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Synthesis, Spectroscopic Study and Crystal Structure Determination by X-ray Powder Diffractometry of [$CdCl_2$(TzTn)] [TzTn=2-(3,4-dichlorophenyl)imino-N-(2-thiazolin-2-yl)tetrahydro-1,3-thiazine]

A. M. Lozano-Vila[a], F. L. Cumbrera[b], F. Luna-Giles[a,*], A. L. Ortiz[c], and A. Bernalte-García[a]

Badajoz/Spain, Universidad de Extremadura, [a] Departamento de Química Orgánica e Inorgánica, Facultad de Ciencias, [b] Departamento de Física, Facultad de Ciencias and [c] Departamento de Ingeniería Mecánica, Energética y de los Materiales, Escuela de Ingenierías Industriales

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Dedicated to Professor Alfonso Castiñeiras Campos on the Occasion of his 65th Birthday

Abstract. The cadmium(II) complex, dichloro[2-(3,4-dichlorophenyl)-imino-κN-N-(2-thiazolin-κN-2-yl)tetrahydro-1,3-thiazin]cadmium(II), was synthesized in the form of fine powder with small crystals unsuitable for structure determination by X-ray single-crystal diffractometry, and was therefore characterized by X-ray powder diffractometry. To that end, the molecular structure was first analyzed using various instrumental techniques including elemental analysis, FAB-mass spectroscopy, and infrared spectroscopy, and then optimized via molecular modeling with a semi-empirical quantum-chemistry model. From the optimized molecule, the crystal structure wasresolved within the methodological framework of the direct-space methods using a 'Monte-Carlo/parallel tempering' search algorithm, and then refined using the Rietveld method. It was found that the title compound crystallizes in the triclinic system, with the space group $P\bar{1}$, two $C_{13}H_{13}Cl_4CdN_3S_2$ molecules in the asymmetric unit, and the following unit cell dimensions: a = 13.558(4) Å, b = 13.579(7) Å, c = 10.117(4) Å, α = 91.07(3)°, β = 95.44(3)°, and γ = 93.03(3)°. It was also found that the environment around the cadmium(II) ion may be described as distorted tetrahedral, with the metallic atom coordinated to two chlorine atoms [Cd(A)-Cl(1A) = 2.44(3) Å; Cd(A)-Cl(2A) = 2.44(3) Å; Cd(B)-Cl(1B) = 2.45(3) Å; Cd(B)-Cl(2B) = 2.45(3) Å], one imino nitrogen atom [Cd(A)-N(3A) = 2.37(10) Å; Cd(B)-N(3B) = 2.37(9) Å], and one thiazoline nitrogen atom [Cd(A)-N(1A) = 2.33(8) Å; Cd(B)-N(1B) = 2.33(10) Å].

Keywords:: Crystal structures; X-ray powder diffractometry; Cadmium; Thiazine; Thiazoline

1 Introduction

Cadmium is a naturally occurring heavy metal typically bound to oxygen (CdO), chlorine ($CdCl_2$) or sulfur (CdS) in the solids of the earth's crust. Since the industrial revolution it has become extensively used in various industrial sectors, such as the battery, pigment, metal coating, and plastic industries, to name a few [1]. One direct consequence of this industrial exploitation is the anthropic release of an important amount of Cd into the environment. Thus, food is in general the principal source of exposure to Cd in non-smokers, although in smokers the cigarette smoke surpasses food in importance as the principal source of contamination by Cd [2].

Cadmium is teratogenic, mutagenic, and carcinogenic [1]. Owing to its bio-availability, persistence, and bioaccumulation, it is potentially lethal [3]. This explains why most of the work on Cd has centred so far on investigating health problems deriving from its toxicity, including Itai Itai disease, renal tubular dysfunction, hypertensive disorders, and respiratory problems. It has been demonstrated recently that Cd causes extreme hyper-mutability via the suppression of post-replication mismatch repair [4, 5], and that it can be a potent non-steroidal endocrine disrupter by mimicking the effects of oestradiol [6].

