and (*M*)-$\mathbf{1}^{4+}$ are shown in Figure 2. The cations lie in a special position on a C_2 axis running through the middle of the N6–N6a bond. The helical axis passes through two symmetry-related nickel(II) ions, which are homochiral. The Ni···Ni separation is of 3.675 Å in (*M*)-$\mathbf{1}^{4+}$, the structure of which was determined more accurately. Both structures consist of three strands wrapped around two metals in a spiral fashion. Two chelate rings formed by each of the three one-stranded ligands are twisted around the rotationally flexible central azine bond. The twist angles can be estimated by torsional angles $\Theta_{C1-N3-N9a-C5a}$, $\Theta_{C3-N6-N6a-C3a}$ and $\Theta_{C5-N9-N3a-C1a}$ at –104.16, –113.24 and –104.16 or $\Theta_{Ni1-N3-N9a-Ni1a}$, $\Theta_{Ni1-N6-N6a-Ni1a}$ and $\Theta_{Ni1-N9-N3a-Ni1a}$ of –35.97, –36.74, –35.97° in (*M*)-$\mathbf{1}^{4+}$. As already noted the driving force of the twisting are the intramolecular S···S repulsions. In addition, the whole structure seems to be stabilized in this sulfur reach environment (Figure 2). The six sulfur atoms form almost a regular hexagon (Figure S3) with S···S contacts at 3.825–4.145 Å for (*M*)-$\mathbf{1}^{4+}$, which are longer than the sum of van der Waals radii (3.600 Å). Each nickel(II) ion has a distorted octahedral geometry with Ni–N1, Ni–N3, Ni–N4, Ni–N6, Ni–N7 and Ni–N9 of 2.129(7), 2.059(7), 2.119(8), 2.051(7), 2.118(8) and 2.050(7) Å, respectively for [(*M*)-$\mathbf{1}^{4+}$].

It should be noted that while the optimal coordination polyhedron for Ni^{II} in mononuclear complex $[Ni(L^1)_2]^{2+}$ is a square, the octahedral coordination geometry for Ni^{II} is favored in the case of dinucleating L^1–L^1 ligand with tail-to-tail arrangement of two L^1 moieties. Thus a better match between electron-donor and conformational characteristics of the three L^1–L^1 ligands and preference of nickel(II) for octahedral coordination environment[21] is achieved in $[Ni^{II}(L^1–L^1)_3Ni^{II}]I_4$.

Solutions of (*P*)-$\mathbf{1^{4+}}\cdot4I^-$ and (*M*)-$\mathbf{1^{4+}}\cdot4I^-$ are indeed optically active and show Cotton effects for both enantiomers (see Figures 3 and S4). As expected, they are roughly mirror images over the 200–800 nm region of the spectrum. In addition, they show very large $[\alpha]_D$ values of +1355 for (*P*)-$\mathbf{1}^{4+}\cdot4I^-$ and –1340 for (*M*)-$\mathbf{1}^{4+}\cdot4I^-$, which remained unchanged over 7 d at room temperature. Each of the enantiomers was repeatedly recrystallized from boiling water without any sign of racemization.

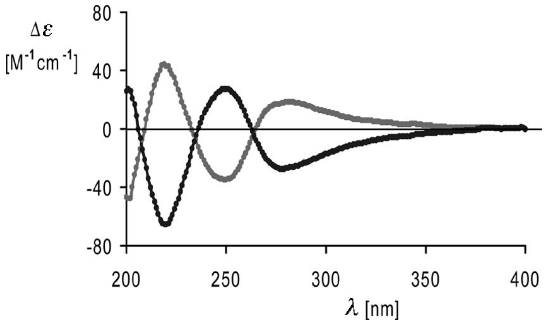

Figure 3. Circular dichroism spectra of the enantiomers of the $[Ni^{II}(L^1–L^1)_3Ni^{II}]I_4$ in water: (*P*)–$\mathbf{1}^{4+}\cdot4I^-$ (black line) and (*M*)–$\mathbf{1}^{4+}\cdot4I^-$ (gray line) in the region 200–400 nm. The spectra between 400 and 800 nm are shown in Figure S4.

