Novel Co(II), Ni(II) and Cu(II) complexes involving a 2-thienyl and trifluoromethyl containing symmetrically-substituted tetradentate Schiff-base ligand: Syntheses, structures, electrochemical and computational studies

Guillermo Ahumada^{a,b}, Mauricio Fuentealba^c, Thierry Roisnel^b, Samia Kahlal^b, David Carrillo^a, Ricardo Cordova^a, Jean-Yves Saillard^b, Jean-René Hamon^{b,*}, Carolina Manzur^{a,*}

^a *Laboratorio de Química Inorgánica, Instituto de Química, Facultad de Ciencias, Pontificia Universidad Católica de Valparaíso, Campus Curauma, Avenida Universidad 330, Valparaíso, Chile*

^b *Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France*

^c *Laboratorio de Cristalografía, Instituto de Química, Facultad de Ciencias, Pontificia Universidad Católica de Valparaíso, Campus Curauma, Avenida Universidad 330, Valparaíso, Chile*

* Corresponding authors.

e-mail address: jean-rene.hamon@univ-rennes1.fr (J.-R. Hamon)

e-mail address: cecilia.manzur@pucv.cl (C. Manzur)

ABSTRACT

Here, we report three novel metal(II) complexes (M = Co, **3a**; Ni, **3b**; Cu, **3c**) involving a symmetrically-substituted N₂O₂-tetradentate Schiff base ligand bearing trifluoromethyl and 2-thienyl substituents. Complexes **3a-c** were readily synthesized upon reaction of the diprotic Schiff base proligand with the appropriate hydrated metal(II) acetates, and isolated as neutral, air and thermally stable solids in good to excellent yields (> 65-85%). All the complexes have been well characterized using elemental analysis and different spectroscopic tools (ESI⁺ HRMS, FT-IR, UV-vis), and single crystal X-ray diffraction analysis for **3b** and **3c**. Their crystal structures revealed a four-coordinate square planar geometry at the Ni(II) and Cu(II) metal ions, with two nitrogen and two oxygen atoms as donors. Complexes **3a-c** displayed similar cyclic voltammetric behavior, exhibiting one anodic and one cathodic wave, both irreversible and of different intensity. They were tentatively assigned to M(II)/M(III) and M(II)/M(I) redox couples, respectively. No deposits of polymeric films on the electrode surface were observed. Structural, electrochemical and electronic parameters of the complexes have been rationalized on the ground of DFT and TD-DFT computation.

Keywords: thiophene; Schiff base complex; N₂O₂-ligand; cyclic voltammetry; single-crystal X-ray diffraction; DFT and TD-DFT calculations

1. Introduction

In the field of new molecular materials for photonic and optoelectronic applications, the impact of organometallic and coordination complexes [1-4] including those containing Schiff base ligands has increased during the last two decades [5-8]. Schiff bases are easily synthesized by condensation of primary amines with aldehydes or ketones and are able to form complexes with almost all metal ions and stabilize many different metals in various oxidation states [9]. These ligands are considered privileged taking into account the structural versatility adopted via incorporation of electron donor or acceptor substituents on their skeletons [9]. The possibility of obtaining “half units” via monocondensation reactions of β -dicarbonyl compounds, which are easily synthesized and modified [10,11] with a primary diamine, opens an important access to the synthesis of symmetrical or unsymmetrical Schiff base ligands [5,12,13].

During the last years, our efforts have been focused on the synthesis of main-chain and side-chain polymers of appropriately-substituted Schiff base metal(II) complexes, exhibiting large second-order nonlinear optics (NLO) responses [14-16]. However, those metallopolymers suffer poor solubility leading to low grafting degrees and oligomers. To avoid such a solubility limitation, especially in the case of main-chain polymers, we thought that electropolymerization of a Schiff base complex with a pendant electroactive 2-thienyl fragment would be of interest, because the polymer is electrogenerated and would grow on the electrode surface [17]. In this context, we recently investigated the electrochemical behavior of the bis-{1-(2-thienyl)-3-(3-thienyl)propane-1,3-dionato} complex of copper (II), and disclosed, for the first time, the generation of a polythienyl-containing β -diketonate complex and its deposition on an electrode using an electrochemical oxidation process [18]. We, therefore, decided to apply this strategy to cobalt(II), nickel(II) and copper(II) Schiff base complexes bearing a pendant 2-thienyl group, employing the dianion of the known symmetrical Schiff base 1,1,1-Trifluoro-4-(2-thienyl)-4-[(2-{[4,4,4-trifluoro-3-oxo-1-(2-thienyl)-but-1-en-1-yl]amino}ethyl)amino]but-3-en-2-one **2**, formally resulting from the condensation of 2-thenoyltrifluoroacetone (TTA) with 1,2-diaminoethane, as ligand [19-21]. Herein, we report modified synthetic procedures to prepare both the known N,N'-Bis[1-(2-thienyl)ethylidene]-1,2-diaminoethane **1** [22] and its bis-trifluoroacetylated derivative **2**, that was reacted with the appropriate metal (II) acetate salt in order to synthesize the symmetrically-substituted N₂O₂-tetradentate Schiff base complexes of Co(II), Ni(II) and Cu(II) **3a-c**, respectively (see formulas in Scheme 1). These compounds were fully characterized by analytical and spectroscopic techniques. Complexes **3b-c** were authenticated

by single crystal X-ray diffraction analysis, and the electrochemical behavior of **3a-c** was investigated by cyclic voltammetry. In addition, the geometries and electronic properties of the three M(II) complex **3a-c** were investigated by density functional (DFT) and time-dependant DFT (TD-DFT) calculation.