Because Cd is a noxious non-essential metal, detoxification has to be tightly controlled. The general agreement that the most effective clinical treatment for heavy-metal poisoning is chelation therapy [7] has motivated the search for and development of chelating agents to treat Cd intoxication. It is not surprising therefore that a large number of therapeutic ligands have been synthesized and investigated for the elimination of Cd accumulation [8, 9].

One group of substances that may hold promise for clinical use as Cd scavengers is that of compounds with thiazine and/or thiazoline rings. This type of compound has been the subject of considerable attention in medicine and pharmacology in recent years due to their attractive biological and pharmaceutical activities [10−15]. In particular, it has been recognized that some of these substances may inhibit

* Prof. F. Luna-Giles
Departamento de Química Orgánica e Inorgánica
Universidad de Extremadura
E-06071 Badajoz/Spain
Fax: +34 924289397
E-mail address: pacoluna@unex.es

cell division [16], which endows them with anti-HIV [17] and anti-cancer activities [18, 19]. Apart from these two activities, many of these compounds also exhibit antibiotic, analgesic, antihistaminic, antiviral, anti-inflammatory, sedative, and anti-tumoral activities [20−23]. With respect to Cd scavenging, the interest in these compounds lies in the fact that they can potentially act as organic ligands to form coordination complexes with this element, and in consequence they have great value as detoxification agents.

Motivated by the great interest in the development of Cd scavengers for clinical use, we have recently synthesized and characterized structurally new coordination compounds with Cd^{II} [24−27]. However, only the crystal structure of those compounds that crystallized as single crystals of appropriate size and quality for conventional X-ray single-crystal diffractometry studies were reported because of the difficulty in resolving organic structures of a certain complexity by X-ray powder diffractometry. Given that the knowledge of the crystal structure is of vital importance to understand in detail how Cd links to the organic ligands, studies in this area are still necessary in the Cd^{II} complexes that crystallize in the form of fine powders.

In comparison with X-ray single-crystal diffractometry, X-ray powder diffractometry is markedly more difficult and very far from being routine. This is because the reflections from different crystal planes are projected onto a single variable, the diffraction angle, and therefore they overlap. When the peak overlap is only moderate, the direct methods borrowed from X-ray single-crystal diffractometry can still be applied to X-ray powder diffraction patterns to resolve crystal structures. However, when peak overlap is very significant, a simple application of these direct methods is ineffective. This situation usually occurs for crystal structures with a low-symmetry space group and large molecules in the unit cell, as is typically the case of coordination compounds such as that investigated in the present study. The methodological strategy that has proven most useful in resolving the crystal structure of such coordination compounds consists of combining spectroscopic techniques and molecular modeling procedures with the direct-space methods and Rietveld method of X-ray diffractometry [28, 29]. Thus, at a first step, a molecular model is elaborated from the information deduced from the different spectroscopic techniques, and the molecular geometry is then optimized by molecular modeling without reference to the XRD data by searching for the absolute minimum in the potential energy surface. At a second step, the optimized molecules constituting the asymmetric unit are placed arbitrarily (but compatible with the chemical constraints) within the unit cell. The remaining molecules in the unit cell are generated by the symmetry operations of the space group. Both the unit cell dimensions and the appropriate space groups are determined by analyzing the experimentally-collected XRD data, whereas the number of molecules in the unit cell is deduced by simple considerations of the volumes of the molecules and the unit cell. The positions of the asymmetric-unit molecules are then modified repeatedly by a global optimization technique with the objective of reaching the best possible agreement between the theoretical XRD pattern calculated for the simulated crystal structure and the experimentally measured XRD pattern. Finally, the best model of the crystal structure is refined using the Rietveld method.

This is the methodological framework of the present study, in which we determined the crystal structure of the title Cd^{II} coordination compound by X-ray powder diffractometry aided by various spectroscopic techniques and molecular modeling.