Racemization requires breaking of at least 10 Ni–N bonds simultaneously, followed by rotation of half the molecule L^1–L^1 in only one allowed direction depending on enantiomer identity, clockwise or anticlockwise. The opposite rotation is prevented by already mentioned S···S steric clashes. The first step event appears to be highly improbable, being in line with high kinetic inertness of enantiomers to racemization, as anticipated for high-spin octahedral nickel(II) complex with maximal ligand field stabilization energy in a row of bivalent d-block transition metal ions.[24] Decomplexation of one ligand with simultaneous break of

4 Ni–N bonds (seems to be difficult, but evidenced by ESI mass spectrometric data) makes an opposite rotation around central azine bond in L^1–L^1 possible. However, rebinding of L^1–L^1 to the $[Ni^{II}(L^1–L^1)Ni^{II}]^{4+}$ moiety needs its conformational accommodation to stereochemical demands of the dinickel(II) moiety, preserving in such a way the original chirality.

To get evidence for the ligand exchange in $[Ni^{II}(L^1–L^1)Ni^{II}]^{4+}$, we have carried out scrambling experiments.[14b,25] Equimolar amounts of $[Ni^{II}(L^1–L^1)_3Ni^{II}]I_4·4H_2O$ and its deuterated analogue, in which SCH_3 groups were replaced by SCD_3 groups $\{[Ni^{II}(L^1SCD_3–L^1SCD_3)_3Ni^{II}]I_4·4H_2O\}$ were dissolved in water, and ESI mass spectra measured immediately after dissolution, thereafter at regular time intervals. Figure S5 shows fragments of the spectra of $[Ni^{II}(L^1–L^1)_3Ni^{II}]I_4$, $[Ni^{II}(L^1SCD_3–L^1SCD_3)_3Ni^{II}]I_4$ and of their equimolar mixture immediately and 15 h after dissolution and heating at 90 °C. The complexes $[Ni^{II}(L^1–L^1)_3Ni^{II}]I_4$ and $[Ni^{II}(L^1SCD_3–L^1SCD_3)_3Ni^{II}]I_4$ give characteristic peaks with *m*/*z* 865 and 883, which were attributed to $[Ni^{II}(L^1–L^1)_3Ni^{II}I–2H]^+$ and $[Ni^{II}(L^1SCD_3–L^1SCD_3)_3Ni^{II}I–2H]^+$, respectively. These two peaks were also found in the mass spectrum of the aqueous solution containing both species with almost equal relative intensities. No peaks between *m*/*z* 865 and 883, which could be attributed to species $[Ni^{II}(L^1–L^1)_x(L^1SCD_3–L^1SCD_3)_{3-x}Ni^{II}I–2H]^+$ ($x = 1, 2$) resulted from ligand exchange (ligand dissociation and binding to nickel-containing ions) were observed in the mass spectra, in line with extraordinary stability of the separated enantiomers to racemization.

The electronic spectrum of *rac*-$\mathbf{1}^{4+}·4I^-$ in water in the visible and NIR region (Figure 4) contains three absorption bands with λ_{max} at 890, 820 and 538 nm (for ε, $M^{-1}\,cm^{-1}$, see Exp. Sect.) which can be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^1E_g(D)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions, correspondingly.[26] Multiplicity- or spin-allowed transitions are known to give broad absorption bands, while multiplicity forbidden transitions are usually sharp. Cyclic voltammogram of *rac*-$\mathbf{1}^{4+}·4BPh_4^-$ in acetonitrile displayed one irreversible electron-transfer wave at 0.90 V relative to Fc^+/Fc couple, which is unambiguously attributed to oxidation of BPh_4^- anion.

