Polyhedron 29 (2010) 1007–1014

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Cobalt(II), nickel(II) and copper(II) compounds derived from template reactions of enantiomerically pure 2-amino-thiazoles

Raúl Ramírez-Trejo [a], Angelina Flores-Parra [b], José Adrián Peña-Hueso [b], Edgar Mijangos [b], Rosalinda Contreras [b,*], Norah Barba-Behrens [a,*]

[a] Departamento de Química Inorgánica, Facultad de Química, Universidad Nacional Autónoma de México, C.U., Coyoacán, México, D.F. 04510, Mexico
[b] Departamento de Química, Centro de Investigación y de Estudios Avanzados, A.P. 14-740, México, D.F. 07000, Mexico

ARTICLE INFO

Article history:
Received 5 September 2009
Accepted 2 December 2009
Available online 5 December 2009

Keywords:
Transition metal bis(tricyclic) compounds
Bis[4,5-dihydrothiazole-2-yl]amine
Template reactions

ABSTRACT

Herein we report the syntheses and structural analyses of three coordination compounds Co(L)$_2$ (**3**), Ni(L)$_2$, (**4**) and Cu(L)$_2$ (**5**) (L = bis[(4R,5R)-4-methyl-5-phenyl-4,5-dihydro-thiazol-2-yl]-amine) prepared by template reactions from the optically active ligand (4R,5R)-4-methyl-5-phenyl-4,5-dihydro-thiazol-2-yl-amine (**1**) and $CoCl_2 \cdot 6H_2O$, $NiBr_2 \cdot 3H_2O$ or $Cu(OAc)_2 \cdot H_2O$ The template reactions involve the condensation of two molecules of thiazol-2-yl-amine and elimination of one NH_3. The resulting bidentate ligand coordinates to the metal ion through the imine nitrogen atoms forming a six-membered ring, presenting an electronic delocalization which averages the four M–N bond lengths. The distorted tetrahedral geometry of the metal atoms gives place to complex electronic spectra for compounds **3**–**5**. A mixed ionic compound (**6**) formed by three cations (4S,5S)-3,4-dimethyl-5-phenyl-thiazolidin-2-ylidene ammonium, one dianion *tris*-(thiocyano)bromide cobaltate and one bromide, obtained from reaction of (4S,5S)-3,4-dimethyl-5-phenyl-thiazolidin-2-ylidene ammonium thiocyanate (**2**) and $CoBr_2$ is also described. Compounds **3**–**6** were characterized in the solid state by UV–Vis–NIR and IR spectroscopy, mass spectrometry and X-ray diffraction analyses. Metal···H–C, S···H–C interactions were observed in **3**–**6**, whereas in **6**, also Br···H–N, Br···H–C and Br···S, S···S short contacts were found.

1. Introduction

Thiazoles have shown fungicide [1] and promising activity for the treatment of Alzheimer disease [2], their derivatives have an important role as nitric oxide synthase inhibitors [3–6] and have been used in the evaluation of possible glycosidase inhibitors [7–9]. They are also found in natural antibiotics, as is the case of micacocidin, which was isolated with Zn^{2+}, Cu^{2+} or Fe^{3+}, where the chelating groups are the imino nitrogens of the thiazole rings [10–13]. Thiazoline derivatives have been applied as ionic liquids, in chiral recognition and asymmetric synthesis [14,15]. Rhodium coordination compounds with chiral thiazolidines have been used as catalysts in asymmetric hydrosilation [16].

Herein we report the reactions of the 2-amino-thiazoles [(4R,5R)-4-methyl-5-phenyl-4,5-dihydro-thiazol-2-yl-amine (**1**) and (4S,5S)-3,4-dimethyl-5-phenyl-thiazolidin-2-ylidene ammonium thiocyanate (**2**)] with transition metal ions. We found that the metal atom induces the template condensation reaction of two 4,5-dihydro-thiazole molecules to give the bis[4,5-dihydrothiazol-2-yl]amine coordinated to the metal atom. To our knowledge, bis[4,5-dihydrothiazol-2-yl]amines have not been reported before, there are only two examples of their unsaturated analogues. One of them is the synthesis of bis[thiazol-2-yl]amine by a traditional method [17] and the other one is a patent [18] where compounds bearing three bis[thiazol-2-yl]amines coordinated to Co(III) are used as optical recording materials. The metallic template reactions to give bis(azolyl)-amines, as far as we know, have not been described before.

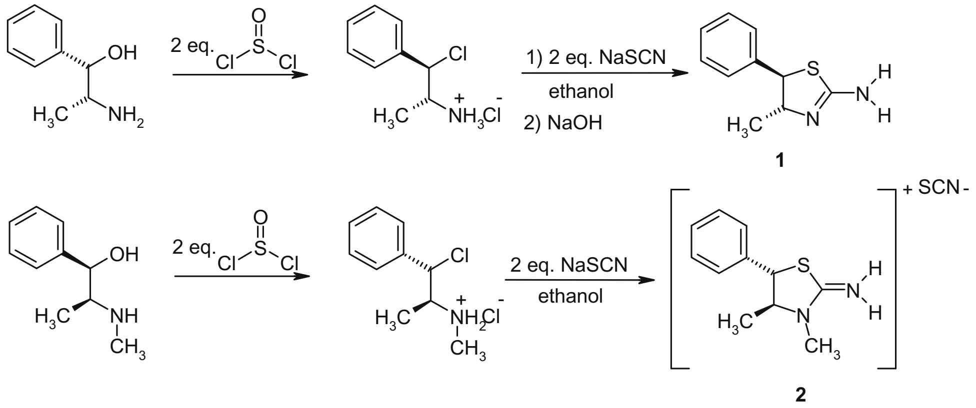
The synthesized compounds are optically active and therefore they could have possible application in asymmetric synthesis, as it has been found for zinc(II) and copper(II) coordination compounds derived from bis-oxazolidines, which are remarkable enantioselective catalysts on Friedel-Crafts or Michael reactions [19–23].

Compounds **1** and **2** were obtained in previous works [24–28], Scheme 1. They are prepared from the optically active ethanolamine, through the synthesis of the chloro derivatives, which afford the thiazolidine by reaction with NaCN. The reaction to obtain compound **1** gives a mixture of two diasteromers the *cis* and *trans* in 85–15 ratio. From crystallization in methanol, the *trans* isomer, is obtained pure. Compound **1** has an imine and a sulfur atom as possible coordination sites, whereas **2** is an ionic compound, where the cation has only a sulfur atom as a basic site. Both

---

* Corresponding authors.
E-mail address: norah@servidor.unam.mx (N. Barba-Behrens).