2. Experimental

2.1. Materials and physical measurements

Reactions were performed under dry dinitrogen or argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures [12]. All starting materials were purchased from commercial sources and used as received. Checking of the purity of the organic compounds was carried out by TLC on silica gel-protected aluminum sheets (type 60 F254, Merck), and the spots were detected by exposure to UV-lamp at $\lambda = 254$ nm. Solid-state FT-IR spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer with KBr disks in the 4000 to 450 cm^{-1} range. Uv/Vis spectra were recorded using a Thermo Scientific, Helios Omega spectrophotometer. NMR spectra were recorded at 298 K with a Bruker Avance III 400 spectrometer. All NMR spectra are reported in parts per million (ppm, δ), and referenced to the residual deuterated solvent peaks (CDCl_3 : ^1H $\delta = 7.26$ ppm, ^{13}C $\delta = 77.16$ ppm). Chemical shifts of ^{19}F NMR spectra are referenced against external CFCl_3 . Coupling constants (J) are reported in Hertz (Hz), and integrations are reported as the number of protons. High Resolution Electrospray Mass Spectra (HR-ESI-MS) were collected on a Bruker MAXI 4G spectrometer at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO) at the Université de Rennes 1, France. Elemental analyses were conducted on a Thermo-Finnigan Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the CRMPO. Melting points were measured in evacuated capillaries on a Kofler Bristoline melting point apparatus and were not corrected. Cyclic voltammetry (CV) measurements were performed at room temperature (r.t. = 20 °C), using a CHI604E potentiostat and a standard three-electrode set-up (purged with dinitrogen and maintained under inert atmosphere) using a platinum working electrode, SCE reference and platinum wire auxiliary electrode, with a voltage scan rate of 100 mVs^{-1} . The concentration of the complex under investigation was 10^{-3} M in acetonitrile solution containing 0.1 M $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$ as supporting electrolyte. Ferrocene (Fc) was added as an internal standard at the end of each experiment. The (Fc/Fc $^+$) couple was located at $E_{1/2} = 0.40$ V ($\Delta E_p = 0.09$ V, i_{pa}/i_{pc}

= 1.0) [24], where $E_{1/2}$ was calculated from the average of the oxidation and reduction peak potentials.

2.2. Synthesis of N,N'-Bis[1-(2-thienyl)ethylidene]-1,2-diaminoethane 1

A Schlenk tube was loaded with a magnetic stirring bar, 0.50 g (4.00 mmol) of 2-acetylthiophene, 20 mL of ethanol and two drops of acetic acid. After 10 min. of stirring, 0.14 mL (2.00 mmol) of ethylenediamine was added dropwise by syringe. The solution turned light yellow and was refluxed for 18 h. The reaction mixture was cooled to r.t., the solvent was evaporated and the oily residue was dried under high vacuum. The oil was then washed several times with cold hexane (0 °C) before being dissolved in ethanol. The solution was kept at -30 °C overnight, leading to the formation of a white precipitate (R_f = 0.1, 1:1 hexane/dichloromethane). It was filtered with a glass frit and washed several times with cold hexane (0 °C) to give 0.88 g (3.20 mmol, 80% yield) of compound **1**. M.p. 139 °C. Anal. calcd for $C_{14}H_{16}N_2S_2$ (276.42 g mol⁻¹): C, 60.83; H, 5.83; N, 10.13; S, 23.20. Found: C, 60.91; H, 5.84; N, 10.25; S, 22.93. FT-IR (KBr, cm⁻¹): 3054(s) ν (C-H arom), 2926(m), 2870(m), 2824(w) ν (C-H aliph), 1616(vs) ν (C=N), 1524(s) ν (C=C), 736(s) δ (C-H SC₄H₃). ¹H NMR (400 MHz, CDCl₃): 2.29 (s, 6 H, CH₃), 3.89 (s, 4 H, CH₂), 7.01 (dd, $J_{H,H}$ = 5.0 and 3.8 Hz, 2 H, SC₄H₃), 7.28 (d, $J_{H,H}$ = 3.7 Hz, 2 H, SC₄H₃), 7.30 (d, $J_{H,H}$ = 4.9 Hz, 2 H, SC₄H₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): 15.73 (CH₃), 52.48 (CH₂), 126.63 (C_{ipso}, SC₄H₃), 127.18 (SC₄H₃), 128.10 (SC₄H₃), 128.36 (SC₄H₃), 160.91 (C=N).

2.3. Synthesis of the tetradentate pro-ligand 2

In a Schlenk tube loaded with a magnetic stirring bar, 1.0 g (3.6 mmol) of **1** were dissolved in 30 mL of dry THF. After 10 min. of stirring, 1.3 mL (9.0 mmol) of trifluoroacetic anhydride was added dropwise by syringe. The solution turned to a light yellow color, and was refluxed for 6 h. The reaction mixture was cooled to r.t. and the volatiles evaporated under high vacuum. The yellow solid residue was dissolved in diethyl ether, kept at -30 °C overnight, leading to the formation of a white solid (R_f = 0.80, 1:1 hexane/dichloromethane). This solid was filtered with a glass frit and washed several times with cold hexane (0 °C) to obtain 1.43 g (3.06 mmol, 85% yield) of compound **2**. M.p. 160 °C. Anal. calcd for $C_{18}H_{14}F_6N_2O_2S_2$ (468.44 g mol⁻¹): C, 46.15; H, 3.01; N, 5.98; S, 13.69. Found: C, 45.99; H, 2.83; N, 5.99; S, 14.03. FT-IR (KBr, cm⁻¹): 3186(w) ν (N-H), 3102(w), 3084(w) ν (C-H arom), 2926(w), 2924(w) ν (C-H aliph), 1604(vs), 1558(s) ν (C=O), ν (C=C) and/or ν (C=N), 1254(m), 1202(m), 1134 (m) ν (CF₃), 716(s) δ (C-H SC₄H₃). ¹H NMR (400 MHz, CDCl₃):

3.80 (s, 4 H, CH₂), 5.58 (s, 2 H, CH=C), 7.15 (dd, $J_{\text{H,H}} = 4.8$ and 3.8 Hz, 2 H, SC₄H₃), 7.27 (d, $J_{\text{H,H}} = 3.7$ Hz, 2 H, SC₄H₃), 7.57 (d, $J_{\text{H,H}} = 4.6$ Hz, 2 H, SC₄H₃) 11.10 (s, 2 H, NH). ¹³C{¹H} NMR (100 MHz, CDCl₃): 45.27 (-CH₂), 91.72 (-CH=C), 117.35 (q, $^1J_{\text{C,F}} = 289$ Hz, CF₃), 128.04 (C_{ipso}, SC₄H₃), 129.93 (SC₄H₃), 130.35 (SC₄H₃), 133.25 (SC₄H₃), 163.09 (CH=C), 176.70 (q, $^2J_{\text{C,F}} = 33$ Hz, C=O). ¹⁹F NMR (376 MHz, CDCl₃): -76.64 (s, CF₃).