The magnetic properties of a polycrystalline (racemic) sample of *rac*-$\mathbf{1}^{4+}·4I^-·4H_2O$ in the temperature range 2–300 K in a field of 1 T is shown in Figure 5. At room temperature the observed value for χ_mT is 2.27 $cm^3\,K\,mol^{-1}$, which is only slightly higher than the theoretical value of 2.0 $cm^3\,K\,mol^{-1}$ for a dinuclear unit of two non-interacting $S = 1$ Ni^{II} ions with $g = 2$. With lowering temperature the value remains almost constant at 2.27–2.28 $cm^3\,K\,mol^{-1}$. Further temperature decrease is accompanied by sharp increase of χ_mT to 2.44 $cm^3\,K\,mol^{-1}$ at 5 K. This implies that the main spin exchange interaction in *rac*-$\mathbf{1}^{4+}·4I^-·4H_2O$ is ferromagnetic in nature. The coupling constant was extracted by modeling the data as a dinuclear system of interacting $S = 1$ ions by applying the spin Hamiltonian $H = -2JS_1·S_2$. Best fit to the experimental data down to low temperature was obtained by using g values of 2.13 for the Ni^{II} ions and a coupling constant of $J = 0.35\ cm^{-1}$, taking into account the TIP of $280 \times 10^{-6}\ cm^{-1}$. The simulation of χ_mT vs. T with these data is shown in Figure 5 as a solid line.

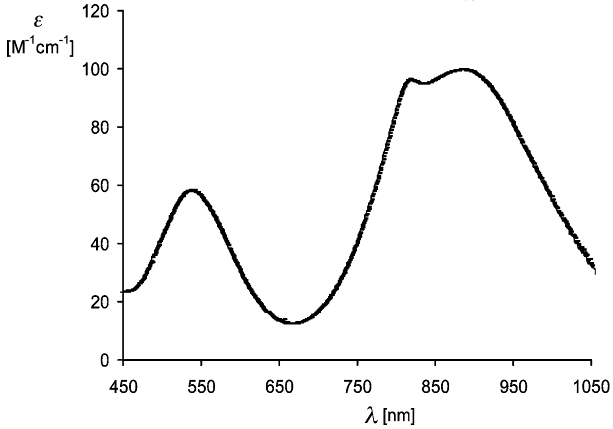

Figure 4. Electronic absorption spectrum of *rac*-$\mathbf{1}^{4+}·4I^-$ in water.

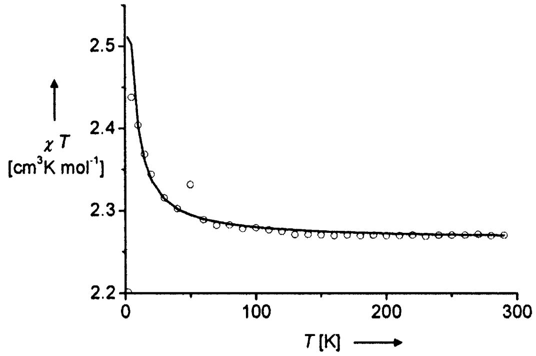

Figure 5. Magnetic susceptibility data for *rac*-$\mathbf{1}^{4+}·4I^-·4H_2O$.

In conclusion, we reported the synthesis of an unprecedented dimetal triple-stranded helicate assembled from nickel(II) and the ligand generated via transamination of *S*-alkylated thiocarbohydrazide. In addition, this is the first example of dinickel(II) helicate which crystallized under spontaneous racemate autoresolution with separation of enantiomers of extraordinary stability to racemization. This inertness to racemization is due to maximal ligand field stabilization energy for high-spin octahedral nickel(II) in a row of bivalent d-block transition metal ions, the spatial arrangement of ligand(s) binding sites matching the optimal coordination polyhedron for the given cation and additional stabilization of the complex in a sulfur-rich environment.

Experimental Section

General: All reagents were used as received from Aldrich. *S*-Methylisothiocarbohydrazide hydroiodide was prepared according to a literature procedure.[27]