0277-5387/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2009.12.003



Scheme 1. Synthesis of compounds **1** and **2**.

heterocycles contain labile amine and iminium protons which can be substituted by heteroatoms generating more complex ligands [29,30]. Compounds **1** and **2** were used in the synthesis of novel transition metal compounds **3**–**6**, which were characterized in the solid state by UV–Vis–NIR reflectance and IR spectroscopy, mass spectrometry and X-ray diffraction analyses, Schemes 2 and 3.

2. Experimental

2.1. Physical measurements

FT IR spectra were recorded with a (Perkin–Elmer 1600) spectrophotometer using KBr pellets (4000–400 cm^{-1}). The UV–Vis–NIR spectra (diffuse reflectance, 40 000–4000 cm^{-1}) were recorded on a Cary-5E (Varian) spectrophotometer. High resolution mass spectra were obtained by LC/MSD TOF on Agilent Technologies instrument with APCI as ionization source. The fast atom bombardment mass spectra (FAB+ mass) were performed with a JEOL SX102A instrument with an inverted geometry, in a matrix of 3-nitrobenzyl alcohol, in the 0–2200 m/z range. NMR spectra were recorded on a JEOL GSX-270. Elemental analyses were carried out with a Fisons EA 1180 analyzer.

2.2. Materials

The inorganic salts $CoCl_2 \cdot 6H_2O$, $CoBr_2$, $NiBr_2 \cdot 3H_2O$, $Cu(OAc)_2 \cdot H_2O$ and methanol (J.T. Baker) were used without further purification.

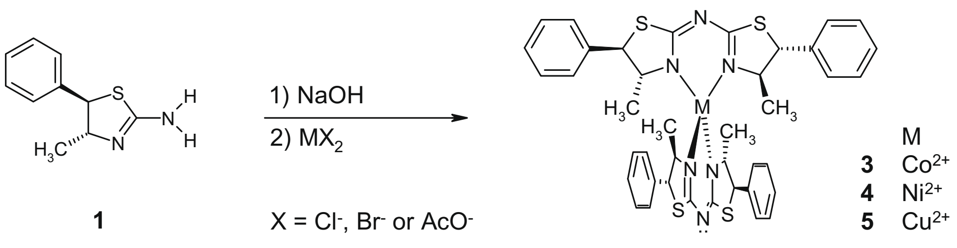
2.3. Synthesis

2.3.1. *(4R,5R)-4-Methyl-5-phenyl-4,5-dihydro-thiazol-2-yl-amine,* **1**

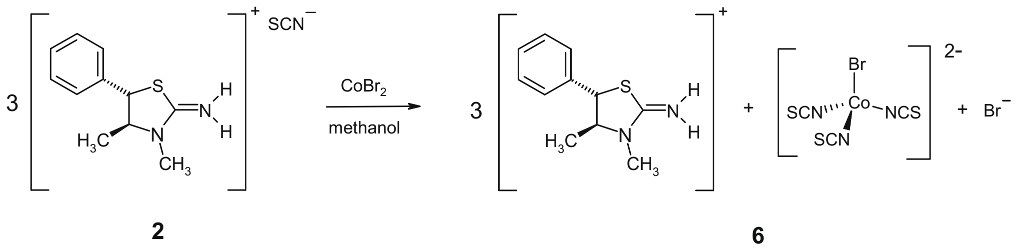
To obtain compound **1**, (1S,2R)-2-methyl-1-phenyl-ethanolamine (25 g, 165 mmol) was reacted with three equivalents of $SOCl_2$ (59 g, 36 mL), after maintaining the reaction mixture at 0° for 4 h, acetone was added (100 mL). (4R,5R)-(2-Chloro-1-methyl-2-phenyl-ethyl)-amine hydrochloride (yield 72%) was recovered as a white solid (24.59 g, 119 mmol). It was washed three times with acetone and then dissolved in ethanol. To this solution, NaSCN (19.29 g, 238 mmol) was added and the reaction mixture maintained under reflux for 4 h. The resultant NaCl was filtered off and the yellow solution concentrated to the half of its original volume under vacuum. Then NaOH (4.8 g, 119 mmol) was added. The reaction product is a 85:15 mixture of the *cis*:*trans* isomers, from this mixture the *trans* isomer (4R,5R) was isolated by crystallization in methanol as colorless needles (1.31 g, 4.1%). Mp. 151–153 °C with dec. NMR (methanol-d_3) ^1H δ: H_5 4.52 (d 6.7 Hz), H_4 4.25 (m), CH_3 1.32 (d 6.5 Hz), NH 4.99, aromatics 7.33 (m). ^{13}C δ: 169.7 (C=N), 141.8 (C_i), 130.2 (C_o), 129.2 (C_m), 129.4 (C_p), 71.4 (C–Ph), 60.8 (C–Me), 20.05 (CH_3). IR (KBr): ν_{max} [cm^{-1}] 3449 (N–H), 3352 (N–H), 1573 (C=N), 1452 (C–N), 698 (C–S). $[\alpha]_{CDCl_3} = -155$. MS: m/z 192 (95) $[M]^+$, 70(100), 177(93), 69(80), 57(69), 149(67). *Anal.* Calc. for $C_{10}H_{12}N_2S$: C, 62.47; H, 6.29; N, 14.57; S, 16.68. Found: C, 62.11; H, 6.32; N, 14.89; S, 17.34%.

2.3.2. *(4S,5S)-3,4-Dimethyl-5-phenyl-thiazolidin-2-ylidene ammonium thiocyanate,* **2**

An ethanolic solution (100 mL) of (1S,2S)-(2-chloro-1-methyl-2-phenyl-ethyl)-methylamine hydrochloride [5.05 g, 23 mmol, prepared from (1R,2S)-*N*-methyl-2-methyl-1-phenyl-ethanolamine] and NaSCN (3.72, 45.9 mmol) was refluxed for 8 h, then the precipitate was filtered and dissolved in ethanol. The solution was concentrated, and crystals were obtained (3.22 g, 53%). Mp. 165–168 °C. NMR (methanol-d_3) ^1H δ: H_5 4.92 (d 4.9 Hz), H_4 4.41 (m), CH_3 1.39 (d 6.3 Hz), N–CH_3 3.22 (s), aromatic 7.43 (m). ^{13}C δ: 32.80 (N–Me), C_4 69.77 C_5 53.39 CH_3 16.64 C_i 138.29, C_o 129.07, C_p 128.66, C_2 167.47. IR (KBr): ν_{max} [cm^{-1}] 3060 (N–H), 3029 (N–H), 1600 (C=N), 1493 (C–N), 1452 (C–N), 699 (C–S).



