Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 24 (2005) 129–136

ELSEVIER

POLYHEDRON

www.elsevier.com/locate/poly

Pseudotetrahedral cobalt(II) complexes with thiazoline and thiazine derivative ligands: synthesis and characterization

F.J. Barros-García, A. Bernalte-García *, A.M. Lozano-Vila, F. Luna-Giles, E. Viñuelas-Zahínos

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Extremadura, 06071 Badajoz, Spain

Received 7 September 2004; accepted 25 October 2004
Available online 8 December 2004

Abstract

The cobalt(II) complexes dichloro[2-(3,4-dichlorophenyl)imino-κN-N-(2-thiazolin-κN-2-yl)thiazolidine]cobalt(II) (**1**) and dichloro[2-(3,4-dichlorophenyl)imino-κN-N-(2-thiazin-κN-2-yl)thiazolidine]cobalt(II) (**2**) have been isolated and characterized in the solid state by X-ray diffraction, elemental analysis, IR spectra, magnetic measurements and UV–Vis–NIR diffuse reflectance spectroscopy. In both complexes, the environment around the cobalt(II) ion may be described as a distorted tetrahedral geometry, with the metallic atom coordinated to two chlorine atoms [Co–Cl(1) = 2.213(1) Å; Co–Cl(2) = 2.226(1) Å], one imino nitrogen [Co–N(3) = 1.992(2) Å] and one thiazoline nitrogen [Co–N(1) = 1.974(2) Å] in complex **1** and to two chlorine atoms [Co–Cl(1) = 2.244(2) Å; Co–Cl(2) = 2.226(1) Å], one imino nitrogen [Co–N(3) = 1.970(4) Å] and one thiazine nitrogen [Co–N(1) = 1.946(4) Å] in complex **2**.

Keywords: Crystal structures; Cobalt(II) complexes; Thiazoline; Thiazolidine; Thiazine

1. Introduction

Multidentate ligands containing N,N donors are extensively used in coordination chemistry with the aim of obtaining new frameworks having potential bioactivity [1]. Among these ligands, thiazoline and thiazine derivative ligands have attracted our attention due to their biological and pharmaceutical activity. The use of compounds containing thiazine, thiazoline or/and thiazolidine rings as antitumoral, analgesic, antibiotic, antiviral, antihistamine, anti-HIV, antiinflammatory and sedative agents, is well known [2–9]. In some cases, the structural and biological properties of the corresponding coordination compounds are more noteworthy than those of the ligands [10].

The synthesis of new siderophore analogues constitutes another pharmacological application example. Microbial siderophores are relatively low molecular weight compounds synthesized in order to solubilize and transport iron (III) into the procariotes cells in the necessary concentrations. New siderophore analogues are prototypes for the synthesis of chelating agents employed for clinical use [11]. Thus, there have been characterized siderophores containing thiazoline and thiazine rings that have been used in the treatment of acute iron poisoning and in chronic iron overload resulting from transfusion therapy of β-thalasemia [12].

Because of the aforementioned, recently we have been investigating the coordination chemistry of compounds containing these heterocycles [13–17]. As a continuation of this research, we report here the synthesis and characterization by elemental analysis, infrared spectra (IR), ultraviolet and visible spectra (UV–Vis), proton nuclear

---

* Corresponding author. Tel.: +34 924 289394; fax: +34 924 289395.
E-mail address: alberga@unex.es (A. Bernalte-García).

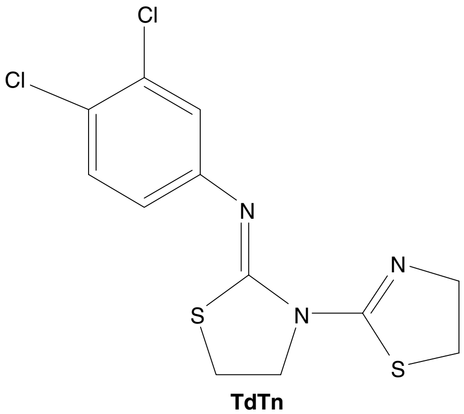
0277-5387/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2004.10.011

magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) of the ligand TdTz [TdTz = 2-(3,4-dichlorophenyl)imino-N-(2-thiazin-2-yl)-thiazolidine]. Likewise, the cobalt(II) complexes [$CoCl_2$(TdTn)] [TdTn = 2-(3,4-dichlorophenyl)imino-N-(2-thiazolin-2-yl)thiazolidine] and [$CoCl_2$(TdTz)] have been isolated and their characterization has been carried out by means of single crystal X-ray diffraction, elemental analysis, spectroscopic and magnetic measurements.

2. Experimental

2.1. Preparation of 2-(3,4-dichlorophenyl)imino-N-(2-thiazolin-2-yl)thiazolidine (TdTn)

The preparation of TdTn has been carried out as described by Outcalt et al. [18]. ^{1}H NMR (deuteriochloroform): δ 7.37 (d, $J = 8.49$ Hz, 1H), 7.10 (d, $J = 2.45$ Hz, 1H), 6.85 (dd, $J = 2.45$, 2.49 Hz, 1H), 4.33 (t, $J = 7.05$ Hz, 2H), 4.01 (t, $J = 8.28$ Hz, 2H), 3.28 (t, $J = 7.05$ Hz, 2H), 3.23 (t, $J = 8.16$ Hz, 2H); ^{13}C NMR (deuteriochloroform): δ 157.58, 155.68, 148.73, 132.47, 130.53, 127.29, 123.30, 120.89, 57.27, 51.30, 33.87, 26.74. *Anal.* Calc. for $C_{12}H_{11}Cl_2N_3S_2$: C, 43.38; H, 3.34; N, 12.64; S, 19.30. Found: C, 43.44; H, 3.36; N, 12.71; S, 18.95%. UV–Vis (EtOH): λ_{max}, nm; (ε, l mol^{-1} cm^{-1}) 205 (35 087), 239 (17 542), 289 (12 351).