$[Ni^{II}(L^1–L^1)_3Ni^{II}]I_4·4H_2O$ ($\mathbf{1}^{4+}·4I^-·4H_2O$): A solution of $NiCl_2·6H_2O$ (0.48 g, 2.0 mmol) and S-methylisothiocarbohydrazide hydroiodide (1.5 g, 6.0 mmol) in water (4 mL) was allowed to stand at room temperature. After 7 d the product precipitated as lilac crystals. It was filtered off, recrystallized from water, and dried in air; yield 0.32 g (24%). $C_{12}H_{44}I_4N_{18}Ni_2O_4S_6$ (1322.00): calcd. C 10.90, H 3.35, N 19.07, S 14.45; found C 10.91, H 2.90, N 18.78, S 13.96. Weight loss at 110 °C is 5.5%. ESI-MS (positive): *m*/*z* = 1121 $[Ni_2(L^1{-}L^1)_3I_3]^+$, 993 $[Ni_2(L^1{-}L^1)_3I_2 - H]^+$, 865 $[Ni_2(L^1{-}L^1)_3I - 2H]^+$, 785 $[Ni_2(L^1{-}L^1)_2I_2 - H]^+$, 739 $[Ni_2(L^1{-}L^1)_3 - 3H]^+$, 657 $[Ni_2(L^1{-}L^1)_2I - 2H]^+$, 601 $[Ni_2(L^1{-}L^1)_2I]^+$, 529 $[Ni_2(L^1{-}L^1)_2 - 3H]^+$, 473 $[Ni(L^1{-}L^1)_2 - H]^+$, 393 $[Ni(L^1{-}L^1)I]^+$, 265 $[Ni(L^1{-}L^1) - H]^+$, 209 $[(L^1{-}L^1)H]^+$. UV-Vis of P–$\mathbf{1}^{4+}\cdot 4I^-$ in water: λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$): 225 (78000), 250 sh (25000), 538 (58), 820 (96), 890 (99). CD [λ, nm ($\Delta\varepsilon/M^{-1}\,cm^{-1}$)], for $\mathbf{1}^{4+}\cdot 4I^-$: band 1 ($c = 6\times10^{-6}$ M): 219 (44), 251 (–35), 282 (18); ($c = 1.2\times10^{-2}$): 550 (0.90); for $\mathbf{1}^{4+}\cdot 4I^-$: band 2 ($c = 6\times10^{-6}$ M): 219 (–65), 251 (27), 278 (–27); ($c = 1.2\times10^{-2}$): 550 (–0.88). $[a]_D$ for (P)–$\mathbf{1}^{4+}\cdot 4I^-$: +1355; for ($M$)–$\mathbf{1}^{4+}\cdot 4I^-$: –1340. IR ($P$)–$\mathbf{1}^{4+}\cdot 4I^-\cdot 2.4H_2O$: $\tilde{\nu}$ = 3421, 3203, 3111, 1601, 1526, 1485, 1422, 1261, 1168, 1108, 1022, 899 cm^{-1}. IR (M)–$\mathbf{1}^{4+}\cdot 4I^-\cdot 3.8H_2O$: $\tilde{\nu}$ = 3436, 3212, 3116, 1601, 1531, 1487, 1426, 1263, 1172, 1110, 1025, 901 cm^{-1}.

$[Ni^{II}(L^1{-}L^1)_3Ni^{II}][BPh_4]_4$ ($\mathbf{1}^{4+}\cdot 4[BPh_4]_4^-$): To a solution of $[Ni^{II}(L^1{-}L^1)_3Ni^{II}]I_4\cdot 4H_2O$ (0.6 g, 0.45 mmol) in water/ethanol, 2:1 (90 mL) was added a solution of $NaBPh_4$ (0.64 g, 1.87 mmol) in water (20 mL). The precipitate formed was filtered off, washed with water and dried in air; yield 0.80 g (87%). $C_{108}H_{116}B_4N_{18}Ni_2S_6$ (2019.22): calcd. Ni 5.81, N 12.49, S 9.53; found Ni 5.86, 5.90, N 12.51, S 9.43. ESI-MS (positive): *m*/*z* = 1697 $[Ni_2(L^1{-}L^1)_3(BPh_4)_3]^+$, 1377 $[Ni_2(L^1{-}L^1)_3(BPh_4)_2 - H]^+$, 1057 $[Ni_2(L^1{-}L^1)_3(BPh_4) - 2H]^+$, 849 $[Ni_2(L^1{-}L^1)_2(BPh_4) - 2H]^+$, 793 $[Ni_2(L^1{-}L^1)_2(BPh_4)]^+$, 739 $[Ni_2(L^1{-}L^1)_3 - 3H]^+$, 529 $[Ni_2(L^1{-}L^1)_2 - 3H]^+$, 473 $[Ni_2(L^1{-}L^1) - H]^+$, 265 $[Ni(L^1{-}L^1) - H]^+$, 209 $[(L^1{-}L^1)H]^+$.