Scheme 2. Synthesis of coordination compounds **3**–**5**.



Scheme 3. Synthesis of the mixed ionic compound **6**.

2.3.3. Cobalt(II) compound **3**, general procedure

Compound **1** (96 mg, 0.5 mmol) was dissolved in methanol (50 mL) and a NaOH solution (1.1 ml, 0.25 M) was added. The mixture was stirred for 15 min followed by the addition of $CoCl_2 \cdot 6H_2O$ (30 mg, 0.125 mmol). The reaction mixture was set aside for 4 days. The coral colored solid was filtered off and redissolved in methanol. After slow evaporation of the solvent, red crystals of **3**, suitable for diffraction analyses were obtained (49 mg, 48%). Dec. at 145 °C. IR (KBr), ν_{max} [cm^{-1}] 1509 (C=N), 1473 (C–N), 698 (C–S). Mass FAB $C_{40}H_{40}N_6S_4Co + H^+$ 792. Mass + TOF calc. for $C_{40}H_{40}N_6S_4Co + H^+$ 792.1607, found: 792.1596. *Anal.* Calc. for $C_{40}H_{40}N_6S_4Co$: C, 60.66; H, 5.09; N, 10.61; S, 16.19. Found: C, 60.91; H, 5.32; N, 10.29; S, 16.35%.

2.3.4. Nickel(II) compound **4**

Following the same procedure for compound **3**. To a methanolic solution (50 mL) of compound **1** (96 mg, 0.5 mmol), a NaOH solution (1.1 mL, 0.25 M) and $NiBr_2 \cdot 3H_2O$ (33 mg, 0.125 mmol) were added. A light green solid was filtered and dissolved in acetone, crystallization from acetone afforded dark green crystals (54 mg, 55%). Dec. at 145 °C. I.R. (KBr) ν_{max} [cm^{-1}]: 1517 (C=N), 1467 (C–N), 698 (C–S). (Mass FAB $C_{40}H_{40}N_6S_4Ni + H^+$ 791, Mass + TOF calc. for $C_{40}H_{40}N_6S_4Ni + H^+$ 791.1629, found: 791.1633). *Anal.* Calc. for $C_{40}H_{40}N_6S_4Ni \cdot 4H_2O$: C, 55.62; H, 5.60; N, 9.73; S, 14.85. Found: C, 55.92; H, 5.40; N, 9.22; S, 14.05%.

2.3.5. Copper(II) compound **5**

Following the same procedure as for compound **3**. Compound **1** (96 mg, 0.5 mmol), methanol (50 mL), a NaOH solution (1.1 mL, 0.25 M) and $Cu(OAc)_2 \cdot H_2O$ (30 mg, 0.125 mmol) were added. Crystallization from methanol afforded dark green needles of compound **5** (20 mg, 20%). IR. (KBr) ν_{max} [cm^{-1}]: 1524 (C=N), 1475 (C–N), 698 (C–S). Mass + TOF calc. for $C_{40}H_{40}N_6S_4Cu + H^+$ 796.1571, found: 796.1574. *Anal.* Calc. for $C_{40}H_{40}N_6S_4Cu \cdot 2H_2O$: C, 57.70; H, 5.33; N, 10.09. S, 15.40. Found: C, 57.27; H, 4.96; N, 10.12; S, 14.75%.

2.3.6. Cobalt(II) compound **6**

Compound **2** (100 mg, 0.38 mmol) was dissolved in methanol (50 mL), followed by the addition of anhydrous $CoBr_2$ (83 mg,

Table 1
Crystal data, data collection and refinement details.

Chemical formula	$C_{40}H_{40}N_6S_4Co$(**3**)	$C_{40}H_{40}N_6S_4Ni$(**4**)	$C_{40}H_{40}N_6S_4Cu$(**5**)	$C_{14}H_{15}N_5S_4Br_2Co$(**6**)
Formula weight (g mol^{-1})	791.97	791.77	796.59	338.31
Crystal size (mm)	0.38 × 0.25 × 0.15	0.45 × 0.1 × 0.02	0.38 × 0.2 × 0.1	0.32 × 0.2 × 0.2
Crystal color	dark pink	dark green	dark green	blue
Crystal system	monoclinic	monoclinic	monoclinic	trigonal
Space group	$P2_1$	$P2_1$	$P2_1$	$P6_3$
a (Å)	9.1170(1)	9.0424(4)	9.15790(10)	15.4208(2)
b (Å)	12.7538(2)	12.6861(7)	12.6488(2)	15.4208(2)
c (Å)	17.2515(3)	17.2486(9)	17.2716(3)	10.9354(2)
α (°)	90.00	90.00	90.00	90.00
β (°)	97.435(1)	97.317(4)	98.2336(7)	90.00
γ (°)	90.00	90.00	90.00	120.00
V ($Å^3$)	1989.37(5)	1962.52(17)	1980.06(5)	2254.49
Z	2	2	2	6
D_{calc} (g/cm^3)	1.322	1.340	1.336	1.495
μ (mm^{-1})	0.678	0.744	0.799	2.468
F(0 0 0)	826	828	830	1034
T (K)	293	293	293	293
θ_{min}	1.19	3.07	1.19	3.05
θ_{max}	30.50	29.46	30.55	30.49
Index range	$-12 \leqslant h \leqslant 12$ $-18 \leqslant k \leqslant 17$ $-23 \leqslant l \leqslant 24$	$-11 \leqslant h \leqslant 11$ $-17 \leqslant k \leqslant 14$ $-22 \leqslant l \leqslant 21$	$-10 \leqslant h \leqslant 12$ $-18 \leqslant k \leqslant 18$ $-24 \leqslant l \leqslant 24$	$-21 \leqslant h \leqslant 21$ $-21 \leqslant k \leqslant 21$ $-15 \leqslant l \leqslant 15$
Reflections measured	26 236	10 516	36 255	46 305
Independent reflections	10 854	6799	24 472	4417
Reflections	7215 [$I > 3.0\sigma(I)$]	4983 [$I > 2.5\sigma(I)$]	11 025 [$I > 2.5\sigma(I)$]	3139 [$I > 2.5\sigma(I)$]
Number of parameters	581	491	581	179
R	0.037	0.031	0.0281	0.048
R_w	0.034	0.030	0.032	0.047
S	1.06	0.95	1.03	0.98
Maximum Δ/σ	0.001	0.000	0.001	0.000
$\Delta\rho$ Maximum (e $Å^3$)	0.39	0.33	0.44	0.47
$\Delta\rho$ minimum (e $Å^3$)	−0.50	−0.38	−0.54	−0.47
Flack parameter	0.00(1)	0.00(1)	0.00(1)	0.22(2)

$R_{int} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum F_o^2$, $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$.