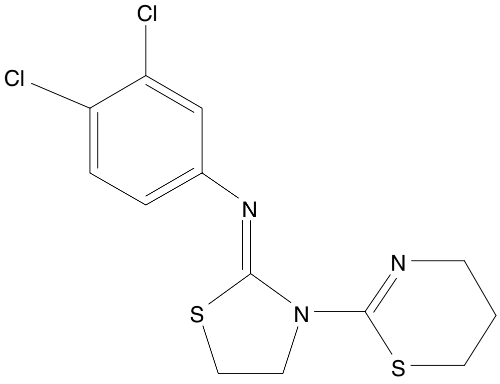


TdTn

2.2. Preparation of 2-(3,4-dichlorophenyl)imino-N-(2-thiazin-2-yl)thiazolidine (TdTz)

A solution of 2.01 g (8.1 mmoles) of 2-(3,4-dichlorobenzylamino)-2-thiazoline (that was obtained by the method of Fanta and Deutsch [19] and by the method of Outcalt et al. [18]) and 1.38 g (10.2 mmoles) of 3-chloropropylisothiocyanate [20] in 30 ml of toluene was stirred and heated to reflux for 4 h. At this point, a white precipitate had separated out and the reaction mixture was allowed to cool to room temperature. A solution of 1.62 g (15.3 mmoles) of sodium carbonate in 20 ml of water was added and the mixture was stirred until dissolution of the solid was complete. The phases were separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give a solid that was recrystallized from ethanol 96% (1.5 g; 53%).

^{1}H NMR (deuteriochloroform): δ 7.32 (d, $J = 8.76$ Hz, 1H), 7.07 (d, $J = 2.24$ Hz, 1H), 6.80 (dd, $J = 2.24$, 8.76 Hz, 1H), 4.19 (t, $J = 7.04$ Hz, 2H), 3.72 (t, $J = 5.62$ Hz, 2H), 3.15 (t, $J = 7.01$ Hz, 2H), 2.95 (t, $J = 6.01$ Hz, 2H), 1.90 (m, $J = 5.88$ Hz, 2H); ^{13}C NMR (deuteriochloroform): δ 156.48, 149.61, 148.31, 132.32, 130.42, 126.86, 123.37, 121.03, 51.42, 46.46, 27.07, 26.46, 20.64. *Anal.* Calc. for $C_{13}H_{13}Cl_2N_3S_2$: C, 45.09; H, 3.78; N, 12.13; S, 18.52. Found: C, 45.26; H, 3.78; N, 11.82; S, 18.07%. UV–Vis (EtOH): λ_{max}, nm; (ε, l mol^{-1} cm^{-1}) 205 (35 140), 247 (19 059), 292 (10 833).



TdTz

2.3. Preparation of [$CoCl_2$(TdTn)]

This complex was isolated from a freshly prepared ethanol solution (1 ml) of $CoCl_2 \cdot 6H_2O$ (71.6 mg, 0.3 mmol) that was added to an ethanol solution (15 ml) of TdTn (100 mg, 0.3 mmol). The resulting solution was allowed to evaporate slowly at room temperature. After a few days, blue crystals were isolated from the solution (124 mg, 89.2%). The crystals were separated by filtration, washed with cold ether and air-dried. *Anal.* Calc. for $C_{12}H_{11}Cl_4CoN_3S_2$: C, 31.19; H, 2.40; N, 9.09; S, 13.88. Found: C, 31.33; H, 2.42; N, 8.97; S, 14.37%.

2.4. Preparation of [$CoCl_2$(TdTz)]

This complex was prepared by reacting an ethanol solution (1 ml) of $CoCl_2 \cdot 6H_2O$ (68.7 mg, 0.3 mmol) with an ethanol solution (15 ml) of TdTz (100 mg, 0.3 mmol), blue crystals being obtained after a slow evaporation of the solution at room temperature (96.5 mg, 67.5%). The crystals were filtered, washed with cold ether and air-dried. *Anal.* Calc. for $C_{13}H_{13}Cl_4CoN_3S_2$: C, 32.79; H, 2.75; N, 8.82; S, 13.47. Found: C, 32.76; H, 2.74; N, 8.58; S, 12.93%.