2.4. Synthesis of the Schiff base complexes 3a-c

2.4.1. General procedure

A Schlenk tube was charged with a magnetic stirring bar, 1.0 g (2.13 mmol) of **2** and 15 mL of methanol. The solution was stirred for 5 min. before adding 2.13 mmol of the hydrated metal acetate salt. The reaction mixture was stirred at r.t. for 4 h. Then, the solvent was evaporated under reduced pressure, the solid material was washed with 100 mL of water, filtered with a glass frit, dissolved in CH₂Cl₂ and dried over MgSO₄. The suspension was filtered off and the solvent evaporated under vacuum.

2.4.2. Complex 3a

Cobalt(II) acetate tetrahydrate used: 0.53 g; brown solid, 0.81 g (1.49 mmol, 70% yield). M.p. 119-120 °C. Anal. calcd for C₁₈H₁₄F₆N₂O₃S₂Co (543.35 g mol⁻¹): C, 39.78; H, 2.21; N, 5.15; S, 11.78. Found: C, 40.15; H, 2.62; N, 4.98; S, 10.52. FT-IR (KBr, cm⁻¹): 3105(w) ν(C-H arom), 2924(w) ν(C-H aliph), 1606(s) and 1524(m) ν(C≡O), ν(C≡C) and/or ν(C≡N), 1295(vs), 1188(vs), 1139(vs) ν(CF₃), 716(s) (C-H SC₄H₃). HRMS positive ESI, [m/z] calcd for [C₁₈H₁₂F₆N₂O₂S₂⁵⁷Co]: 524.9584; found: 524.9576 [M]⁺.

2.4.3. Complex 3b

Nickel(II) acetate tetrahydrate used: 0.53 g; light green solid, 0.94 g (1.79 mmol, 84% yield). M.p. 179-180 °C. Anal. calcd for C₁₈H₁₂F₆N₂NiO₂S₂ (525.11 g mol⁻¹): C, 41.17; H, 2.30; N, 5.33; S, 12.21. Found: C, 41.07; H, 1.95; N, 5.31; S, 12.33. FT-IR (KBr, cm⁻¹): 3106(w) ν(C-H arom), 2924(w) ν(C-H aliph), 1604(s) and 1518(m) ν(C≡O), ν(C≡C) and/or ν(C≡N), 1302(vs), 1184(s), 1150(s) ν(CF₃), 716(s) δ(C-H SC₄H₃). HRMS positive ESI, [m/z] calcd for [C₁₈H₁₂N₂O₂F₆S₂Na⁵⁸Ni]: 546.94956; found: 546.94910 [M + Na]⁺.

2.4.4. Complex 3c

Copper(II) acetate monohydrate used: 0.39 g; dark green solid, 0.73 g (1.38 mmol, 65% yield). M.p. 141-142 °C. Anal. calcd for C₁₈H₁₂CuF₆N₂O₂S₂ (529.96 g mol⁻¹): C, 40.79; H, 2.28; N, 5.29; S, 12.10. Found: C, 41.18; H, 2.46; N, 5.04; S, 10.50. FT-IR (KBr, cm⁻¹):

3100(w) $\nu(\text{C-H arom})$, 2923(w), 2854 $\nu(\text{C-H aliph})$, 1613(s) and 1530(m) $\nu(\text{C}\equiv\text{O})$, $\nu(\text{C}\equiv\text{C})$ and/or $\nu(\text{C}\equiv\text{N})$, 1294(vs), 1185(s), 1134(s) $\nu(\text{CF}_3)$, 716(s) $\delta(\text{C-H SC}_4\text{H}_3)$. HRMS positive ESI, $[m/z]$ calcd for $[\text{C}_{18}\text{H}_{12}\text{F}_6\text{N}_2\text{O}_2\text{S}_2\text{Na}^{63}\text{Cu}]$: 551.9433; found: 551.9433 $[\text{M} + \text{Na}]^+$.

2.5. X-ray Crystal Structure Determinations

Crystallographic measurements were carried out for **3b** at $T = 296(2)$ K on a Bruker D8 QUEST diffractometer equipped with a bidimensional CMOS Photon100 detector, and for **3c** at $T = 150(2)$ K on a APEXII Bruker-AXS diffractometer equipped with a bidimensional CCD detector, using in both cases graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). A single crystal of **3b** was mounted on top of glass fiber in a random orientation while a crystal of **3c** was coated in Paratone-N oil, mounted onto a nylon loop and transferred to the cold gas stream of the cooling device. The structure of **3b** was solved by direct methods using OLEX2 [25] and refined by full matrix l.s. methods based on F^2 [26]. DFIX instruction restrains were used on the bond lengths of one 2-thienyl moiety with a standard uncertainty of 0.01 Å. FLAT constrain instructions were applied in order to keep the planarity of one 2-thienyl ring with a standard uncertainty of 0.1 Å³. Finally, EADP constraints were used on the disordered ring in order to keep the same anisotropic displacement parameters. The structure of **3c** was solved by dual-space algorithm using the SHELXT program [27], and then refined with full-matrix L.S. methods based on F^2 (SHELXL-2014) [28]. The disorder observed in **3c** for the carbon and sulfur atoms of the two thiophene units of the full molecule of the asymmetric unit were modelled using two positions per ring with fixed occupancy factors of 0.80 and 0.20. In both compounds, non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were included in their calculated positions, assigned fixed isotropic thermal parameters and constrained to ride on their parent atoms. A summary of the details about crystal data, collection parameters and refinement are documented in Table 1, and additional crystallographic details are in the CIF files. ORTEP views were drawn using Olex2 software [25].

Table 1 Crystallographic data, details of data collection and structure refinement parameters for compounds **3b** and **3c**.