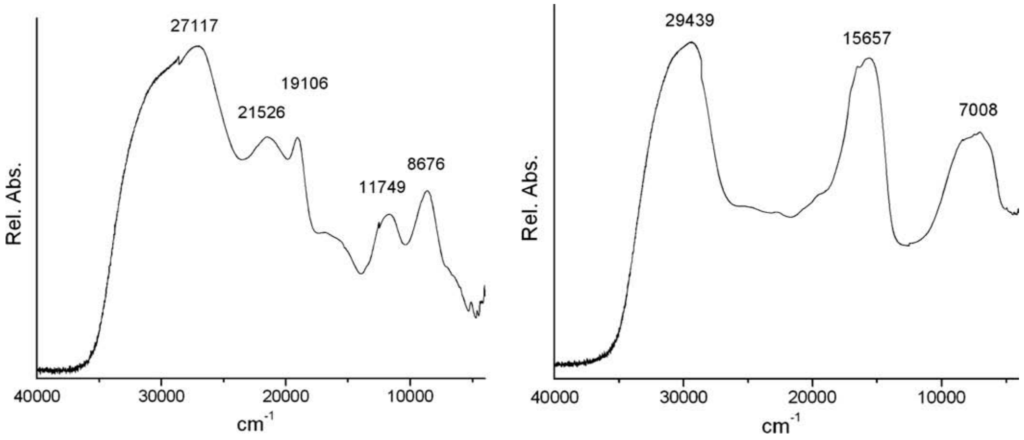


Fig. 1. (a) Tetrahedral cobalt(II) compound **3**, electronic transitions due to low symmetry effects; (b) electronic transitions for $[Co(SCN)_3Br]^{2-}$ in compound **6**.

0.38 mmol). The solution was stirred for 72 h. Solvent evaporation let blue crystals of compound **6** (20 mg, 16%). MS: *m*/*z* 207(12) $[M]^+$, 58(100), 118(78), 206(71), 117(66), 122(47). Mass + TOF calc. for $C_{10}H_{13}N_2S$ 207.0954, found: 207.0954. Mass – TOF calc. for $C_3N_3S_3Co$ 232.8586, found: 232.8592. *Anal.* Calc. for $C_{36}H_{45}N_9S_6CoBr_2{\cdot}HSCN$: C, 43.11; H, 4.79; N, 12.23; S, 18.66. Found: C, 43.51; H, 4.91; N, 12.13; S, 18.96%.

2.4. X-ray crystallographic study

Suitable single crystals of compounds **3**–**6** were mounted on a glass fiber and covered with a small amount of perfluoro ether oil. Data were collected at 293 K. Crystal data, data collection and structure refinement details are given in Table 1. All data were measured using standard procedures [31] on a Nonius Kappa CCD instrument with CCD area detector using graphite-monochromated Mo Kα radiation at 293 K. Intensities were measured using φ + ω scans. A summary of data collection and refinements is given in Table 1. All structures were solved using direct methods, using SHELX-97 [32] and the refinement (based on F^2 of all data) was performed by full-matrix least-squares techniques with Crystals 12.87 [33]. All non-hydrogen atoms were refined anisotropically. For compounds **3** and **5**, all hydrogen atoms were found in the difference map and their positions refined, while for compounds **4** and **6**, all hydrogen atoms were found in the difference map and allowed to ride on their respective atoms, except for H18, H24, H25, H35, H48, H51, H121, H193, H421 and H493 for compound **4** and H7, H8, H141 and H142 for compound **6**, whose coordinates were refined.

Table 2
Selected bond lengths (Å) for **3**–**5**.

	$C_{40}H_{40}N_6S_4Co$ (**3**)	$C_{40}H_{40}N_6S_4Ni$ (**4**)	$C_{40}H_{40}N_6S_4Cu$ (**5**)
Bond lengths			
(M1)–(N3)	1.969(2)	1.934(3)	1.959(2)
(M1)–(N9)	1.963(2)	1.935(2)	1.936(2)
(M1)–(N33)	1.950(2)	1.946(2)	1.938(2)
(M1)–(N39)	1.956(2)	1.943(3)	1.932(2)
(C2)–(N3)	1.310(4)	1.301(4)	1.293(4)
(C2)–(N6)	1.343(4)	1.338(4)	1.348(4)
(C8)–(N6)	1.334(4)	1.330(4)	1.335(4)
(C8)–(N9)	1.313(4)	1.305(4)	1.308(4)
(C32)–(N33)	1.305(3)	1.298(4)	1.304(4)
(C32)–(N36)	1.345(4)	1.343(5)	1.347(4)
(C38)–(N36)	1.338(3)	1.328(4)	1.337(4)
(C38)–(N39)	1.320(3)	1.297(4)	1.309(4)

3. Results and discussion

Reactions of compound **1** with cobalt(II) and nickel(II) halides or with copper(II) acetate, afforded compounds **3**–**5** (Scheme 2). The coordination compounds were prepared by a template reaction which involves condensation of one pair of 2-amino-thiazoles and elimination of one NH_3 molecule. In the coordination compounds **3**–**5**, the ligand forms three fused rings. The central ring is a six-membered metallocycle. Two ligands are bound to a metal atom, giving tetracoordinated metal centers.

The electronic spectra of the tetrahedral cobalt(II) **3** and nickel(II) **4** compounds merit some comments. As we will discuss below, the X-ray structures show that the metal ion geometry is far from a regular tetrahedron, giving place to several electronic transitions due to low symmetry effects, where the T terms, $^4T_2(F)$, $^4T_1(F)$ and $^4T_1(P)$, split into ^4E and ^4A, and the spin orbit coupling is a less important perturbation than the lower symmetry field [34]. For the orange cobalt(II) compound **3**, these electronic transitions were observed

Table 3
Selected bond angles (°) for **3**–**5**.