2.5. Instrumental procedures

Chemical analyses of carbon, hydrogen, nitrogen and sulfur were performed by microanalytical methods using a Leco CHNS-932 microanalyser. IR spectra were recorded on a Perkin–Elmer FT-IR 1720 spectrophotometer, from KBr pellets in the 4000–370 cm^{-1} range and on a Perkin–Elmer FT-IR 1700X spectrophotometer, from polyethylene pellets in the 500–150 cm^{-1} range. Electronic spectra of the ligands in solution were measured on a Shimadzu UV-3101 PC using a 10 mm quartz cell. UV–Vis–NIR reflectance spectra for complexes in the 200–2000 nm range were obtained from a pellet of the samples, using a Shimadzu UV-3101 PC spectrophotometer and $BaSO_4$ as a reference. Magnetic measurements were made at room temperature on a magnetometer with a pendulum MANICS DSM8, equipped with a helium continuous-flow cryostat and an electromagnetometer DRUSCH EAF 16 UE. Data were corrected for temperature-independent paramagnetism and diamagnetic contributions, which were estimated from Pascal constants. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AM 400 instrument at 400 and 100 MHz, respectively, in $CDCl_3$ using Me_4Si as internal standard.

2.6. Crystal structure determinations

Experimental details of the crystal structure determinations including crystal data, data collection, structure determination and refinement for complexes **1** and **2** are listed in Table 1. X-ray diffraction measurements were

Table 1
Crystal data, data collection and refinement details for $[CoCl_2(TdTn)]$ (**1**) and $[CoCl_2(TdTz)]$ (**2**)

	$[CoCl_2$ (TdTn)] (**1**)	$[CoCl_2(TdTz)]$ (**2**)
Crystal shape	prism	prism
Colour	blue	blue
Size (mm)	0.34 × 0.18 × 0.14	0.50 × 0.32 × 0.13
Chemical formula	$C_{12}H_{11}Cl_4CoN_3S_2$	$C_{13}H_{13}Cl_4CoN_3S_2$
Formula weight	462.09	476.11
Crystal system	monoclinic	monoclinic
Space group	*P2₁/a*	*Cc*
Unit cell dimensions		
a (Å)	9.699(1)	7.637(1)
b (Å)	17.336(1)	18.273(2)
c (Å)	10.825(1)	13.709(1)
β (°)	104.06(1)	101.54(1)
Cell volume ($Å^3$)	1765.4(2)	1874.3(3)
Z	4	4
T (K)	298(2)	298(2)
D_{calc} (g cm^{-3})	1.739	1.687
μ (mm^{-1})	1.810	1.708
F (0 0 0)	924	956
Diffractometer	Bruker SMART CCD	Bruker SMART CCD
Radiation	Mo-Kα ($\lambda = 0.71073$Å)	Mo-Kα ($\lambda = 0.71073$ Å)
Collection method	ϕ–ω	ϕ–ω
2θ Range	3.8–56.6	5.4–51.4
Index ranges	$-10 \leqslant h \leqslant 12$, $-22 \leqslant k \leqslant 22$, $-12 \leqslant l \leqslant 14$	$-6 \leqslant h \leqslant 9$, $-22 \leqslant k \leqslant 21$, $-16 \leqslant l \leqslant 14$
Independent reflections	4222	2298
Observed reflections	3220 [$F > 4.0\sigma(F)$]	2230 [$F > 4.0\sigma(F)$]
Absorption correction	empirical	empirical
Maximum/minimum transmission	0.7857/0.5781	0.8085/0.4822
Number of refined parameters	199	208
R [$I > 2\sigma(I)$][a]	0.0347	0.0317
wR [all data][b]	0.0875	0.0844
GOF[c]	1.027	1.060
ρ_{max}, ρ_{min} (e $Å^{-3}$)	0.824, −0.679	0.267, −0.260

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$.

[b] $wR = \left\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\right\}^{1/2}$.

[c] The goodness-of-fit (GOF) equals $\left\{\sum[w(F_o^2 - F_c^2)^2]/(N_{rf\ln s} - N_{params})\right\}^{1/2}$.

performed using a Bruker SMART CCD diffractometer. The first fifty frames were recollected at the end of the data collection to monitor for decay. Absorption corrections were applied using the program SADABS. The structures were solved by direct methods and subsequent Fourier differences using the WINGX package [21] and refined by full-matrix least-squares. The H atoms were placed from a differential Fourier synthesis and included in the final refinement cycles in calculated positions.

3. Results and discussion

3.1. Description of the crystal structures

3.1.1. [CoCl$_2$(TdTn)] (**1**)

The structure of **1** consists of discrete neutral monomeric units in which the environment around the cobalt(II) atom may be described as a distorted tetrahedral geometry. The metallic atom is coordinated by two chlorine atoms [Co–Cl(1) = 2.213(1) Å; Co–Cl(2) = 2.226(1) Å], one thiazoline nitrogen [Co–N(1) = 1.974(2) Å] and one imino nitrogen [Co–N(3) = 1.992(2) Å]. A diagram of the molecular structure and the atom numbering system used is shown in Fig. 1. The most relevant bond lengths and angles are given in Table 2.

The Co–Cl bond lengths are similar and comparable to the calculated average value [2.240(26) Å] for 100 tetrahedral cobalt(II) complexes with a chromophore group CoCl$_2$N$_2$, obtained from CONQUEST software [22] from the Cambridge Structural Database (CSD) [23]. Likewise, the Co–N$_{\text{imino}}$ bond distance is slightly shorter than the mean value [2.027(24) Å] calculated for 16 cobalt(II) complexes with an Cl$_2$N$_2$ environment collected in the CSD. The Co–N$_{\text{thiazoline}}$ bond distance is closer to that found in [CoCl$_2$(PyTT)] (1.982 Å) [13], but shorter than those observed in [Co(2,2′-bithiazoline)-(N$_3$)$_2$]$_n$ (average 2.155 Å) [24]. The ligand–metal–ligand bite angles differ from the ideal value of 109.5°, varying between 116.6(1)° [Cl(1)–Co–N(3)] and 90.8(1)° [N(3)–Co–N(1)].

