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Single-, double- and triple-stranded helical metal complexes of chiral tetradentate pyridyl-thiazole ligands: Stereoselective synthesis, spectroscopic properties and structural characterization

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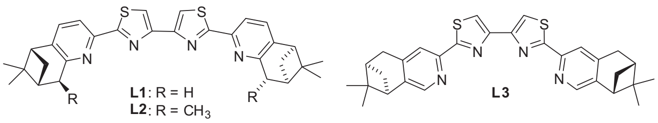
ABSTRACT

With a series of chiral pyridine-based tetradentate pyridyl-thiazole ligands **L**, three types of binuclear helical metal complexes were synthesized. They were the Re(I) single-stranded complexes of formula $[Re_2(\mathbf{L})(CO)_6Br_2]$, the Ag(I) double-stranded complexes of formula $[Ag_2(\mathbf{L})_2](ClO_4)_2$ and the Cu(II) triple-stranded complex of formula $[Cu_2(\mathbf{L})_3](ClO_4)_4$. Each type of them has been characterized using CD spectroscopy and if possible ^1H NMR spectroscopy. Three single crystal structures, one from each type, have been determined.

1. Introduction

With two distinct binding motifs, bis-bidentate ditopic ligands are of great interest to chemists because they can afford multimetallic coordination complexes. Various bis-bidentate ligands have been reported and different binding motifs, such as 2,2′-bipyridine, [1] pyridyl-pyrazole, [2,3] bis-catechol, [4] pyridyl-thiazole, [5–7] have been used. Depending on the geometrical relationship between the bis-bidentate ligands and the metal ions, coordination polymers, [8] metallodendrimers [9] or metallosupramolecules, such as helicates, [10] grids [11] and coordination cages, [12] have been prepared.

Upon the coordination with two bis-bidentate ligands, a tetrahedral or octahedral metal center becomes chiral [13]. Ligands bearing chiral moieties can result in the formation of optically pure multinuclear coordination complexes [3] and terpenoid moiety is one such chiral group that has been incorporated into pyridine ligands [14–26]. Herein, we report the coordination chemistry of a new series of chiral bis-bidentate pyridyl-thiazole ligands **L1**–**L3** bearing different terpenoid moieties. Having two thiazole rings bridging two chiral pyridines, this series of tetradentate ligands complex with Re(I), Ag(I) and Cu(II) ions to afford three types of binuclear metal complexes, single-, double- and triple-stranded, respectively. Each type has been characterized by circular dichroism (CD) spectroscopy and X-ray diffraction method and stereochemical pure complexes have been obtained in each type of complexes.



2. Experimental

2.1. Materials and instrumentation

All air and moisture sensitive manipulations were carried out in an oven-dried apparatus under a dry nitrogen atmosphere with magnetic stirring. Anhydrous acetonitrile was distilled over calcium hydride. Dimethylformamide was stirred with activated magnesium sulfate overnight and distilled under vacuum. The α,β-unsaturated ketones, (1*R*,2*S*,5*R*)-2,6,6-trimethyl-4-methylenebicyclo[3.1.1]heptan-3-one and (1*R*,5*R*)-6,6-dimethyl-3-methylenebicyclo[3.1.1]heptan-2-one were prepared according to our previous reported procedures [18a,27]. Compounds **1a** and **1c**, and **2a** and **2c** were prepared according to the literature methods. [17,28] Chemicals of reagent grade were obtained commercially. Chromatographic separations were performed with silica gel (60–200 μm; Merck) flash column chromatography. All ^1H, ^{13}C

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NMR and ^1H–^1H correlation spectra were recorded on a Varian 300 MHz Mercury instruments or Bruker 400 MHz instruments with tetramethylsilane (Sigma–Aldrich) as internal standard. Electron ionization mass spectra were recorded on a Hewlett Packard 5890II GC instrument coupled with a 5970 mass selective detector. Elemental analyses were performed on a Vario EL elemental analyzer. CD spectra were accorded with BioKin MOS-450.