	$C_{40}H_{40}N_6S_4Co$ (**3**)	$C_{40}H_{40}N_6S_4Ni$ (**4**)	$C_{40}H_{40}N_6S_4Cu$ (**5**)
Bond angles			
(N3)–(M1)–(N9)	92.9(11)	90.6(1)	91.7(1)
(N3)–(M1)–(N33)	126.2(1)	123.5(1)	134.7(1)
(N3)–(M1)–(N39)	108.0(1)	107.6(1)	102.8(1)
(N9)–(M1)–(N33)	107.5(1)	107.1(1)	102.2(1)
(N9)–(M1)–(N39)	134.3(1)	141.6(1)	142.6(1)
(N33)–(M1)–(N39)	92.4(1)	90.8(1)	91.8(1)
(N3)–(C2)–(N6)	130.3(3)	130.4(3)	130.1(3)
(C2)–(N6)–(C8)	121.1(2)	119.0(3)	119.4(3)
(N6)–(C8)–(N9)	130.9(3)	130.5(3)	131.6(3)
(N33)–(C32)–(N36)	130.2(3)	129.9(3)	130.5(3)
(C32)–(N36)–(C38)	120.1(3)	119.6(3)	119.0(3)
(N36)–(C38)–(N39)	131.2(3)	130.7(3)	131.0(3)

Table 4
Selected data for $C_{12}H_{15}N_3SCoBr_2$ (**6**).

Bond lengths (Å)		Bond angles (°)	
Co15)–(N17)	1.97(1)	(Br16)–(Co15)–(N17)	109.6(2)
(Co15)–(Br16)	2.366(3)	(N9)–(C10)–(S11)	114.8(7)
(C10)–(N9)	1.32(1)	(N9)–(C10)–(N14)	124.8(7)
(C10)–(N14)	1.29(1)	(S11)–(C10)–(N14)	120.4(7)
(C10)–(S11)	1.728(7)	(C7)–(S11)–(C10)	92.0(4)
(C7)–(S11)	1.83(1)		

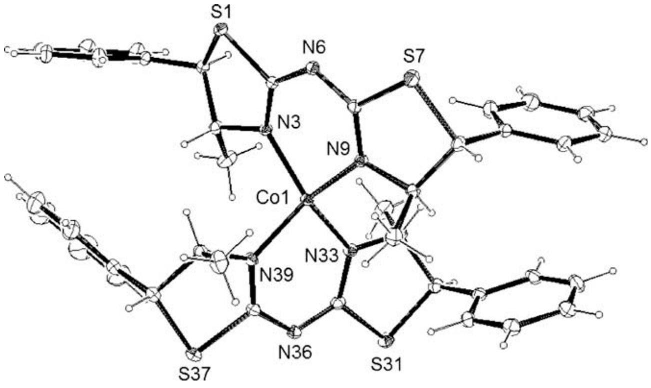
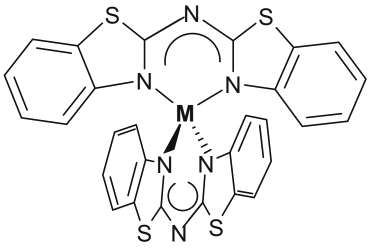


Fig. 2. Compound **3** ORTEP diagram with ellipsoids at 20% of probability.



Scheme 4. Coordination compounds derived from 2-(2-benzothiazolylamino)benzothiazole M^{2+} = Co, Ni, Zn, Hg [35].

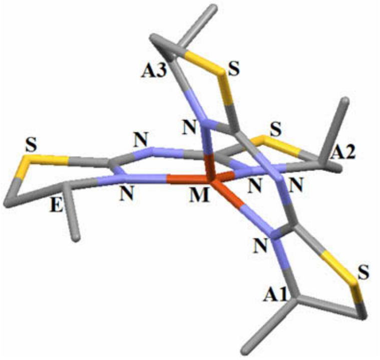
at 8676, 11 749, 19 106, 21 526 cm^{-1} and a broad charge transfer band at 27 117 cm^{-1} as shown in Fig. 1. In this figure, for comparison purposes, the electronic spectrum of the cobalt(II) compound **6** is included, which its X-ray structure will be discussed below. Compound **6** contains a cobaltate ion, $[Co(SCN)_3Br]^{2-}$, where the expected electronic transitions for a cobalt(II) center in a regular tetrahedral geometry, ν_2 $^4T_1(F) \leftarrow {}^4A_2(F)$ at 7008 cm^{-1} and ν_3 $^4T_1(P) \leftarrow {}^4A_2(F)$ at 15 657 cm^{-1}, are observed. Nickel(II) compound **4**, presents a similar tetrahedral low symmetry field spectrum, with electronic transitions at 6793, 8745, 11 991, 16 917, 21 292 cm^{-1} and a broad charge transfer band at 25 658 cm^{-1}. For the copper(II) compound **5**, transitions at 8646 and 15 714 cm^{-1}, and a broad charge transfer band at 23 796 cm^{-1}, are observed.

X-ray diffraction analyses of coordination compounds **3**–**5**, showed the same general structure. The metal atom is bound by two bis(thiazolyl)amines through the imine nitrogen atoms. Selected bond lengths and angles are summarized in Tables 2–4. Fig. 2 shows the atom numbering scheme of the cobalt(II) compound **3**.

In compounds **3**–**5**, the metal atom participates in two six-membered rings. The four metal–nitrogen bond lengths in each compound are similar and relatively short (from 1.93 to 1.97 Å), while the C–N bond lengths in the six-membered metallacycles vary from 1.29 to 1.34 Å in between single and double bonds (the average distance of C–N and C=N bonds is 1.33 Å), indicating an electronic delocalized π-system with the participation of the metal atom. The broad charge transfer band (10 000 cm^{-1}) in their electronic spectra also shows the electronic delocalization, as it has been observed in similar coordination compounds with six-membered delocalized metallacycles derived from 2-(2-benzothiazolylamino)benzothiazole [35], Scheme 4.

In these compounds, the pentacyclic aromatic systems are almost perpendicular, which is not the case, of the present compounds.

Molecules **3**–**5** are not symmetric. The four M–N bond lengths present small differences as well as the angles around the metal atoms. This effect is the result of a significant distortion, originated



M	Cu	Ni	Co
N_E-M-N_{A1}	142.6	141.7	134.3
N_{A1}-M-N_{A2}	102.2	107.5	107.5
N_E-M-N_{A3}	102.8	107.1	108.0
N_{A3}-M-N_{A2}	134.7	123.7	126.2

Fig. 3. Structure for the copper(II) compound **5**, showing the rings conformation. C–Me is marked as E for equatorial position and A for axial position. Hydrogen and phenyl groups have been omitted for clarity. The table shows the N–M–N angles in degrees for **3**–**5**.