2 Experimental Section

2.1 Preparation and characterization of 2-(3,4-dichlorophenyl)imino-N-(2-thiazolin-2-yl)tetrahydrothiazine (TzTn)

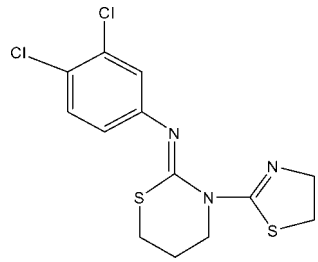
A volume of 3 mL (21.0 mmoles) of 3,4-dichlorophenyl isothiocyanate was treated with 1.5 mL (19.6 mmoles) of 3-amine-1-propanol in 15 mL of dichloromethane. The resulting thiourea was heat-treated to reflux in 100 mL of 3N hydrochloric acid for 3 hours, then cooled and the solution made basic with a solution of 12.5 g of sodium hydroxide in 50 mL of water. Extraction with dichloromethane, then drying over anhydrous magnesium sulfate and concentration resulted in 5.3 g of 2-(3,4-dichlorobenzylamino)-4H-5,6-dihydro-1,3-thiazine. Subsequently, a solution was prepared with 2.12 g (8.1 mmoles) of this compound, 1 mL (10.2 mmoles) of 2-chloroethylisothiocyanate [30], and 30 mL of chloroform, which was stirred and heated to reflux. After 4 hours, a white powder had precipitated, 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 again to completely dissolve the solid phase. 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 result in a solid that was recrystallized from ethanol 96 % (1.9 g; 68 %).

The TzTn ligand was subjected to various characterizations as described next. Chemical analyses of carbon, hydrogen, nitrogen, and sulfur were performed by microanalytical methods using a Leco CHNS-932 microanalyzer. Measured (in wt%): C, 45.17; H, 3.79; N, 12.13; S, 18.77; calculated (in wt%) for $C_{13}H_{13}Cl_2N_3S_2$: C, 45.09; H, 3.78; N, 12.13; S, 18.52.

^{1}H- and ^{13}C-NMR spectra were both measured with a Bruker AM 400 instrument at 400 and 100 MHz, respectively, in $CDCl_3$ using Me_4Si as internal standard.

Measured by **^{1}H-NMR** (deuterochloroform): δ 7.36 (d, J = 8.47 Hz, 1H), 7.04 (d, J = 2.37 Hz, 1H), 6.77 (dd, J = 2.39, 8.70 Hz, 1H), 4.14 (t, J = 6.09 Hz, 2H), 4.02 (t, J = 7.98 Hz, 2H), 3.15 (t, J = 7.98 Hz, 2H), 2.99 (t, J = 6.40 Hz, 2H), 2.24 (m, J = 6.42 Hz, 2H); measured by **^{13}C-NMR** (deuterochloroform): δ 160.41, 146.49, 146.49, 132.42, 130.44, 127.02, 123.20, 121.07, 57.62, 46.91, 34.29, 27.26, 23.89.

Finally, a UV-Vis spectrum in the 350-200 nm range was collected on a Shimadzu UV-3101TC spectrophotometer from a sample in EtOH solution.Measured by UV-Vis (λ_{max}, nm; ε, L mol^{-1} cm^{-1}): 202 (35855), 237 (17000), 298 (7855).



Scheme 1 Two-dimensional chemical drawing of the TzTn molecule.

2.2 Preparation and characterization of [$CdCl_2$(TzTn)]

The [$CdCl_2$(TzTn)] complex was isolated from a freshly prepared 96 % ethanol solution (2 ml) of $CdCl_2 \cdot 2^1/_2H_2O$ (65.9 mg, 0.3 mmol) that was added to a 96 % ethanol solution (15 ml) of TzTn (100 mg, 0.3 mmol). The resulting solution was allowed to evaporate slowly at room temperature. After a few hours, a fine powder was isolated from the solution (109 mg, 71 %). The powder particles were first separated by filtration, then washed with cold ether, and finally air-dried.