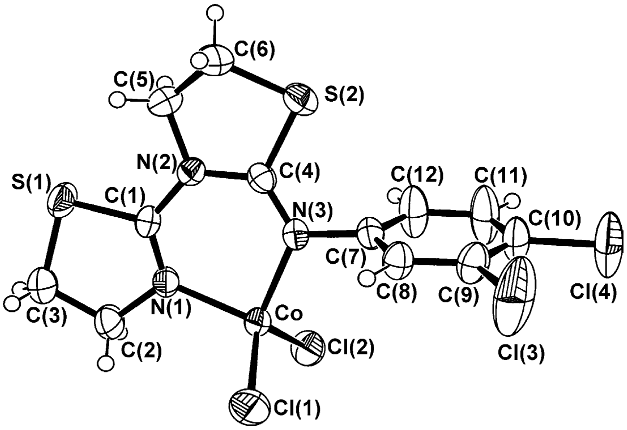


Fig. 1. Molecular structure of [CoCl$_2$(TdTn)] (**1**), showing the atom numbering scheme. The thermal ellipsoids are drawn at the 50% level.

Table 2
Selected bond lengths (Å) and bond angles (°) for [CoCl$_2$(TdTn)] (**1**)

Bond lengths			
Co–Cl(1)	2.213(1)	Co–Cl(2)	2.226(1)
Co–N(1)	1.974(2)	Co–N(3)	1.992(2)
C(1)–N(1)	1.280(3)	N(2)–C(4)	1.381(3)
N(2)–C(1)	1.382(3)	C(7)–N(3)	1.445(3)
C(4)–N(3)	1.292(3)		
Bond angles			
Cl(1)–Co–Cl(2)	114.4(4)	Cl(1)–Co–N(3)	116.6(1)
Cl(2)–Co–N(3)	109.4(1)	Cl(1)–Co–N(1)	108.7(1)
Cl(2)–Co–N(1)	114.8(1)	N(3)–Co–N(1)	90.8(1)
C(4)–N(2)–C(1)	126.4(2)	N(2)–C(4)–N(3)	124.5(2)
Co–N(3)–C(4)	126.3(2)	Co–N(3)–C(7)	115.5(2)
C(4)–N(3)–C(7)	118.1(2)	Co–N(1)–C(1)	126.9(2)
C(1)–N(1)–C(2)	112.6(2)	N(2)–C(1)–N(1)	125.0(2)
N(3)–C(4)–N(2)	124.5(2)		

The six-membered chelate ring Co–N(1)–C(1)–N(2)–C(4)–N(3) is essentially planar with maximum mean-plane deviation for C(4) (0.020 Å). In the organic ligand, the values of the puckering parameters for the 2-thiazoline ring, calculated according to Cremer and Pople [25], are q = 0.143 Å and ϕ = 251.2°, whereas for the thiazolidine ring these are q = 0.330 Å and ϕ = 289.3°. These values indicate that both five-membered rings show a conformation near to envelope, with the apex at C(3) [deviating 0.230 Å from the plane formed by S(1)–C(1)–N(1)–C(2), maximum mean plane deviation for N(1) = 0.001 Å] for the 2-thiazoline ring, and at C(6) [deviating 0.514 Å from the plane formed by S(2)–C(4)–N(2)–C(5), maximum mean plane deviation for N(2) = 0.004 Å] for the thiazolidine ring.

3.1.2. [CoCl$_2$(TdTz)] (**2**)

The X-ray study revealed that the crystals of **2** are made up of monoclinic unit cells, each containing four complex molecules. A diagram of the molecular structure and the atom numbering system used is shown in Fig. 2. Selected bond lengths and angles are given in Table 3.

The cobalt(II) is bound to two chlorine atoms [Co–Cl(1) = 2.244(2) Å; Co–Cl(2) = 2.226(1) Å], one thiazine nitrogen [Co–N(1) = 1.946(4) Å] and one imino nitrogen [Co–N(3) = 1.970(4) Å] in a distorted tetrahedral geometry. The distortion of the tetrahedral environment of the cobalt(II) ion is smaller than in complex **1**, being indicated by the ligand–metal–ligand bite angles that vary between 115.1(2)° [Cl(1)–Co–N(1)] and 92.5(2)° [N(3)–Co–N(1)]. This compound is the first structurally characterized compound having a 1,3-thiazine link to cobalt(II). The Co-ligand bond lengths were compared with the same values collected from the CSD used during discussion of complex **1**. Thus, the Co–Cl bond

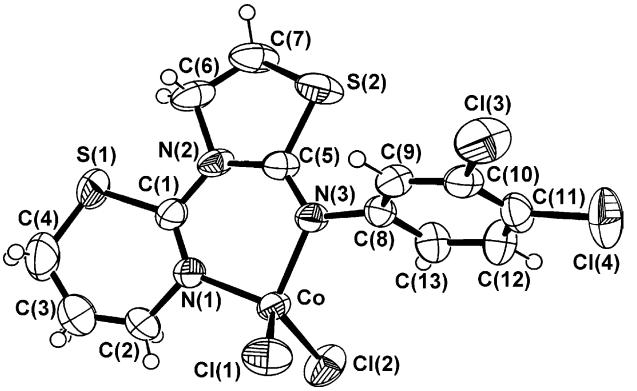


Fig. 2. Molecular structure of $[CoCl_2(TdTz)]$ (**2**), showing the atom numbering scheme. The thermal ellipsoids are drawn at the 50% level.