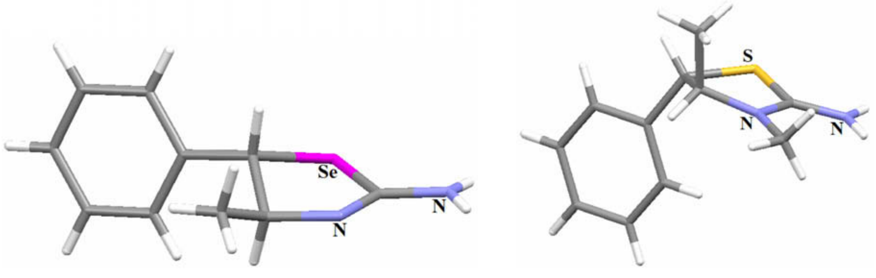


Fig. 4. X-ray diffraction structures of 4-methyl-5-phenyl-4,5-dihydro-selenazol-2-yl-amine (left) and (4S,5S)-3,4-dimethyl-5-phenyl-thiazolidin-2-yliden-ammonium ion (right) [25].

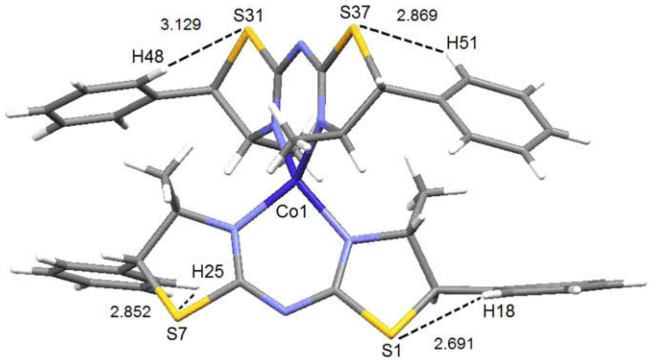


Fig. 5. Intramolecular S···H–C hydrogen bond distances in Å for compound **3**.

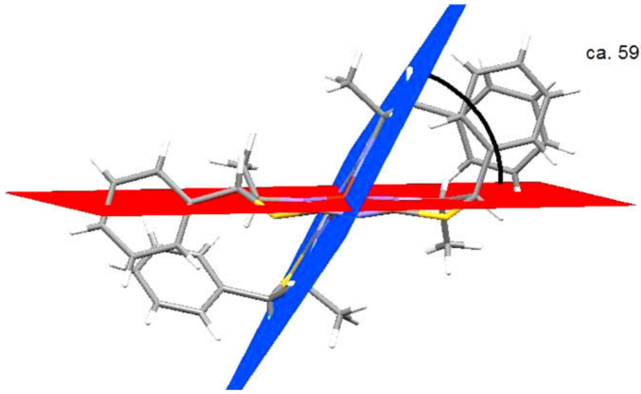


Fig. 7. Dihedral angle between the planes of the fused tricycles in compound **5**.

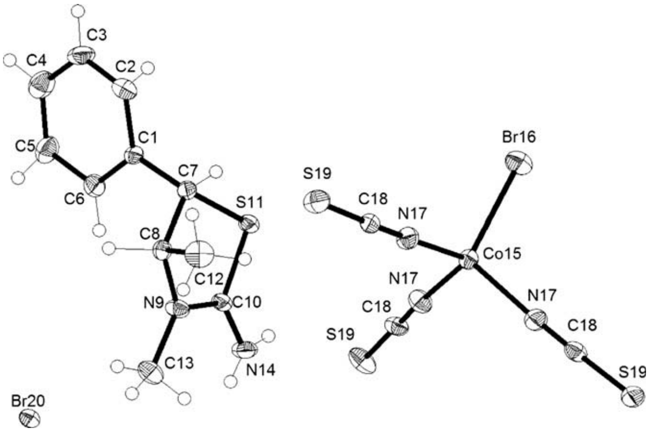


Fig. 8. Compound **6** ORTEP diagram with ellipsoids at 50% of probability.

by the thiazole rings conformation. The three compounds present the same conformational arrangement. Three of the thiazolyl rings in each compound presents two substituents (methyl and phenyl) in axial positions, whereas the fourth ring presents the substituents in equatorial position as is shown in Fig. 3 for the copper(II) compound. The equatorial C–Me is marked as E, the axial C–Me as A.

A possible explanation of this peculiar conformational behavior can be found from the comparison between the solid state structure of the selenium analogue of compound **1** and the thiazolidinium cation of compound **6** (Fig. 4).

In the thiazolidinium ion, the steric effect of the endocyclic N–Me group, which is in the ring plane, induces the C–Me and C–phenyl to adopt axial positions. On the other hand, in the selenium compound, the lack of a substituent at the endocyclic nitrogen atom drives the C–Me group to adopt an equatorial position. In compounds **3**–**5**, one ring may adopt the more favored conformation with the methyl and phenyl groups in equatorial positions, by opening the contiguous N_E–M–N_{A1} angle. However, for the other three rings, the steric effect makes their substituents to be in axial positions (Fig. 3). The fact that one of the four rings has a different conformation, explains the significant distortion in the discussed compounds.

The structure adopted by the compounds is driven by the rings conformation, which is also favored by different intramolecular hydrogen bonding interactions. In Fig. 5, S···H–C hydrogen bonds (between an *ortho* proton of the phenyl group and the sulfur atom) for compound **3** are shown, where the sulfur is acting as a Lewis base. The S···H contacts (2.69–3.13 Å) are similar or shorter than the reported distance of the highest incidence (3.21 Å) of this type of contacts [36]. Other hydrogen interactions are depicted in Fig. 6, where the three equatorial C–H protons have shorter distances than the sum of van der Waals radii ($\sum_{vdWr}$ C–H···M, M^{2+} = Ni, Co or Cu (2.0 (M) + 1.2 (H) = 3.2 Å [37]), indicating a hydrogen bonding interaction, while for the axial hydrogen (C–H, 3.286 Å) this interaction does not occur. Additionally, protons from the methyl groups may interact with the metal ions [38].