The [$CdCl_2$(TzTn)] complex was characterized using the microanalytical method described above for the TzTn ligand. Measured (in wt%): C, 29.75; H, 2.53; N, 7.98; S, 12.47; calculated (in wt%) for $C_{13}H_{13}Cl_4CdN_3S_2$: C, 29.48; H, 2.47; N, 7.93; S, 12.11 %. Additionally, the [$CdCl_2$(TzTn)] complex was also characterized using FAB-mass and IR spectroscopies, as described next. The FAB-mass spectrum was collected on a Micromass AUTOSPEC spectrophotometer using nitrobenzyl alcohol as matrix (mnba). 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.

2.3 Crystal structure determination of [$CdCl_2$(TzTn)]

The [$CdCl_2$(TzTn)] complex was analyzed using X-ray powder diffractometry to determine its crystal structure. Before being installed in the XRD holder, the particles resulting from the synthesis of the [$CdCl_2$(TzTn)] complex were ground to an ultra-fine powder to avoid texture and granulation effects in the XRD pattern. The resulting powder was then loaded into the XRD holder (3 mm thick) and pressed slightly with a glass slide to ensure a flat surface and thus the absence of instrumental shift in the position of the XRD peaks. The operating conditions for the XRD data collection were CuKα radiation (λ = 1.54183 Å), 5-100° scanning interval, 0.02° step size, and 20 seconds count time per step, using a D5000 Siemens diffractometer equipped with a graphite secondary monochromator.

3 Results and Discussion

3.1 FAB-mass spectrum

The FAB-mass spectrum of the [$CdCl_2$(TzTn)] complex shows a fragmentation pattern characteristic of a monomeric nature, with no peaks at m/z values greater than the molecular mass calculated from the elemental chemical analysis. The peak at m/z 346 is due to the ($TzTn^+$) ligand, which is also the base peak of the spectrum. Similarly, the peak at m/z 494 is assigned to the $[CdCl(TzTn)]^+$ fragment. One may hence deduce from these observations the integrity of the ligand in the complex.

3.2 IR spectra

The IR spectrum of the TzTn ligand in the 4000-370 cm^{-1} region shows the presence of bands due to the tetrahydro-1,3-thiazine ring vibrations at 1024 ($\nu\theta_1$), 919 ($\nu\theta_2$), 819 ($\nu\theta_3$), 700 ($\nu\theta_4$), 667 ($\nu\theta_5$), 588 ($\delta\theta_1$), 488 ($\delta\theta_2$), and 393 (ε_1) cm^{-1} [31, 32]. Likewise, characteristic bands of the thiazoline ring vibrations are detected at 1576 (W_1), 998 (W_2), 945 (W_3), 768 (W_4), 711 (W_5), 633 (W_6), 611 (W_8), 560 (W_7), and 438 (Γ_1) cm^{-1} [33]. In addition, bands of 3,4-dichlorophenyl ring vibrations are registered at 1576 (8b), 1545 (8a), 1463 (19b), 1398 (19a), 1240 (14), 1123 (1), 690 (6a), 633 (12), and 541 (16a) cm^{-1} [34]. Other relevant bands are observed at 1598 [$\nu(C{=}N)_{imine}$], 1353 [ν(C-N)], and 1051 [$\nu(C\text{-}Cl)_{orto}$] cm^{-1} [35, 36].

The IR spectrum of the [$CdCl_2$(TzTn)] complex in the 4000-370 cm^{-1} region shows the presence of bands due to organic moiety ring vibrations. Comparison of relevant stretching vibration modes between the free TzTn ligand and the [$CdCl_2$(TzTn)] complex would thus shed light on the ligand coordination. Indeed, this comparison showed that the strong $\nu(C{=}N)_{imine}$ absorption band at 1598 cm^{-1} in the TzTn ligand is shifted towards the higher wavenumber of 1618 cm^{-1} in the [$CdCl_2$(TzTn)] complex. In addition, the in-plane stretching vibrations due to $\nu(C{=}N)$ skeletal vibration of the heterocyclic ring (W_1) in the [$CdCl_2$(TzTn)] complex appears at 1542 cm^{-1}, in contrast to the higher wavenumber of 1576 cm^{-1} for the uncoordinated thiazolinic nitrogen band in the TzTn ligand. Based on these two observations, it can be concluded that the coordination of the [$CdCl_2$(TzTn)] complexes has taken place via the imino nitrogen atoms of the TzTn ligands [37−40].