	3b	3c
Empirical Formula	$\text{C}_{18}\text{H}_{12}\text{F}_6\text{N}_2\text{NiO}_2\text{S}_2$	$\text{C}_{18}\text{H}_{12}\text{CuF}_6\text{N}_2\text{O}_2\text{S}_2$

Formula mass, g mol ⁻¹	525.13	529.96
Collection T, K	296(2)	150(2)
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Pbnb
<i>a</i> (Å)	8.9753(10)	11.3637(4)
<i>b</i> (Å)	9.6659(9)	19.3774(5)
<i>c</i> (Å)	12.3426(13)	27.7795(9)
α (°)	75.909(3)	90
β (°)	84.730(4)	90
γ (°)	78.475(3)	90
<i>V</i> (Å ³)	1016.56(18)	6117.0(3)
<i>Z</i>	2	12
<i>D</i> _{calcd} (g cm ⁻³)	1.716	1.726
<i>F</i> (000)	528	3180
abs coeff (mm ⁻¹)	1.232	1.348
θ range (°)	2.210 to 26.401	2.93 to 27.53
range <i>h,k,l</i>	-11/11, -12/12, -15/15	-14/14, -25/13, -36/36
No. total refl.	57668	73885
No. unique refl.	4156	7023
Comp. to θ_{max} (%)	99.8	99.6
Data/Restraints/Parameters	4156/16/305	7023/0/422
Final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0355 <i>wR</i> ₂ = 0.0957	<i>R</i> ₁ = 0.0418 <i>wR</i> ₂ = 0.1055
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0374 <i>wR</i> ₂ = 0.0979	<i>R</i> ₁ = 0.0615 <i>wR</i> ₂ = 0.1175
Goodness of fit / <i>F</i> ²	1.037	1.045
Largest diff. Peak/hole (eÅ ⁻³)	0.609/-0.581	1.113/-0.969

2.6. Computational details

DFT calculations were carried out for complexes **3a-c** using the ADF2013 package [29,30], employing the PW91 functional [31] and the TZ2P basis set [32]. Spin-unrestricted calculations were performed on the open-shell systems. The geometry optimizations were carried out assuming the X-ray structures as input data, without any symmetry constraint. The optimized geometries were characterized as true minima on the potential energy surface using vibration frequency calculations (no imaginary values). The UV-vis transitions were calculated by means of TD-DFT calculations on the optimized geometries, at the same PW91/TZ2P level of theory.

3. Results and discussion

3.1. Syntheses and characterization

In order to synthesize complexes **3a-c**, it was necessary to prepare the symmetrical 2-thienyl and trifluoromethyl-containing Schiff base **2**. Asiri et al. [19,20] reported that light yellow crystals of **2**, characterized by X-ray diffraction analysis, were formed upon heating

equimolar amounts of 2-thenoyltrifluoroacetone and ethylenediamine in benzene, using a Dean-Stark trap, for about 2 h. We were unable to reproduce this work and have recently shown that double condensation of 2-thenoyltrifluoroacetone with ethylenediamine in a 2:1 stoichiometric ratio does not provide the expected Schiff base **2**, but leads instead to the formation of the 7-(thiophene-2-yl)-5-(trifluoromethyl)-2,3-dihydro-1H-1,4-diazepine, whatever the experimental conditions used [33]. By contrast, Sosnovskikh and Kutsenko have shown that standing a mixture of the same two reagents in a 1:3 ratio at -20 °C under solventless conditions for 3 h afforded N,N'-Bis[1-(2-thienyl)ethylidene]-1,2-diaminoethane **1**, isolated in 78% yield [34]. To circumvent these problems in the synthesis of **2**, we applied a procedure developed by Asiri and co-workers [20] *i.e.*, the trifluoroacetylation of the diimine **1**. Diimine **1** was, indeed, previously prepared by condensation of ethylenediamine with 2 equivalents of 2-acetylthiophene in refluxing dry benzene, using Dean-Stark apparatus, either with a catalytic amount of toluene-*p*-sulfonic acid for 18 h (60% yield) [22] or without any catalytic agent for about 2 h (84% yield) [21]. However, this latter procedure did not give satisfactory yields (<10%) in our hands. Even upon substituting the highly toxic benzene solvent for toluene the yield remained very low. Thus, for the preparation of **1**, the condensation was carried out in refluxing ethanol containing acetic acid as catalyst for 18 h (Scheme 1). N,N'-Bis[1-(2-thienyl)ethylidene]-1,2-diaminoethane **1** was isolated as a white solid in 80% yield. Treatment of **1** with a slight excess (25%) of trifluoroacetic anhydride under dry and anaerobic conditions in THF for the optimized 6 h period of refluxing time, provided the desired symmetrical Schiff base **2** as a white powder in 85% isolated yield (Scheme 1). Starting material **1** is slightly soluble in THF, but after 2 h of reflux, all the solid dissolved and the solution turned to a pale yellow color, indicating that the reaction occurred. Prolonged periods of refluxing time decreased the yield of **2** with concomittent formation of side products that complicated the purification process, whereas 2 h of reflux as originally stated [21] afforded **2** in very poor yields (~10%). Analytical and spectroscopic characterization, in agreement with reported data [20-22,34], confirmed the purity and nature of both compounds **1** and **2** (see section 2.1 and 2.2, respectively, for details).

Scheme 1 Syntheses of diimine **1**, Schiff base **2** and complexes **3a-c**.

Complexes **3a-c** were straightforwardly obtained by reacting the Schiff base **2** with the appropriate hydrated metal (II) acetate salt in methanol at r.t. for 4 h (Scheme 1). To facilitate their purification, it is important to copiously wash the formed solids with water, in order to eliminate all the acetic acid formed during the reaction. Upon work-up, the three compounds were isolated as air and thermally stable brown **3a**, light green **3b** and dark green **3c** solids in good yields (~65-85%). They are insoluble in hexane and diethyl ether, but soluble in polar organic solvents such as dichloromethane, tetrahydrofurane, methanol or acetonitrile. Compounds **3a-c** were characterized by mass spectrometry and elemental analyses (see section 2.4) which were found to be in concordance with the proposed structures. Furthermore, **3b** and **3c** were further authenticated by X-ray diffraction studies (see section 3.2). From elemental analysis, it appears that the coordination sphere of Co(II) in complex **3a** contains one molecule of water.