The tetrahedral distortion of the metal centers can be evaluated according to Houser and co-workers [39] as a seesaw geometry (λ_4 = 0.62, 0.67 and 0.70 for copper(II) **5**, nickel(II) **4** and cobalt(II) **3** compounds). The distortion is also appreciated from the dihedral angle between the planes of the fused tricycles. For cobalt(II) and

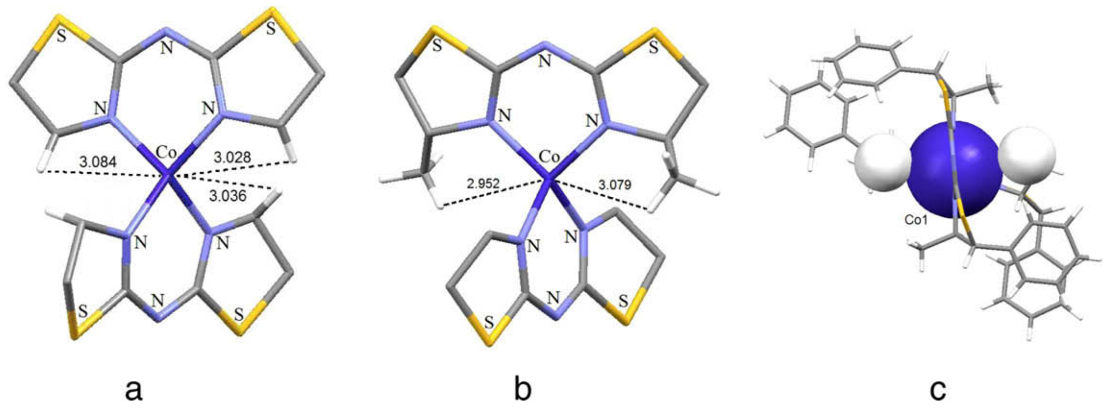


Fig. 6. Co···H–C hydrogen bond distances in Å for compound **3**, (a) and (b). Spacefill representation of (b) is depicted in (c).

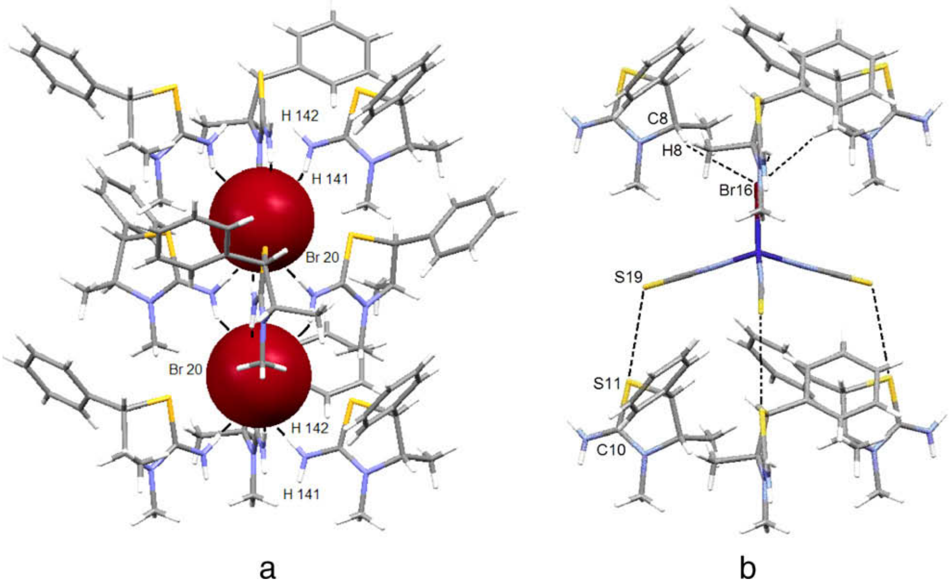


Fig. 9. Intermolecular N–H···Br^- (a) and C–H···Br^- (b) hydrogen bonds and S···S interactions (b) in compound **6**.

nickel(II) compounds, the dihedral angle between the planes described by the N–M bonds is near 70°, whereas in the copper(II) compound this angle is only 59° (Fig. 7).

The reaction of the thiocyanate salt **2** with $\mathrm{CoBr_2}$ in methanol gave blue crystals of compound **6**, which is a mixed ionic compound (Scheme 3). X-ray diffraction analysis for this compound shows three thiazol-2-ylidin ammonium cations, a bromide ion and a tetrahedral cobaltate dianion. The latter has three thiocyanate groups and one bromide, Fig. 8. This compound presents diverse intermolecular interactions which are described below.

The Co–N (1.97(1) Å) and Co–Br (2.366(3) Å) bond lengths indicate a strong coordination of the thiocyanate and the bromide to the cobalt(II) atom, Table 4. The uncoordinated bromide is in close contact with six N–H protons (2.59–2.83 Å), forming a slightly irregular trigonal antiprism arrangement, with the bromide ion is in its center. Sulfur–bromide short contacts are also present, where the sulfur atom acts as a Lewis acid and the bromide anion as an electron donor (Fig. 9a).

Sulfur–sulfur interactions are important in the structural stabilization of crystalline arrangements of thiazolidines [40]. In the present compound, three thiazolidine rings are interacting with one cobaltate molecule. These are strong interactions, due to their almost perfect alignment and distance (3.44 Å), which is shorter than the sum of the van der Waals radii ($\sum_{\mathrm{vdWr}}$ 3.6 Å, [34]). In Fig. 9b, this type of contacts is shown, where the thiazolidine S11, behaves as an electron acceptor, while the cobaltate S19, as an electron donor [41–42]. In this way, the sulfur–sulfur interactions, together with Br–H bonds (2.9 Å) constitute a columnar motive of alternating thiazolidines and cobaltate dianions.

4. Summary

Novel polydentate enantiomerically pure ligands were obtained by metal template reactions. Condensation of two molecules of the (4R,5R)-4-methyl-5-phenyl-4,5-dihydro-thiazol-2-yl-amine, in the presence of cobalt(II), nickel(II) and copper(II) ions, gave the corresponding coordination compounds **3**–**5**. These transition metals compounds have in common a planar electronic delocalized six-membered metallaring, where the metal ions show a great distortion from a regular tetrahedral geometry, originating complex electronic spectra. Two conformations for the bis-thiazolyl ligand are stabilized in the coordination compounds, where one ligand has both heterocycles with the phenyl and methyl groups in axial positions, while the second ligand has a heterocycle with these groups in equatorial positions, and on the other one, in axial positions. A mixed ionic compound formed by three (4S,5S)-3,4-dimethyl-5-phenyl-thiazolidin-2-ylidene ammonium cations, one *tris*-(thiocyano)bromide cobaltate dianion and one bromide, obtained from reaction of (4S,5S)-3,4-dimethyl-5-phenyl-thiazolidin-2-yliden-ammonium thiocyanate (**2**) and $\mathrm{CoBr_2}$ is described. Metal···H–C, S···H–C interactions were observed in **3**–**6**, whereas in **6**, also Br···H–N, Br···H–C and Br···S, S···S short contacts were found.

5. Supplementary data

CCDC 741947, 741948, 741949 and 741950 contains the supplementary crystallographic data for **3**, **4**, **5** and **6**. 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) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

R.R. thanks for the post-doctoral DGAPA-UNAM fellow scholarship. J.A.P.-H. thanks the Conacyt scholarship. E.M. post-doctoral scholarship from Conacyt-060894. Financial support by DGAPA IN206707 and Conacyt-060894 is acknowledged.