In the low-frequency region, the C_1 symmetry of the [$CdCl_2$(TzTn)] complex predicts the appearance of four bands assignable to the metal−ligand stretching vibrations. The IR spectrum of the complex shows the appearance of four such bands at 312, 265, 243, and 199 cm^{-1}. The band at 312 cm^{-1} is attributed to the $\nu(Cd\text{-}N_{imino})$ vibration mode, which has been detected before in Cd^{II} complexes in the range 365-302 cm^{-1} [24, 40]. The bands at 265 cm^{-1} and 243 cm^{-1} are assigned to the $\nu(Cd\text{-}Cl_{terminal})$ vibration, which have been observed previously in several Cd^{II} complexes in the 324-200 cm^{-1} range [41−45]. Finally, the band at 199 cm^{-1} is due to the $\nu(Cd\text{-}N_{thiazoline})$ vibration, which has appeared before in several Cd^{II} complexes in the 222-202 cm^{-1} range [24, 46]. Taken together, IR, FAB-mass, and elemental chemical analyses show that the [$CdCl_2$(TzTn)] complex has a tetra-coordinated geometry.

3.3 Molecular modeling

A first approximation to the molecular structure in the crystalline state was made by determining the most stable conformation of the isolated molecule through molecular modeling with a semi-empirical quantum-chemical model. The principle behind this approximation is that the molecular structure of this kind of coordination compound hardly changes at all with the crystallization process. The molecular modeling was done using the *HyperChem* software package.*HyperChem*'s front-end launches back-end calculations including HyperNDO (*), which performs the semi-empirical calculations. In this approach the main scheme is based on the neglect of certain differential overlap terms in the Schrödinger equation, which incorporates adjustable parameters fitted to experimental results. The input to initialize the molecular optimization process was the raw two-dimensional model of the $C_{13}H_{13}Cl_4CdN_3S_2$ molecule elaborated from the connectivity information deduced from the various spectroscopic techniques. Different, independent optimization sessions were performed using the semi-empirical AM1, PM3, MNDO and MNDO/d quantum-chemical models. The geometry of the molecule was optimized by searching for the absolute minimum of the potential energy surface. The algorithms used are designed to determine the next point to sample by using the previous trajectory points. The best optimization was obtained with the MNDO/d model (binding energy $E_b = -3508$ kcal mol^{-1}), with the considerable difference in E_b of 320.7 kcal mol^{-1} with respect to the second-best optimized model.

3.4 Crystal structure determination

The sequence followed to resolve the crystal structure of the novel[$CdCl_2$(TzTn)] complex synthesized in the present study consisted of the following three stages.

3.4.1 Data reduction and indexing

Firstly, the Bragg angles of the peaks in the XRD pattern were determined using a derivative-based algorithm included in the *CELREF* program [47]. The first 30 Bragg reflections of the total of 4067 identified as such were then indexed using the *CRYSFIRE* software package [48], which launches the commonest indexing programs: *ITO*, *TREOR90*, *DICVOL91*, *KOHL*, *TAUP*, *FJZN* and *LZON*. The best indexing had a de Wolff figure-of-merit of $M(20) = 19.5$ and was obtained with *TREOR90*, which indexed the XRD pattern in the triclinic system. Subsequent detailed analysis of the indexed peaks with the *CHECKCELL* program [49] yielded a triclinic unit cell of approximate dimensions $a = 13.294$ (4) Å, $b = 13.304$ (4) Å, $c = 9.930$ (4) Å, $\alpha = 91.023$ (13)°, $\beta = 95.393$ (11)°, $\gamma = 93.017$ (8)°, $V = 1746$ (1) Å^3. There was ambiguity between the two possible crystallographic space groups: P1 and P$\bar{1}$. However, the reasonableness of the P1 space group is very low since the number of molecules within the unit cell, as determined from the ratio of the unit cell volume ($V = 1746$ Å^3) to the expected $C_{13}H_{13}Cl_4CdN_3S_2$ molecule volume ($V = 427$ Å^3), is four and the possibility of four independent molecules in the triclic unit cell is extremely low.