Table 3
Selected bond lengths (Å) and bond angles (°) for $[CoCl_2(TdTz)]$ (**2**)

Bond lengths			
Co–Cl(1)	2.244(2)	Co–Cl(2)	2.226(1)
Co–N(1)	1.946(4)	Co–N(3)	1.970(4)
C(1)–N(1)	1.284(6)	N(2)–C(5)	1.384(6)
N(2)–C(1)	1.403(6)	C(8)–N(3)	1.433(6)
C(5)–N(3)	1.288(6)		
Bond angles			
Cl(1)–Co–Cl(2)	112.8(1)	Cl(1)–Co–N(3)	108.2(1)
Cl(2)–Co–N(3)	115.0(1)	Cl(1)–Co–N(1)	115.1(2)
Cl(2)–Co–N(1)	111.7(1)	N(3)–Co–N(1)	92.5(2)
C(5)–N(2)–C(1)	127.0(4)	N(2)–C(5)–N(3)	125.6(4)
Co–N(3)–C(5)	124.4(3)	Co–N(3)–C(8)	117.1(3)
C(5)–N(3)–C(8)	118.5(4)	Co–N(1)–C(1)	127.8(3)
C(1)–N(1)–C(2)	119.2(4)	N(2)–C(1)–N(1)	122.1(4)
N(3)–C(5)–N(2)	125.6(4)		

lengths are similar to those collected, whereas the Co–N_{imino} bond length is shorter to those collected.

The six membered chelate ring Co–N(1)–C(1)–N(2)–C(5)–N(3), similarly to complex **1**, is essentially planar with maximum mean-plane deviation for C(1) (0.047 Å). The 1,3-thiazine ring shows a conformation near to boat with S(1) and C(2) deviating 0.350 and 0.215 Å, respectively, above the plane formed by C(1), N(1), C(3), C(4) [maximum mean-plane deviation for N(1) = 0.051 Å]. This geometry is proved by the puckering parameters $q = 0.336$ Å, $\phi = 303.4°$ and $\theta = 82.9°$ [25]. For the thiazolidine ring, the puckering parameters $q = 0.356$ Å and $\phi = 303.4°$ [25] indicate a conformation near to envelope with the apex at C(7), deviating 0.546 Å from the plane formed by C(5), N(2), C(6), S(2) [maximum mean-plane deviation for N(2) = 0.038 Å].

Finally, it should be pointed out that the organic moiety in both complexes presents a different degree of rotation of the 3,4-dichlorophenyl ring around the N(3)–C(7) [or N(3)–C(8)] bond, which could be due to the molecular packing of the crystal structures [torsion angle C(4)–N(3)–C(7)–C(12) = −78.5° in complex **1**; torsion angle C(5)–N(3)–C(8)–C(13) = −119.2° in complex **2**].

3.2. Physical measurements

A pseudotetrahedral stereochemistry may be assigned to the two complexes reported in this paper on the basis of their diffuse reflectance spectra, which closely resemble those of other Co(II) tetrahedral complexes.

Complex **1** exhibits one intense band at 34 720 cm^{-1} (288 nm), which is assigned to the $\pi \rightarrow \pi^*$ transition of the organic ligand. Moreover, the spectrum shows two multicomponent absorptions in the near infrared and visible regions with intensities consistent with spin-allowed d–d transitions. These bands may be assigned to ν_2 $[^4A_2(F) \rightarrow {}^4T_1(F)]$ (10 800, 8300, 6930 cm^{-1}) and ν_3 $[^4A_2(F) \rightarrow {}^4T_1(P)]$ (18 870 and 16 290 cm^{-1}) transitions, respectively, in an idealized T_d symmetry.

The very large splitting for these bands suggests a marked effect of a low symmetry component of the crystal field, C_1, prevailing on the spin-orbit coupling effects, although such a mechanism may contribute [26].

The ligand field parameters, 10 Dq and B, were calculated from the average values of the ν_2 and ν_3 bands taking the centre of gravity of the total intensity, using the following known relationships [27] for tetrahedral d^7 complexes:

$$\nu_2[^4A_2(F) \rightarrow {}^4T_1(F)] = 15Dq + (15/2)B - 1/2[(-6Dq + 15B)^2 + 64(Dq)^2]^{1/2} \tag{1}$$

$$\nu_3[^4A_2(F) \rightarrow {}^4T_1(P)] = 15Dq + (15/2)B + 1/2[(-6Dq + 15B)^2 + 64(Dq)^2]^{1/2} \tag{2}$$

The calculated values of the ligand field parameters 10 Dq = 4870 cm^{-1} and B = 746 cm^{-1} are in fair agreement with the predicted values for tetrahedral complexes and are consistent with the presence of a chromophore group $[CoCl_2N_2]$ [13,28–30].

The electronic spectra of **1** and **2** resemble each other closely. Thus, complex **2** shows one intense band at 34 480 cm^{-1} (290 nm) which can be assigned to the $\pi \rightarrow \pi^*$ transition of the organic ligand.