References

[1] M. Kaeriyama, S. Suga, A. Hashimoto, S. Sakai, Jpn. Kokai Tokkyo Koho (1983). CODEN: JKXXAF JP 58157794 A 19830919 Showa. CAN 100:103397 AN 1984:103397.

[2] N. Kobayashi, K. Ueda, N. Itoh, S. Suzuki, G. Sakaguchi, A. Kato, A. Yukimasa, A. Hori, Y. Kooriyama, H. Haraguchi, K. Yasui, Y. Kanda, PCT Int. Appl. (2008) 2. CODEN: PIXXD2 WO 2008133273 A1 20081106 CAN 149:534229 AN 2008:1339943.

[3] K. Shankaran, K.L. Donelly, S.K. Shah, R.N. Guthikonda, M. MacCoss, J.L. Humes, S.G. Pacholok, S.K. Grant, T.M. Kelly, K.K. Wong, Bioorg. Med. Chem. Lett. 14 (2004) 4539.

[4] A.A. Mandrugin, T.P. Trofimova, V.M. Fedoseev, S.Y. Proskuryakov, L.I. Shtein, A.N. Proschin, A.N. Pushin, Pharm. Chem. J. 41 (2007) 640.

[5] T. Castaño, A. Encinas, C. Pérez, A. Castro, N.E. Campillo, C. Gil, Bioorg. Med. Chem. 16 (2008) 6193.
[6] H. Li, C.S. Raman, P. Martásek, V. Král, B.S.S. Masters, T.L. Poulos, J. Inorg. Biochem. 81 (2000) 133.
[7] S. Knapp, D. Vocadlo, Z. Gao, B. Kirk, J. Lou, S.G. Withers, J. Am. Chem. Soc. 118 (1996) 6804.
[8] G.E. Whitworth, M.S. Macauley, K.A. Stubbs, R.J. Dennis, E.J. Taylor, G.J. Davies, I.R. Greig, D.J. Vocadlo, J. Am. Chem. Soc. 129 (2007) 635.
[9] T.K. Ritter, C.H. Wong, Tetrahedron Lett. 42 (2001) 615.
[10] S. Kobayashi, H. Nakai, Y. Ikenishi, Y. Sun, M. Ozaki, Y. Hayase, R. Takeda, J. Antibiot. 51 (1998) 328.
[11] S. Kobayashi, S. Hidaka, Y. Kawamura, M. Ozaki, Y. Hayase, J. Antibiot. 51 (1998) 323.
[12] A. Ino, Y. Hasegawa, A. Murabayashi, Tetrahedron Lett. 39 (1998) 3509.
[13] A. Ino, A. Murabayashi, Tetrahedron 55 (1999) 10271.
[14] J. Levillain, G. Dubant, I. Abrunhosa, M. Gulea, A.C. Gaumont, Chem. Commun. (2003) 2914.
[15] P. Wasserscheid, A. Bösmann, C. Bolm, Chem. Commun. (2002) 200.
[16] H. Li, J. Yao, B. He, Sci. China, B: Chem. 40 (1997) 485.
[17] H. Beyer, G. Berg, Chem. Ber. 89 (1956) 1602.
[18] R. Takahashi, K. Kunimoto, P. Sutter, U. Lehmann, PCT Int. Appl. (2005) 2. CODEN: PIXXD2 WO 2005081239, A1 20050901, CAN 143:257116, AN 2005:962534.
[19] W. Zhuang, T. Hansen, K.A. Jørgensen, Chem. Commun. (2001) 347.
[20] K.B. Jensen, J. Thorhauge, R.G. Hazell, K.A. Jørgensen, Angew. Chem., Int. Ed. 40 (2001) 160.
[21] J. Zhou, Y. Tang, Chem. Commun. (2004) 432.
[22] S. Yamazaki, Y. Iwata, J. Org. Chem. 71 (2006) 739.
[23] R. Rasappan, M. Hager, A. Gissibl, O. Reiser, Org. Lett. 8 (2006) 6099.
[24] A. Cruz, I.I. Padilla-Martínez, E.V. García-Báez, R. Contreras, Tetrahedron Asymmetry 18 (2007) 123.
[25] R. Ramírez-Trejo, Ph.D. Thesis, Cinvestav México, 2005.
[26] A. Cruz, D. Macías-Mendoza, E. Barragán-Rodríguez, H. Tlahuext, H. Nöth, R. Contreras, Tetrahedron Asymmetry 8 (1997) 3903.
[27] A. Cruz, A. Flores-Parra, H. Tlahuext, R. Contreras, Tetrahedron Asymmetry 6 (1995) 1933.
[28] A. Flores-Parra, P. Suarez-Moreno, S.A. Sánchez-Ruíz, M. Tlahuextl, R. Sálas-Coronado, A. Cruz, H. Nöth, R. Contreras, Tetrahedron Asymmetry 9 (1998) 1661.
[29] E.V. Bakhmutova, H. Nöth, R. Contreras, B. Wrackmeyer, Z. Anorg. Allg. Chem. 627 (2001) 1846.
[30] E.V. Bakhmutova, A. Cruz, R. Ramírez-Trejo, R. Contreras, B. Wrackmeyer, Magn. Reson. Chem. 39 (2001) 739.
[31] Siemens, XSCAnS (release 2.21) Users Manual, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1996.
[32] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
[33] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, J. Appl. Crystallogr. 36 (2003) 1487.
[34] A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, Amsterdam, 1984.
[35] F. Téllez, A. Peña-Hueso, N. Barba-Behrens, R. Contreras, A. Flores-Parra, Polyhedron 25 (2006) 2363.
[36] J.A. van den Berg, K.R. Seddon, Cryst. Growth Des. 3 (2003) 643.
[37] S.S. Batsanov, Inorg. Mater. 37 (2001) 871.
[38] M. Brookhart, M.L.H. Green, G. Parkin, Proc. Natl. Acad. Sci. USA 17 (2007) 6908.
[39] L. Yang, D.R. Powell, R. Houser, Dalton Trans. 2 (2007) 955.
[40] D.E. Lynch, Acta Crystallogr., Sect. C C60 (2004) o677.
[41] F. Téllez, A. Cruz, A.H. López-Sandoval, I. Ramos-García, M. Gayosso, R. Castillo-Sierra, B. Paz-Michel, H. Nöth, A. Flores-Parra, R. Contreras, Eur. J. Org. Chem. (2004) 4203.
[42] A. Esparza-Ruiz, A. Peña-Hueso, J. Hernández-Díaz, A. Flores-Parra, R. Contreras, Cryst. Growth Des. 7 (2007) 2031.