3,6-Bis(methylthio)-1,4-dihydro-1,2,4,5-tetrazine (2): To a solution of $[Ni^{II}(L^1{-}L^1)_3Ni^{II}]I_4\cdot 4H_2O$ (0.1 g, 0.07 mmol) in 0.2 M hydrochloric acid (1 mL) at 60 °C was added a solution of $Na_2S\cdot 9H_2O$ (0.12 g, 0.5 mmol) in water (2 mL). The black precipitate formed (NiS) was filtered off and washed with water. The filtrate produced colorless crystals suitable for X-ray diffraction[20] upon evaporation.

3,6-Bis(methylthio)-1,2,4,5-tetrazine (3): An aqueous solution of $[Ni^{II}(L^1{-}L^1)_3Ni^{II}]I_4\cdot 4H_2O$ was allowed to stand at room temperature for one month and then evaporated under reduced pressure. The collected solvent contained a small amount of volatile compound, which made it slightly red colored. This was extracted by chloroform and allowed to crystallize by slow evaporation at room temperature. The red crystals formed were suitable for X-ray diffraction study.[20]

$[Ni(L^1)_2]I_2$ (4): To a solution of $Ni(CH_3COO)_2\cdot 4H_2O$ (1.3 g, 5.0 mmol) in ethanol (10 mL) was added a solution of *S*-methylisothiosemicarbazide hydroiodide (3.45 g, 15.0 mmol) in ethanol (20 mL). The blue solution generated red crystals of X-ray diffraction quality.[20] Compound with the same composition was already reported in the literature.[28]

IR spectra were recorded on a Bruker FTIR VERTEX70 instrument in the region 4000–400 nm. Circular dichroism spectra were recorded in thermostatted (±0.5 °C) quartz cuvettes (1 cm path length) on a CD6 circular dichrograph (I.S.A. Jobin-Yvon). Optical rotation was measured on Perkin–Elmer Polarimeter Model 341. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 20 UV/Vis spectrophotometer. Electrospray ionization mass spectrometry was carried out with a Bruker Esquire 3000 instrument Bruker Daltonic, Bremen, Germany. Predicted and experimental isotope distributions were compared. Cyclic voltammograms were measured in a two-compartment three-electrode cell using a 0.5-mm-diameter carbon disk working electrode, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode, and a platinum auxiliary electrode. Measurements were performed by cyclic voltammetry (CV) at room temperature using an EG & G PARC 273A potentiostat/galvanostat. Deaeration of solutions was accomplished by passing a stream of high-purity nitrogen through the solution for 10 min prior to the measurements and then maintaining a blanket atmosphere of nitrogen over the solution during the measurements. The potentials were measured in 0.15 M $[nBu_4N][BF_4]/CH_3CN$ using the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ ($E_{1/2}$ = +0.66 V vs. NHE) as internal standard. Magnetic susceptibility measurements were carried out with a Quantum Design MPMS SQUID magnetometer between 2 and 290 K in an applied field of 1 T. Diamagnetic correction of $-500\times10^{-6}\,cm^3\,mol^{-1}$ for *rac*-$\mathbf{1}^{4+}$ $4I^-\cdot 4H_2O$, was estimated from Pascal's constants.[29]

Supporting Information (see also the footnote on the first page of this article): ORTEP views of molecular structures of **2** (a) and **3** (b) (Figure S1), details of data collection and refinement for **2**–**4**, crystals of enantiomers grown from water (Figure S2), projection of the structure of the (M)-$[Ni^{II}(L^1{-}L^1)_3Ni^{II}]^{4+}$ cation along the Ni···Ni vector, showing the arrangement of the sulfur atoms (Figure S3), circular dichroism spectra of the enantiomers of the $[Ni^{II}(L^1{-}L^1)_3Ni^{II}]I_4$ in water (Figure S4), ESI mass spectra of $[Ni^{II}(L^1{-}L^1)_3Ni^{II}]I_4$ and its SCD_3 analogue (Figure S5).