Likewise, in a similar form to **1**, the electronic spectrum exhibits a splitting of the ν_2 and ν_3 transitions. Thus, the bands at 18 670 and 16 500 cm^{-1} are assigned to the ν_3 $[^4A_2(F) \rightarrow {}^4T_1(P)]$ transition, whereas the bands at 11 130 cm^{-1}, 8200 cm^{-1} and 7130(sh) cm^{-1} are assigned to the ν_2 $[^4A_2(F) \rightarrow {}^4T_1(F)]$ transition.

Attention is now given to the splitting of the ν_2 transition of **2** (two bands and a shoulder) that is smaller than that of **1** (three bands). This fact may possibly be explained in terms of geometrical effects, since in accordance with the X-ray crystallographic results, the distortion of the coordination polyhedron around the cobalt(II) atom in **1** is greater than that in **2** [31].

The ligand field parameters, 10 Dq and B, were collected in the same way as for **1** using the Eqs. (1) and (2). Likewise, the calculated values of the ligand field parameters, 10 Dq = 4861 cm^{-1} and B = 754 cm^{-1}, are consistent with the presence of the chromophore group [$CoCl_2N_2$] [13,28–30].

The observed molar magnetic susceptibilities for **1** and **2** were corrected for diamagnetism and temperature-independent paramagnetism to provide the fully corrected magnetic moments at room temperature of 4.37 and 4.44 MB, respectively. These values are consistent with an ion with an $e^4t_2^3$ electronic configuration in a tetrahedral field [32,33].

It should be pointed out that the magnetic moment of **2** is a little higher than that of **1**, this fact can be explained by considering, according to Cotton [34,35], that the orbital contribution to the spin only value of the magnetic moment varies inversely with the strength of the ligand field, and that is lower for **2** than for **1**.

The IR spectra of TdTn and TdTz in the 4000–370 cm^{-1} region show the presence of bands due to thiazolidine ring vibrations at 1027 (νn_1), 906 (νn_2), 828 (νn_3), 704 (νn_4), 673 (νn_5) and 477 cm^{-1} (δn_2) for TdTn, and at 1024 (νn_1), 923 (νn_2), 891 (νn_3), 701 (νn_4), 675 (νn_5) and 475 cm^{-1}(δn_2) for TdTz [36,37].

Likewise, the spectrum of TdTn exhibits bands assignable to the thiazoline ring vibrations at 1602 (W_1), 985 (W_2), 937 (W_3), 799 (W_4), 733 (W_5), 644 (W_6), 593 (W_8), 526 (W_7) and 445 cm^{-1} (Γ_1) [38], whereas the spectrum of TdTz shows bands assignable to the thiazine ring vibrations at 1604 (Ψ_1), 1010 (Ψ_2), 947 (Ψ_3), 823 (Ψ_4), 765 (Ψ_5), 710 (Ψ_6), 628 (Ψ_7), 592 (Ψ_8) and 528 cm^{-1} (ϕ_1) [14,39,40].

Moreover, the bands of 3,4-dichlorophenyl ring vibrations are detected at 1586 (8b), 1550 (8a), 1470 (19b), 1384 (19a), 1253 (14), 1131 (1) and 433 cm^{-1} (16b) for TdTn, and at 1585 (8b), 1548 (8a), 1466 (19b), 1372 (19a), 1244 (14), 1136 (1) and 428 cm^{-1} (16b) for TdTz [41].

Other relevant bands are registered at 1635 [$\nu(C{=}N)_{imine}$] and 1035 cm^{-1} [$\nu(C–Cl)_{orto}$] for TdTn, and at 1631 [$\nu(C{=}N)_{imine}$], 1358 [ν(C–N)] and 1048 cm^{-1} [$\nu(C–Cl)_{orto}$] for TdTz [42,43].

Table 4
Infrared bands (cm^{-1}) due to ring vibrations of TdTn, [$CoCl_2$(TdTn)] (**1**), TdTz and [$CoCl_2$(TdTz)] (**2**)

Assignment		TdTn	**1**	TdTz	**2**
Thiazoline	W_1	1602 (vs)	1540 (s)		
	W_2	985 (w)	1001 (w)		
	W_3	937 (w)	949 (m)		
	W_4	799 (w)	774 (w), 753 (vw)		
	W_5	733 (vw)	730 (w), 717 (w)		
	W_6	644 (m)	631 (w)		
	W_8	593 (m)	588 (w)		
	W_7	526 (w)	542 (w)		
	Γ_1	445 (w)	444 (w)		
Thiazine	Ψ_1			1604 (vs)	1598 (vs)
	Ψ_2			1010 (m)	1022 (m)
	Ψ_3			947 (w)	942 (w)
	Ψ_4			823 (m)	839 (m)
	Ψ_5			765 (w)	760 (w), 746 (w)
	Ψ_6			710 (w)	721 (w)
	Ψ_7			628 (w)	631 (w)
	Ψ_8			592 (w)	594 (w)
	ϕ_1			528 (w)	545 (w)
Thiazolidine	νn_1	1027 (m)		1024 (m)	1031 (m)
	νn_2	906 (m)	912 (w)	923 (m)	912 (w)
	νn_3	828 (m)	830 (w)	891 (m)	893 (m)
	νn_4	704 (m)	696 (w)	701 (w)	702 (w)
	νn_5	673 (m)	672 (w)	675 (w)	673 (w)
	δn_2	477 (w)	484 (w)	475 (w)	478 (w)
	Γ_1	445 (w)	444 (w)		
3,4-Dichlorophenyl	8b	1586 (s)	1606 (vs)	1585 (s)	1563 (m)
	8a	1550 (m)	1558 (m)	1548 (m)	1538 (m)
	19b	1470 (s)	1463 (m)	1466 (s)	1467 (m)
	19a	1384 (s)	1391 (s)	1372 (m)	1377 (s)
	14	1253 (m)	1237 (m)	1244 (m)	1233 (m)
	1	1131 (m)	1121 (m)	1136 (m)	1147 (w)
	6a				686 (w)
	16a		550 (w)		584 (w)
	16b	433 (w)	435 (w)	428 (w)	425 (w)