3.4.2 Monte Carlo methods

The crystal structure of the [$CdCl_2$(TzTn)] complex was resolved within the methodological framework of the direct-space methods by Monte Carlo algorithms, using the "parallel tempering" formulation implemented in the *FOX* software package [50]. The structure was described using the Z-matrix formalism, which is extremely useful for organic molecules of relative complexity. In this formalism the geometry of the molecules is described by the bond distances, the bond angles, and the dihedral angles between the different atoms. From the optimized molecule structure, the corresponding Fenske-Hall Z-matrix was constructed using the *BABEL* program [51], with the heavy Cd atom as pivot. The Monte Carlo/parallel tempering search algorithm was applied by first choosing the P$\bar{1}$ space group and taking the molecules to be rigid bodies during the first 500 000 movements, and then relaxing the rigid-body constraints imposed on the Z-matrix parameters during the next 2 000 000 movements. Thus, the aim with the first step was to refine only the six translational and rotational degree of freedom, whereas with the second step it was to allow a certain variation in the bond distances, and bond and dihedral angles. The molecular geometry is therefore mainly (but not exclusively) a result of the molecular modeling, and the Monte Carlo/parallel tempering search algorithm is used basically to determine the optimal packing of the molecules within the unit cell. The final weighted residual was $R_{wp} = 0.24$. To check for uniqueness, the entire procedure was repeated several times using different random starting positions for the Cd pivot and molecule orientations. All these attempts converged to the same final crystallographic configuration and R_{wp} value. Finally, the Z-matrix coordinates were converted to crystallographic coordinates for the Rietveld refinement.

To check for correctness of the P$\bar{1}$ space group, the entire procedure described above was repeated taking the P1 space group as input. The final R_{wp} value was markedly greater than 0.24, and thus the P1 space group was ruled out.

3.4.3 Rietveld refinement

Finally, the crystal structure determined by the Monte Carlo/parallel tempering search algorithm was finally refined by the Rietveld method, using the *FULLPROF* Rietveld code [52] included in the *WinPLOTR* software packαge [53].In the Rietveld analysis, the peak shape was assumed to be a pseudo-Voigt function and the refinement included the following aspects: (i) the background, which was interpolated by cubic splines, (ii) the scale factor, (iii) the global instrumental shifts (zero-point shift, and systematic shifts depending on transparency and off-centring of the sample), (iv) the cell parameters, (v) the profile parameters (Caglioti half-width parameters, the mixing parameters of the pseudo-Voigt function, and the asymmetry parameter for diffraction angles less than 15° 2θ), (vi) the atomic positions excluding the H atoms that were rigidly

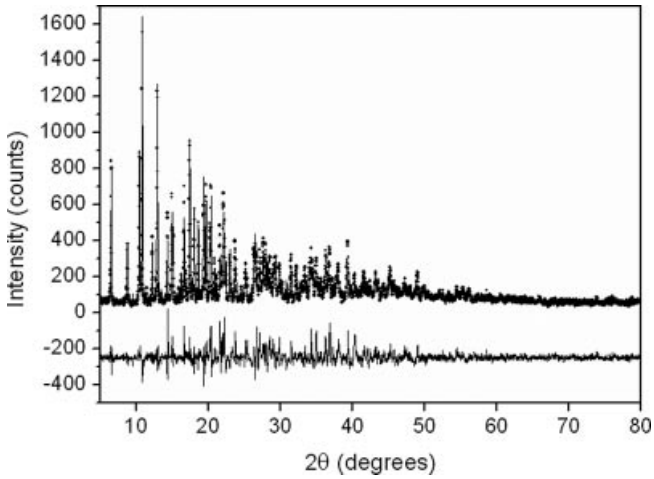


Figure 1 Plot output from the Rietveld analysis of the X-ray diffraction pattern corresponding to the [$CdCl_2$(TzTn)] complex. Points are the experimental X-ray diffraction data; the solid line is the calculated pattern; the residuals are plotted at the bottom.