The solid-state FT-IR spectra of **3a-c** present similar patterns, exhibiting two strong and medium intensity bands in the 1613-1606 and 1530-1518 cm^{-1} ranges, respectively, attributed to $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{C})$ and/or $\nu(\text{C}=\text{N})$ stretching modes of the chelating Schiff base skeleton [14-16]. The disappearance of the $\nu(\text{N-H})$ vibration observed at 3186 cm^{-1} in proligand **2** clearly suggests that the Schiff base is coordinated to the metal ion through the imine nitrogen atoms. Besides, a series of three strong bands were observed in the 1300-1100 cm^{-1} , which have been assigned to the stretching vibration mode of the C-F bonds of the CF_3 groups [33,35,36]. The presence of the thienyl moiety was also confirmed by the strong vibration at 716 cm^{-1} due to the bending vibration mode out of the plane of the C-H groups

pertaining to this ring [37,38]. This strong band was also present in the spectrum of precursor **2**, thus indicating that the thiophene sulfur atoms are not coordinated to the metal center in complexes **3a-c** [18].

Based on the preceding analytical and structural (see below) data confirmed by DFT calculations (see Section 3.5), the square planar Ni(II) derivative **3b** is expected to be diamagnetic. Surprisingly, all attempts to run a well-resolved ^1H NMR spectrum failed. The obtained spectra showed broad and shifted unassignable resonances whatever the solvent used. Interestingly, we made a similar observation when running the ^1H NMR spectrum of a Ni(II) complex supported by an unsymmetrically-substituted Schiff base ligand bearing both fluoro and nitro substituents [39]. This unexpected solution behavior might be due to a tetrahedral distortion of the coordination sphere about the metal ion caused by the powerful electron withdrawing ability of the Schiff base ligand substituents.

3.2. X-ray Crystallographic Study

Whereas it was not possible to obtain single crystals of **3a** suitable for X-ray diffraction analysis, good quality crystals of **3b** and **3c** were obtained by slow evaporation of a saturated methanol solution of the respective compound. Perspective views of **3b** and **3c** with partial atom labelling scheme are displayed in Fig. 1, in similar orientations for the sake of comparison. Selected bond lengths and angles of the $[\text{M}(\text{N}_2\text{O}_2)]$ coordination cores are given in Table 2, whereas other selected bond distances and angles are provided in Table S1 (Supplementary material). Complex **3b** crystallizes in the triclinic group P-1 with a single molecule in the asymmetric unit, whereas complex **3c** is arranged in the orthorhombic crystal system in the centrosymmetric space group Pbnb with 1.5 molecule in the asymmetric unit. The entire molecule is labelled **3c** while the half one is noted **3c'**. This extra symmetry-independent half molecule is related to its other half through a C_2 axis passing through the metal atom and the middle of the $\text{CH}_2\text{-CH}_2$ bond. The molecular structure of **3c'** is shown in Fig. S1 (Supplementary Material). Complexes **3b** and **3c** consist of a metal(II) ion tetracoordinated by the N_2O_2 donor set of the same dianionic Schiff base ligand symmetrically substituted with 2-thienyl and trifluoromethyl groups, and forming monomeric units. The structures are very similar, differing only by the M(II)-centered metal ion, $\text{M} = \text{Ni}$ for **3b** and Cu for **3c/3c'**. Orientational disorder of the 2-thienyl rings is observed in both compounds [18,33,40], and all close intermolecular contacts correspond to van der Waals interactions.

Fig. 1 Molecular structures of **3b** (top) and **3c** (bottom) with partial atom numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

The crystal structures of **3b** and **3c** revealed that the symmetrically-substituted Schiff base ligand coordinates to the metal(II) ion as a doubly deprotonated form in a tetradentate fashion with a N_2O_2 *cis*-configuration (Fig. 1). This leads to the formation of a six-, five-, and six-membered chelate ring arrangement around the central metal. In each compound, the Ni(II) and Cu(II) ions adopt a slightly distorted square planar geometry with O-M-N diagonal angles and sum of bond angles involving the metal and the N_2O_2 donor atoms set of $175.10(7)^\circ$ and 360.4° for **3b**, and of $177.47(10)^\circ$ and 360.2° for **3c**, respectively. The geometry is more distorted in **3c'** with corresponding angle values of $171.29(10)^\circ$ and 361.3° (Table 2). This distortion towards a tetrahedral environment could arise from the strong electron withdrawing power of the trifluoromethyl groups, although the effect of packing forces cannot be excluded. We have previously noticed such an observation for complexes

supported by unsymmetrically-substituted Schiff base ligands bearing 3,5-difluorosalicylidene ring [41].

Table 2 Bond distances and angles of the first coordination sphere of the $[M(N_2O_2)]$ core for **3b**, **3c** and **3c'** (from X-ray structures).

	3b	3c	3c' [#]
Bond distances (Å)			
M-O(1)	1.8570(15)	1.921(2)	1.901(2)
M-O(2)	1.8540(16)	1.917(2)	-
M-N(1)	1.8610(17)	1.947(2)	1.943(3)
M-N(2)	1.8550(17)	1.960(2)	-
Bond angles (°)			
O(1)-M-N(2)	175.10(7)	177.47(10)	171.29(10)
O(2)-M-N(1)	175.30(8)	175.93(10)	-
O(1)-M-O(2)	85.36(7)	86.47(9)	85.74(15)
O(1)-M-N(1)	94.91(7)	93.40(9)	94.58(11)
O(2)-M-N(2)	93.90(7)	94.42(9)	-
N(1)-M-N(2)	86.22(8)	85.88(10)	86.43(15)