Abbreviations: (s) strong; (m) medium; (w) weak; (v) very.

The IR spectra of **1** and **2** in the 4000–370 cm^{-1} region show the presence of bands due to the organic moiety ring vibrations as is shown in Table 4.

The two complexes showed a strong $\nu(\text{C=N})_{\text{imine}}$ absorption, at 1606 cm^{-1} in **1** and at 1598 cm^{-1} in **2**, suffering a shift to a lower wavenumber when compared with that for the uncoordinated imine function of the respective ligands. Likewise, the in-plane stretching vibrations corresponding to ν(C=N) skeletal vibrations of the heterocyclic rings (W_1 of **1** and ψ_1 of **2**), were also shifted to lower wavenumbers compared with that for the respective free ligands (Table 4). From this a coordination via the imino nitrogens of the ligands can be deduced [44–47].

In the low-frequency region, the C_1 symmetry of both complex cations predicts the appearance of four bands assignable to metal–ligand stretching vibrations. The IR spectrum of **1** shows three such bands at 345, 322 and 226 cm^{-1}. The band at 345 cm^{-1} could include the $\nu(\text{Co–N}_{\text{imino}})$ vibration [13,44–46,48] and one ν(Co–Cl) vibration [13,49–52], whereas the band at 322 cm^{-1} is assigned to the other ν(Co–Cl) vibration [13,49–52]. Finally, the band at 226 cm^{-1} is assignable to $\nu(\text{Co–N}_{\text{thiazoline}})$ [13,29,30]. In a similar form, only three such bands are observed for **2**. Of these, the band at 337 cm^{-1} can include the $\nu(\text{Co–N}_{\text{imino}})$ vibration [13,44–46,48] and one ν(Co–Cl) vibration [13,49–52], whereas the band at 320 cm^{-1} is assigned to the other ν(Co–Cl) vibration [13,49–52]. The last band at 230 cm^{-1} is tentatively assigned to $\nu(\text{Co–N}_{\text{thiazine}})$, in good accord with literature data for several complexes containing thiazoline or thiazine derivative ligands [13,29,30].

4. Supplementary material

CCDC 247453, corresponding to $[\text{CoCl}_2(\text{TdTn})]$, and CCDC 247454, to $[\text{CoCl}_2(\text{TdTz})]$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We would like to thank the Spanish Ministerio de Ciencia y Tecnología, [Project BQU01-0374], the Junta de Extremadura (Consejería de Educación, Ciencia y Tecnología) and the FEDER [Project 2PR02A098] for financial support. A.M. Lozano-Vila thanks the Spanish Ministerio de Ciencia y Tecnología and E. Viñuelas-Zahínos thanks the Junta de Extremadura (Consejería de Educación, Ciencia y Tecnología) and the FEDER for their Ph.D. fellowships.