2.2. X-ray diffraction study

The data of crystal structures of ligand **L3** and helical complexes [Re_2(**L1**)$(CO)_6Br_2$], [Ag_2(**L2**)$_2$]$(PF_6)_2$ and [Cu_2(**L3**)$_3$]$(ClO_4)_4$ were collected by Bruker SMART 1000 CCD diffractometer or Oxford Diffraction CrystAlisPro. All the structures were solved by direct method with SHELX-97 by full matrix least-squares based on F^2. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms were placed in idealized positions and assigned isotropic thermal parameters. In all cases, Friedel pairs were measured to enable refinement of the Flack parameter, which converged at −0.01(1) for **L3**, 0.06(1) for [Re_2(**L1**)$(CO)_6Br_2$], −0.008(6) for [Ag_2(**L2**)$_2$]$(PF_6)_2$ and 0.06(3) for complex [Cu_2(**L3**)$_3$]$(ClO_4)_4$ to confirm the absolute configurations. Details of the crystal parameters, data collection and refinement are collected in Table 1, and selected metric parameters are in Table 2–4.

2.3. Synthesis of compound **1b**

1-(2-Amino-2-oxoethyl)pyridinium chloride (12.8 g, 74 mmol), (1*R*,2*S*,5*R*)-2,6,6-trimethyl-4-methylenebicyclo[3.1.1]heptan-3-one (10 g, 67 mmol), and piperidine (7.7 ml, 80 mmol) were dissolved in methanol (252 ml). The yellow mixture was refluxed for 3 h. The resulting brown mixture was cooled down and methanol was evaporated under vacuum which afforded brown oily product. Formamide (176 ml) and glacial acetic acid (15.2 ml) were added into the brown oil, and the resulting mixture was heated at 200–210 °C for 1 h. The reaction mixture was cooled down and diluted with CH_2Cl_2 and water. The organic layer was collected and the aqueous layer was basified with 1 N NaOH solution. The resulting solution was extracted with CH_2Cl_2. The extract was collected and dried with $MgSO_4$. Solvent was removed under vacuum and brown oily product was afforded. The product was purified with column chromatography using petroleum ether (40–60 °C)/ethyl acetate/methanol (20:8:2) as eluent (R_f = 0.4). Removal of solvent afforded yellow oily product. Yield: 7.7 g (38%); ^1H NMR (300 MHz, $CDCl_3$): δ 13.80 (broad, 1H), 6.98 (d, 1H, *J* = 8.8 Hz), 6.17 (d, 1H, *J* = 8.8 Hz), 2.90–2.96 (m, 1H), 2.41 (t, 1H, *J* = 5.6 Hz), 2.32–2.35 (m, 1H), 1.87–1.90 (m, 1H), 1.25 (d, 3H, *J* = 6.8 Hz), 1.23 (s, 3H), 1.17 (d, 1H, *J* = 8.0 Hz), 0.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.57, 146.33, 141.05, 124.31, 115.36, 46.89, 45.05, 41.95, 35.02, 29.28, 26.13, 20.62, 17.55, 14.58; ESI-MS: *m/z* 190 (M+H$^+$).

Table 2
Selected bond distances and bond angles of binuclear single-stranded helical complex [Re_2(**L1**)$(CO)_6Br_2$].