M = Ni, **3b**; Cu, **3c** and **3c'**. Symmetry code: #1 -x+1/2, y, -z+1/2

The fused five- and six-membered heterometallacycles formed upon coordination of Schiff base **2** to the metal(II) ion are essentially co-planar, albeit in each complex the five-membered ring adopts an envelop conformation with one carbon deviating from the mean $[MN_2C_2]$ plane by 0.262 Å in **3b**, 0.215 Å in **3c**, and 0.212 Å in **3c'**. Inspection of the bond length patterns and angles (Table S1) of the six-membered metallacycles suggests a significant electron delocalization within the chelating rings, as the O-C, C-C and C-N bond distances fall between the measured values for related normal single and double bonds involving those sp^2 hybridized atoms [42]. The 2-thienyl rings are planar within experimental error and make with their respective attached six-membered metallacycles (Figs. 1 and S2), dihedral angles of 65.15° and 108.3° in **3b**, 68.2° and 38.6° in **3c**, and 45.95° in **3c'**. On the other hand, there is not rotational disorder associated with the CF_3 groups, so all the C-F bond distances are quite similar (Table S1). On average, the C-F bond lengths are about 1.329(3) and 1.305(4) Å in **3b**, 1.327(4) and 1.335(4) Å in **3c**, and 1.329(4) Å in **3c'**.

3.3. Electronic absorption spectra

The electronic absorption spectra of Schiff base proligand **2** and of its metal(II) complexes **3a-c** were recorded at room temperature in 10^{-3} M and 10^{-6} M dichloromethane solutions in the ranges 450-900 nm and 250-450 nm, respectively (Fig. 2). Absorption spectral data are presented in Table 3. The two bands observed in **2** in the UV region can be

assigned to $\pi \rightarrow \pi^*$ transitions. These two bands are also found at similar wavelengths in complexes **3a-c**. On grounds of our previous TD-DFT calculation [39], the bands at 362, 398 and 344 nm observed for **3a-c**, respectively, are assumed to originate from ligand-to-metal charge transfer (LMCT). From our present TD-DFT investigations discussed below in Section 3.5, the low-energy absorption bands appearing at 610 (**3a**) and 560 (**3c**) nm are tentatively assigned to LMCT transitions while the absorption band observed at 580 nm for diamagnetic **3b** is attributed to a MLCT transition. Participation of some d-d transitions could not, however, be excluded [39,43,44].

Fig. 2 UV spectra (top) and Vis spectra (bottom) measured in CH_2Cl_2 solutions at r.t. for **2** (solid line) and complexes **3a** (dashed line), **3b** (dotted line) and **3c** (dashed-dotted line).

Table 3 Electronic spectral data of compounds **2** and **3a-c**.

Compd.	$\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) (CH_2Cl_2)
2	294 (4.16)
	346 (4.60)
3a	293 (5.40)
	362 (5.70)
	610 (2.20)

3b	292 (6.10)
	330 (5.91)
	398 (5.45)
	580 (2.00)
3c	292 (4.38)
	320 (4.35)
	344 (4.00)
	560 (2.34)

3.4. Electrochemical studies

The electrochemical behavior of complexes **3a-c** was investigated by cyclic voltammetry (CV) in acetonitrile solutions, at 293 K, in the potential range -0.5 to 1.8 V versus external Fc/Fc⁺. The three complexes present a similar potentiodynamic behavior where each stabilized profile exhibits one anodic and one cathodic wave, both being irreversible (Fig. 3). The oxidation peaks are located at 1.35, 1.24 and 1.10 V whereas the reverse reduction waves appeared at 0.12, 0.90 and 0.95 V vs. Fc/Fc⁺ for **3a**, **3b** and **3c**, respectively. In all cases, the anodic charge involved is always greater than the respective cathodic one. From our DFT calculations (see below), these redox events could be assigned to the M(II)/M(III) and M(II)/M(I) couples, respectively. By contrast to what we previously observed with the bis-{1-(2-thienyl)-3-(3-thienyl)propane-1,3-dionato} copper(II) complex [18], in the present case no deposits of polymeric species on the electrode surface occurred whatever the metal center used.

Fig. 3 Cyclic voltammograms of complexes **3a** (dashed line), **3b** (dotted line) and **3c** (dashed-dotted line), recorded at a Pt working electrode in acetonitrile containing 0.1 M *n*-Bu₄N⁺PF₆⁻, at T=293 K with a sweep rate $\nu = 0.1 \text{ Vs}^{-1}$ and SCE as reference electrode. Potentials are referenced to the Fc/Fc⁺ redox couple at +0.40 V vs. SCE [14].

3.5. Theoretical investigations

In order to get a better insight into the bonding and properties of compounds **3a-c**, DFT calculations were performed on these compounds. Details of the calculations are given in the experimental section. Their fully optimized geometries were characterized as true energy minima by vibrational frequency calculations. That of **3c** was found to be of C_2 symmetry, with the C_2 axis passing through the metal and the middle of the H_2C-CH_2 ethylidene bond. Those of **3a** and **3b** were found to be of C_1 symmetry, but with a structure not that much different from the C_2 configuration adopted by **3c**. This C_2 symmetry can be easily understood from considering the five-membered MNCCN ring constraint which is somewhat minimized by rotating the CH_2-CH_2 bond out of from the coordination plane. Selected computed metrical data are given in Table 4. They are in a good overall agreement with the X-ray structures of **3b-c** (Table 2), with a slight overestimation by DFT of the metal-ligand distances (2-5%), as usually observed for this type of complexes.

Table 4 Selected DFT metrical data of complexes **3a**, **3b** and **3c** (optimizations in the gas phase).

	3a (C_1)	3b (C_1)	3c (C_2)
Bond distances (Å)			
M-O(1)	1.872	1.879	1.965
M-O(2)	1.874	1.885	1.965
M-N(1)	1.881	1.892	1.985
M-N(2)	1.873	1.881	1.985
Bond angles (°)			
O(1)-M-N(2)	173	177	169
O(2)-M-N(1)	174	178	169
O(1)-M-O(2)	85	84	89
O(1)-M-N(1)	94	95	94
O(2)-M-N(2)	94	94	94
N(1)-M-N(2)	87	87	86

M = Co, **3a**; Ni, **3b**; Cu, **3c**.