References

[1] W.Y. Sun, J. Fan, T. Okamura, N. Ueyama, Inorg. Chem. Commun. 3 (2000) 541.
[2] A. Korolkovas, J.H. Burckhalter, in: Compendio Esencial de Química Farmacéutica, Reverte, Barcelona, 1983.
[3] R.F. Schinazi, R.A. Floyd, PCT Int. Appl. WO 90 13,296 (Cl. A61K31/54) (1991) Chem. Abstr. 115 (1991) 105989.
[4] D. Bozsing, P. Sohar, G. Gigler, G. Kovacs, Eur. J. Med. Chem. 31 (1996) 663.
[5] I.A. Shehata, H.I. Elsubbagh, A.M. Abdelal, M.A. Elsherbeny, A.A. Alobaid, Med. Chem. Res. 6 (1996) 148.
[6] B. Tozkoparan, G. Aktay, E. Yesilada, Il Farmaco 57 (2002) 145.
[7] P. Wipf, P. Fritch, Tetrahedron Lett. 35 (1994) 5377.
[8] M. Premanathan, R. Arakaki, S. Ramanan, S. Jinno, M. Baba, S. Yamashita, H. Nakashima, Antiviral Chem. Chemother. 9 (1998) 423.
[9] C. Della Monica, A. Randazzo, G. Bifulco, P. Cimino, M. Aquino, I. Izzo, F. De Riccardis, L. Gomez-Paloma, Tetrahedron Lett. 43 (2002) 5707.
[10] C.A. Bolos, K.T. Papazisis, A.H. Kortsaris, S. Voyatzi, D. Zambouli, D.A. Kyziakidis, J. Inorg. Biochem. 88 (2002) 25.
[11] M.L. Guerinot, Annu. Rev. Microbil. 48 (1994) 743.
[12] R.J. Bergeron, C.Z. Liu, J.S. McManis, M.X.B. Xia, S.E. Algee, J. Wiegand, J. Med. Chem. 37 (1994) 1411.
[13] A. Bernalte García, F.J. García Barros., F.J. Higes Rolando, F. Luna Giles, Polyhedron 20 (2001) 3315.
[14] A. Bernalte García, F.J. García Barros, F.J. Higes Rolando, F. Luna Giles, R. Pedrero Marín, J. Inorg. Biochem. 98 (2004) 15.
[15] F.J. Barros García, A. Bernalte García, F.J. Higes Rolando, F. Luna Giles, R. Pedrero Marín, Polyhedron 23 (2004) 1453.
[16] F.J. Barros García, A. Bernalte García, F.J. Higes Rolando, F. Luna Giles, R. Pedrero Marín, E. Viñuelas-Zahínos, Inorg. Chim. Acta 357 (2004) 1457.
[17] F.J. Barros García, A. Bernalte García, F.J. Higes Rolando, F. Luna Giles, M.A. Maldonado Rogado, E. Viñuelas-Zahínos, Inorg. Chim. Acta 357 (2004) 3574.
[18] R.J. Outcalt, J. Heterocyclic Chem. 24 (1987) 1425.
[19] A.S. Deutsch, P.E. Fanta, J. Org. Chem. 21 (1956) 892.
[20] H.W. Schubert, O. Behner, Arch. Pharm. 301 (1968) 752.
[21] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.
[22] F.H. Allen, Acta Cryst. B58 (2002) 380.
[23] I.J. Bruno, J.C. Cole, P.R. Edington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Cryst. B58 (2002) 389.
[24] T.F. Liu, D. Fu, S. Gai, Y.Z. Zhang, H.L. Sun, G. Su, Y.J. Liu, J. Am. Chem. Soc. 124 (2003) 13976.
[25] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354.
[26] B.B. Garrett, V.L. Goedken, J.V. Quagliano, J. Am. Chem. Soc. 11 (1970) 489.
[27] D.K. Rastogi, K.C. Sharma, S.K. Dua, M.P. Teotia, J. Inorg. Nucl. Chem. 37 (1975) 685.
[28] Y.J. Weaver, J.A. Weaver, J. Inorg. Nucl. Chem. 37 (1975) 1309.
[29] J.A. Weaver, P. Hambright, P.T. Talbert, E. Kang, A.N. Thorpe, Inorg. Chem. 9 (1970) 268.
[30] A.C. Fabretti, G. Peyronel, G.C. Franchini, Inorg. Chim. Acta 35 (1979) 49.
[31] G. Marcotrigiano, L. Menabue, G.C. Pellacani, Inorg. Chim. Acta 26 (1978) 57.
[32] B.N. Figgis, J. Lewis, Prog. Inorg. Chem. 6 (1964) 37.
[33] R.L. Carlin, Transit. Metal Chem. 1 (1965) 21.
[34] F.A. Cotton, O.D. Fant, D.M.L. Goodgame, R.H. Holm, J. Am. Chem. Soc. 83 (1961) 1780.
[35] F.A. Cotton, D.M.L. Goodgame, M. Goodgame, J. Am. Chem. Soc. 83 (1961) 4690.
[36] M. Guiliano, G. Mille, J. Choteau, J. Mol. Struct. 50 (1978) 233.

[37] M. Guiliano, G. Mille, T. Avignon, J. Chouteau, J. Raman Spectrosc. 7 (1978) 214.

[38] G. Mille, J.L. Meyer, J. Choteau, J. Mol. Struct. 50 (1978) 247.

[39] A.I. Meyers, J. Org. Chem. 26 (1961) 218.

[40] A. Pastura, K. Thewalt, J. Prakt. Chem. 38 (1968) 177.

[41] G. Varsanyi, in: Vibrational Spectra of Benzene Derivatives, Academic Press, New York, 1969.

[42] R.T. Conley, in: Espectroscopía Infrarroja, Alhambra, Madrid, 1979.

[43] E. Pretsch, T. Clerc, J. Seibl, W. Simon, in: Tablas para la determinación estructural por métodos espectroscópicos, Springer-Verlag Ibérica, Barcelona, 2000.

[44] M. Shakir, S.P. Varkey, F. Firdaus, P.S. Hameed, Polyhedron 13 (1994) 2319.

[45] B. Singh, R.N. Singh, R.C. Aggarwal, Polyhedron 4 (1985) 401.

[46] M.M. Mostafa, M.A. Khattab, K.M. Ibrahim, Polyhedron 2 (1983) 583.

[47] J. Nelson, S. Martin Nelson, W.D. Perry, J. Chem. Soc., Dalton Trans. (1976) 1282.

[48] N.K. Singh, S. Agrawal, R.C. Aggarwal, Polyhedron 3 (1984) 1271.

[49] E.J. Duff, M.N. Hughes, K.J. Rutt, J. Chem. Soc. (1969) 2101.

[50] C.E. Taylor, A.E. Underhill, J. Chem. Soc. A (1969) 368.

[51] W.J. Eilbeck, F. Holmes, C.E. Taylor, A.E. Underhill, J. Chem. Soc. A (1968) 128.

[52] W.J. Eilbeck, F. Holmes, C.E. Taylor, A.E. Underhill, J. Chem. Soc. A (1969) 1189.