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[20] Crystal data for **2**: $C_4H_8N_4S_2$, M_r = 176.26, monoclinic, space group $C2/c$, a = 11.3538(8), b = 7.0853(8), c = 10.5678(10) Å, β = 118.514(8)°, V = 747.01(12) Å^3, Z = 4, $\rho_{calcd.}$ = 1.567 g cm^{-3}, Mo-K_α radiation (λ = 0.71073 Å, μ = 0.639 mm^{-1}), T = 100 K, R = 0.0245 ($F^2 > 2\sigma$), R_w = 0.0654 (for 7018 data and 50 refined parameters). Crystal data for **3**: $C_4H_6N_4S_2$, M_r = 174.25, monoclinic, space group $P2_1/c$, a = 8.5962(12), b = 10.2017(12), c = 8.6899(12) Å, β = 100.435(10)°, V = 749.46(17) Å^3, Z = 4, $\rho_{calcd.}$ = 1.544 g cm^{-3}, Mo-K_α radiation (λ = 0.71073 Å, μ = 0.636 mm^{-1}), T = 100 K, R = 0.0412 ($F^2 > 2\sigma$), R_w = 0.1169 (for 17559 data and 91 refined parameters). Crystal data for **4**: $C_4H_{14}I_2N_6S_2$, M_r = 522.84, monoclinic, space group $P2_1/n$, a = 4.3552(1), b = 18.7024(6), c = 8.6247(3) Å, β = 100.828(2)°, V = 690.00(4) Å^3, Z = 2, $\rho_{calcd.}$ = 2.517 g cm^{-3}, Mo-K_α radiation (λ = 0.71073 Å, μ = 6.164 mm^{-1}), T = 100 K, R = 0.0157 ($F^2 > 2\sigma$), R_w = 0.0313 (for 20968 data and 86 refined parameters). Details of data collection and structure refinement are given as Supporting Information

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[23] Crystal data for (P)–$[Ni_2(L^1–L^1)_3]I_4 \cdot 2.4H_2O$: $C_{12}H_{40.8}I_4N_{18}Ni_2O_{2.40}S_6$, M_r = 1293.21, tetragonal, space group $P4_12_12$, a = b = 14.825(1), c = 20.201(1) Å, V = 4439.8(5) Å^3, Z = 4, $\rho_{calcd.}$ = 1.935 g cm^{-3}, Mo-K_α radiation (λ = 0.71073 Å, μ = 3.950 mm^{-1}), T = 243 K, R = 0.0997 ($F^2 > 2\sigma$), R_w = 0.2391 [for 88427 data, 3953 unique reflections (R_{int} = 0.1154) and 215 refined parameters], Flack parameter 0.07(10). Crystal data for (M)–$[Ni_2(L^1–L^1)_3]I_4 \cdot 3.8H_2O$: $C_{12}H_{43.6}I_4N_{18}Ni_2O_{3.80}S_6$, M_r = 1318.43, tetragonal, space group $P4_32_12$, a = b = 14.8489(3), c = 20.4632(3) Å, V = 4511.93(14) Å^3, Z = 4, $\rho_{calcd.}$ = 1.941 g cm^{-3}, Mo-K_α radiation (λ = 0.71073 Å, μ = 3.891 mm^{-1}), T = 100 K, R = 0.0512 ($F^2 > 2\sigma$), R_w = 0.1442 [for 171651 data, 4607 unique reflections (R_{int} = 0.0931) and 230 refined parameters], Flack parameter –0.01(4). A single crystal of suitable size was attached to a glass fiber using acrylic resin and mounted on a goniometer head 40 mm off the detector. Data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated X-radiation (λ = 0.71073 Å) at 100 and 243 K. 2667 and 664 frames were measured, each for 20 and 50 s over 1° scan width. The data were processed using SAINT software. The structure was solved by direct methods and refined by full-matrix least-squares techniques using the SHELX program. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were placed in calculated positions and refined as riding atoms with isotropic displacement parameters, set to be a multiple of that of the parent atoms. CCDC-680517 (for **4**), -680518 [for (M)–$\mathbf{1}^{4+} \cdot 4I^- \cdot 3.8H_2O$], -680519 [for ($P$)–$\mathbf{1}^{4+} \cdot 4I^- \cdot 2.4H_2O$], -680520 (for **3**), -680521 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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