3a, **3b** and **3c** are 15-, 16- and 17-electron square planar transition-metal complexes, respectively. Whereas the ground-state of **3b** is a singlet, those of **3a** and **3c** are doublets. The MO diagrams of **3b** and **3c** are shown in Fig. 4. Due to the spin-unrestricted nature of the calculations, each Kohn-Sham MO level in the diagrams of **3a** and **3c** is split into two spinorbitals: one spin-up (left) and one spin-down (right). Considering first the closed-shell situation of **3b**, its 3d atomic shell generates in the complex a set of four non-bonding or weakly antibonding metal-based MOs which are occupied and a σ -antibonding $d_{x^2-y^2}$ orbital which is the LUMO. The substantial computed HOMO-LUMO gap is consistent with the

stability and diamagnetism of **3b**. The level energy diagram of **3a** (not shown in Fig. 4) is similar to that of **3b**, but with one electron less in the HOMO. On the other hand, that of **3c** (Fig. 4) corresponds to the addition of a supplementary electron in the $d_{x^2-y^2}$ -based orbital. However, the occupied 3d-type levels of **3c** are lying much lower than in the case of **3b** where they constitute the four highest occupied orbitals. The spin densities of the odd-electron **3a** and **3c** (Fig. 5) reflect the shape of their singly occupied orbital. Both have significant ligand participation. The redox properties of **3a-c** (see above) are readily understood from their different electron counts. It is easier to oxidize **3c** because its unpaired electron lies in the somehow high-lying antibonding $d_{x^2-y^2}$ orbital, whereas removing that of the unsaturated **3a** requires more energy. On the other hand, reducing **3a** to complete its closed-shell configuration is easier than adding an extra electron in the high-lying $d_{x^2-y^2}$ orbital of **3c**.

Fig. 4 Kohn-Sham orbital diagrams of **3b** and **3c**. The localizations (in %) are given in the following order: metal/ligand. HOSO: highest occupied spin-orbital; LUSO: lowest unoccupied spin-orbital.

Fig. 5 Spin density plots of **3a** and **3c**.

TD-DFT calculations were performed in order to index the optical transitions of low energy. The transition of lowest energy was computed at 573, 599 and 474 nm for **3a**, **3b** and **3c**, respectively. In the cases of **3a** and **3c**, it is a transition from an occupied ligand-type level to the half-vacant metal-based HOMO, whereas in the case of **3b**, it is a MLCT transition.

4. Conclusion

In conclusion, a series of Co(II), Ni(II) and Cu(II) complexes featuring a symmetrically-substituted N₂O₂-tetradentate Schiff base ligand bearing trifluoromethyl and 2-thienyl substituents, was synthesized and fully characterized by analytical and spectroscopic methods, as well as by X-ray crystallography for the nickel and copper derivatives. In addition, the geometry, bonding and electronic structure have been analysed by DFT calculations. Single crystal X-ray diffraction analysis showed slightly distorted square planar geometry of the M(N₂O₂) cores, and revealed the partial delocalization of bonding electron density throughout the six-membered heterometallacycle frameworks. Indexation of the optical transitions of low energy were supported by TD-DFT calculations. Cyclic voltammetry experiments showed one irreversible oxidation wave and one irreversible reduction wave, of different intensity, for each complex. DFT calculations indicate that those waves are associated to M(II)/M(III) and M(II)/M(I), respectively, and that the relative redox potentials depend on the electronic structure of the complexes. However, in any case no formation of polymeric deposit occurred.

Acknowledgments

We thank F. Lambert (CRMPO, Rennes) for helpful assistance with MS measurements. Financial support from the Fondo Nacional de Desarrollo Científico y Tecnológico [FONDECYT (Chile), grant no. 1140903 (C.M. and D.C.)], FONDEQUIP

[EQM130154], the Vicerrectoría de Investigación y Estudios Avanzados, Pontificia Universidad Católica de Valparaíso, Chile (C.M. and D.C.), the CNRS and the Université de Rennes 1 is gratefully acknowledged. The GENCI-CINES and GENCI-IDRISS French national computer centers are acknowledged for computational resources (grant a0010807367). This research has been performed as part of the Chilean-French International Associated Laboratory for “Multifunctional Molecules and Materials” (LIA M3 - CNRS N°1027). G.A. thanks the CONICYT (Chile) for support of a graduate fellowship N°21120098.

Appendix A. Supplementary data

CCDC 1510918 for **3b** and 1826566 for **3c** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk.

Appendix B. Supplementary Material

Molecular structure of **3c'** (Fig. S1), selected bond distances and angles for **3b**, **3c** and **3c'** (Table S1), and cartesian coordinates of the DFT-computed compounds (Table S2). Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.poly.2018.xxx>.

References

- [1] B.J. Coe, *Coord. Chem. Rev.* 257 (2013) 1438-1458.
- [2] O. Maury, H. Le Bozec, *Metal-Based Quadratic Nonlinear Optical Materials*, in *Metal-Based Quadratic Nonlinear Optical Materials* in D.W. Bruce, D. O'Hare, R.I. Walton (Eds), *Molecular Materials*, John Wiley & Sons, Ltd, Chichester, UK, 2010, pp. 1-59.
- [3] D. Astruc, *Eur. J. Inorg. Chem.* (2017) 6-29.
- [4] S. Kaur, M. Kaur, P. Kaur, K. Clays, K. Singh, *Coord. Chem. Rev.* 343 (2017) 185-219.
- [5] X. Liu, C. Manzur, N. Novoa, S. Celedon, D. Carrillo, J.-R. Hamon, *Coord. Chem. Rev.* 357 (2018) 144-172.
- [6] C. R. Nayar, R. Ravikumar, *J. Coord. Chem.* 67 (2014) 1-16.
- [7] S. Di Bella, C. Dragonetti, M. Pizzotti, D. Roberto, F. Tessore, R. Ugo, *Top. Organomet. Chem.* 28 (2010) 1-55.
- [8] P. G. Lacroix, *Eur. J. Inorg. Chem.* (2001) 339-348.