Bond distances (Å)			
Re1–C2	1.74 (3)	Re3–C7	1.83 (3)
Re1–C3	1.86 (3)	Re3–C8	1.85 (2)
Re1–C1	1.90 (2)	Re3–C9	1.89 (3)
Re1–N2	2.18 (2)	Re3–N6	2.23 (2)
Re1–N1	2.27 (2)	Re3–N5	2.26 (2)
Re1–Br1	2.616 (3)	Re3–Br3	2.615 (3)
Re2–C5	1.91 (3)	Re4–C10	1.91 (2)
Re2–C4	1.94 (3)	Re4–C12	1.92 (2)
Re2–C6	1.98 (3)	Re4–C11	1.96 (3)
Re2–N3	2.12 (2)	Re4–N7	2.18 (1)
Re2–N4	2.22 (2)	Re4–N8	2.22 (2)
Re2–Br2	2.620 (2)	Re4–Br4	2.584 (3)
Bond angles (°)			
C2–Re1–N2	92.6 (9)	C7–Re3–N6	173 (1)
C3–Re1–N2	97 (1)	C8–Re3–N6	96 (1)
C1–Re1–N2	175 (1)	C9–Re3–N6	97 (1)
C2–Re1–N1	89 (1)	C7–Re3–N5	103 (1)
C3–Re1–N1	172 (1)	C8–Re3–N5	88.4 (9)
C1–Re1–N1	104.2 (9)	C9–Re3–N5	174 (1)
N2–Re1–N1	75.4 (7)	N6–Re3–N5	78.1 (7)
N2–Re1–Br1	87.9 (4)	N6–Re3–Br3	82.3 (4)
N1–Re1–Br1	86.6 (4)	N5–Re3–Br3	87.2 (4)
C5–Re2–N3	97.6 (9)	C10–Re4–N7	98.3 (8)
C4–Re2–N3	100 (1)	C12–Re4–N7	176.4 (9)
C6–Re2–N3	171.8 (9)	C11–Re4–N7	94.6 (9)
C5–Re2–N4	87 (1)	C10–Re4–N8	172.3 (8)
C4–Re2–N4	171 (1)	C12–Re4–N8	102 (1)
C6–Re2–N4	103 (1)	C11–Re4–N8	92 (1)
N3–Re2–N4	71.9 (7)	N7–Re4–N8	74.2 (6)
N3–Re2–Br2	82.7 (4)	N7–Re4–Br4	85.0 (5)
N4–Re2–Br2	86.8 (4)	N8–Re4–Br4	84.9 (5)

2.4. Synthesis of compound **2b**

Compound **1b** (1.9 g, 10 mmol) was dissolved in anhydrous dimethylforamide (3.7 ml) with stirring. Phosphorous(III)

Table 1
Crystallographic data.

Compound	**L3**[a]	[Re_2(**L1**)$(CO)_6Br_2$][b]	[Ag_2(**L2**)$_2$]$(PF_6)_2$[a]	[Cu_2(**L3**)$_3$]$(ClO_4)_4$[a]
Formula	$C_{30}H_{30}N_4S_2$	$Re_2C_{36}H_{30}N_4S_2O_6Br_2$	$AgC_{34.25}H_{39.50}N_4S_2\text{-}P_1F_6Cl_{0.5}O_{0.5}$	$Cu_2C_{90}H_{90}N_{12}S_6Cl_4O_{16}$
M_r	510.70	1210.98	849.88	2056.98
Color, habit	colorless, plate	yellow, plate	transparent, rectangle	green, needle
T (K)	133	296	133	293
Lattice type	monoclinic	triclinic	tetragonal	orthorhombic
Space group	$P2_1$	*P*1	$P4_12_12$	$P2_12_12$
a (Å)	10.9603 (3)	9.1400(9)	16.03159 (7)	12.5358 (3)
b (Å)	10.0242 (2)	15.543(2)	16.03159 (7)	31.7074 (6)
c (Å)	12.2518 (4)	16.441(2)	28.9709 (2)	14.3703 (3)
V (Å^3)	1309.61 (6)	2234.7(4)	7445.87 (7)	5711.9 (2)
Z	2	2	8	2
D_x [g m^{-3}]	540	1.800	1.516	1.196
F(000)	−0.01 (1)	0.06(1)	−0.008(6)	0.06(3)
Radiation used	Cu Kα	Mo Kα	Cu Kα	Cu Kα
μ (mm^{-1})	2.039	7.34	6.67	2.83
θ Range (°)	3.71–67.00	22.7–27.5	3.9–71.6	3.38–66.99
Unique reflections measured	3266	16134	6431	9419
Unique reflections observed, $I > 2\sigma(I)$	3311	9746	6625	5528
R	0.0347	0.047	0.0329	0.0653
wR_2	0.0944	0.135	0.0902	0.1689

[a] Details: graphite monochromatic radiation, Oxford Diffraction CrysAlisPro, 133 K, refinement based on F^2.
[b] Details: graphite monochromatic radiation, Bruker SMART 1000 CCD diffractometer, refinement based on F^2.