- [9] P.G. Cozzi, *Chem. Soc. Rev.* 33 (2004) 410-421.
- [10] N. Novoa, T. Roisnel, V. Dorcet, J.-R. Hamon, D. Carrillo, C. Manzur, F. Robin-Le Guen, N. Cabon, *J. Organomet. Chem.* 762 (2014) 19-28, and references cited therein.
- [11] G. Ahumada, T. Roisnel, S. Sinbandhit, C. Manzur, D. Carrillo, J.-R. Hamon, *J. Organomet. Chem.* 737 (2013) 1-6.
- [12] R. Hernandez-Molina, A. Mederos, Acyclic and Macrocyclic Schiff Base Ligands, in: J.A. McCleverty, T.J. Meyer (Eds.), *Comprehensive Coordination Chemistry II*, Elsevier Pergamon, Oxford, 2004, vol. 1, pp. 411-458.
- [13] J.-P. Costes, *Polyhedron* 6 (1987) 2169-2176 and references cited therein.
- [14] S. Celedón, V. Dorcet, T. Roisnel, A. Singh, I. Ledoux-Rak, J.-R. Hamon, D. Carrillo, C. Manzur, *Eur. J. Inorg. Chem.* (2014) 4984-4993.
- [15] S. Celedón, M. Fuentealba, T. Roisnel, I. Ledoux-Rak, J.-R. Hamon, D. Carrillo, C. Manzur, *Eur. J. Inorg. Chem.* (2016) 3012-3023.
- [16] S. Celedón, T. Roisnel, I. Ledoux-Rak, J.-R. Hamon, D. Carrillo, C. Manzur, *J. Inorg. Organomet. Polym. Mater.* 27 (2017) 795-804.
- [17] A. Pietrangelo, B.C. Sih, B.N. Boden, Z. Wang, Q. Li, K.C. Chou, M.J. MacLachlan, M.O. Wolf, *Adv. Mater.* 20 (2008) 2280-2284.
- [18] J. Oyarce, L. Hernández, G. Ahumada, J. P. Soto, M. A. del Valle, V. Dorcet, D. Carrillo, J.-R. Hamon, C. Manzur, *Polyhedron* 123 (2017) 277-284.
- [19] A.M. Asiri, A.O. Al-Youbi, H.M. Faidallah, S.W. Ng, *Acta Crystallogr.* E67 (2011) o2659-o2660.
- [20] K.A. Khan, H. Faidallah, A.M. Asiri, *J. Chem.* 2013, <http://dx.doi.org/10.1155/2013/478635>.
- [21] A.M. Asiri, A.O. Al-Youbi, H.M. Faidallah, K.A. Alamry, S.W. Ng, *Acta Cryst.* E67 (2011) o2465.
- [22] J.F. Modder, R.J. Leijen, K. Vrieze, W.J.J. Smeets, A.L. Spek, G. van Koten, *J. Chem. Soc. Dalton Trans.* (1995) 4021-4028.
- [23] W.L.F. Armarego, C.L.L. Chai, *Purification of Laboratory Chemicals*, Fifth ed., Butterworth-Heinemann, Elsevier Inc., Amsterdam, The Netherlands, 2003.
- [24] N.G. Conelly, W.E. Geiger, *Chem. Rev.* 96 (1996) 877-910.
- [25] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 42 (2009) 339-341.
- [26] G.M. Sheldrick, *Acta Crystallogr.* A64 (2008) 112-122.
- [27] G.M. Sheldrick, *Acta Crystallogr.* A71 (2015) 3-8.
- [28] G.M. Sheldrick, *Acta Crystallogr.* C71 (2015) 3-8.
- [29] G. te Velde, F.M. Bickelhaupt, S.J.A. van Gisbergen, C. Fonseca Guerra, E.J. Baerends, J.G. Snijders, T. Ziegler, *J. Comput. Chem.* 22 (2001) 931-967.
- [30] ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>.
- [31] J.P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B* 54 (1996) 16533-16539.
- [32] E. Van Lenthe, E.J. Baerends, *J. Comput. Chem.* 24 (2003) 1142-1156.
- [33] G. Ahumada, D. Carrillo, C. Manzur, M. Fuentealba, T. Roisnel, J.-R. Hamon, *J. Mol. Struct.* 1125 (2016) 781-787.
- [34] V.Ya. Sosnovskikh, P.A. Kutsenko, *Russ. Chem. Bull.* 48 (1999) 540-551 (Engl. Transl.).
- [35] R.L. Redington, K.C. Lin, *Spectrochim. Acta A* 27 (1971) 2445-2460.
- [36] S.P. Gejji, K. Hermansson, J. Lindgren, *J. Phys. Chem.* 97 (1993) 3712-3715.
- [37] (a) P. Molina, A. Arques, I. Cartagena, *Comprehensive Heterocyclic Chemistry III*, Elsevier, New York, 2008, Vol. 3, Chapter 09, pp. 625-739.

- [38] J.J. Peron, P. Saumagne, J.M. Lebas, *Spectrochim. Acta A* 26 (1970) 1651-1666.
- [39] J. Cisterna, V. Artigas, M. Fuentealba, P. Hamon, C. Manzur, V. Dorcet, J.-R. Hamon, D. Carrillo, *Inorg. Chim. Acta* 462 (2017) 266-280.
- [40] G. Ahumada, T. Roisnel, S. Kahlal, D. Carrillo, R. Córdova, J.-Y. Saillard, J.-R. Hamon, C. Manzur, *Inorg. Chim. Acta* 470 (2018) 221-231.
- [41] J. Cisterna, V. Dorcet, C. Manzur, I. Ledoux-Rak, J.-R. Hamon, D. Carrillo, *Inorg. Chim. Acta* 430 (2015) 82-90.
- [42] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor. *J. Chem. Soc. Perkin Trans.*, (1987) S1-S19.
- [43] A.P.B. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1980.
- [44] M. A. Al-Anber, *Am. J. Phys. Chem.* 2 (2013) 1-7.

Graphical Abstract Synopsis

The three new four-coordinate Co(II), Ni(II) and Cu(II) complexes featuring a symmetrical N₂O₂-tetradentate Schiff base ligand substituted with trifluoromethyl and 2-thienyl groups, adopt a square planar geometry (pictured). DFT and TD-DFT calculations were performed to rationalize structural, electrochemical and electronic parameters of the complexes.