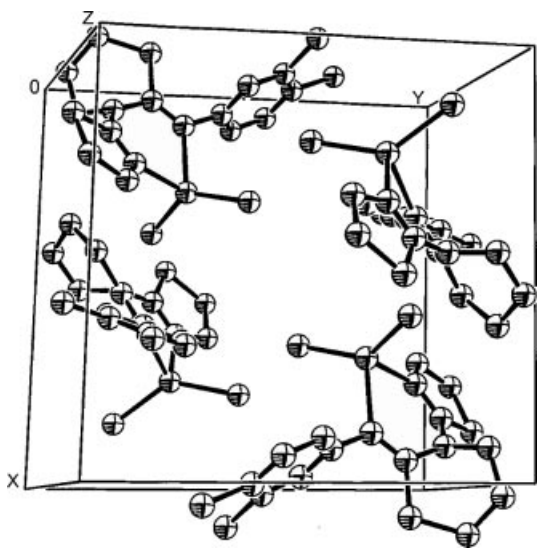


Figure 2 Representation of the crystal structure of the [$CdCl_2$(TzTn)] complex after refinement using the Rietveld method.

linked to their bonding atoms, and (vii) the overall Debye-Waller temperature factor.This makes a total of 180 refined parameters.The Rietveld refinement was made by first taking the molecules to be rigid bodies and then replacing the rigid-body constraints by soft restraints on the atom-atom angles and distances. The residuals at the completion of the Rietveld refinement were R_{wp} = 0.189, R_p = 0.147, and R_F = 0.065, and the refined cell parameters were a = 13.558(4) Å, b = 13.579(7) Å, c = 10.117(4) Å, α = 91.07(3)°, β = 95.44(3)°, and γ = 93.03(3)°. Figure 1 shows the plotted output from the Rietveld refinement, Figure 2 shows a representation of the refined crystal structure, and Table 1 lists the most representative crystallographic parameters of such a crystal structure.

Table 1 Main crystallographic data for the [$CdCl_2$(TzTn)] complex obtained by X-ray powder diffractometry.

Chemical formula	$C_{13}H_{13}Cl_4CdN_3S_2$
Space group	$P\bar{1}$
Cell parameters	
a (Å)	13.558(4)
b (Å)	13.579(7)
c (Å)	10.117(4)
α (°)	91.07(3)
β (°)	95.44(3)
γ (°)	93.03(3)

Coordinates Atoms	*x*	*y*	*z*
CdA	0.287(1)	−0.678(1)	0.718(1)
N1A	0.235(8)	−0.824(6)	0.602(9)
N2A	0.088(7)	−0.865(6)	0.722(8)
N3A	0.116(7)	−0.685(6)	0.751(8)
C1A	0.155(4)	−0.882(4)	0.622(4)
C2A	0.290(8)	−0.857(5)	0.488(4)
C3A	0.240(4)	−0.956(4)	0.420(3)
C4A	0.055(4)	−0.766(4)	0.752(3)
C5A	0.083(4)	−0.939(4)	0.833(4)
C6A	−0.027(4)	−0.963(4)	0.868(3)
C7A	−0.111(7)	−0.900(7)	0.801(7)
C8A	0.079(7)	−0.587(7)	0.776(6)
C9A	0.019(6)	−0.540(4)	0.673(3)
C10A	−0.021(4)	−0.446(4)	0.700(3)
C11A	−0.000(4)	−0.399(4)	0.830(4)
C12A	0.060(7)	−0.447(6)	0.933(6)
C13A	0.099(6)	−0.540(5)	0.906(3)
S1A	0.130(2)	−0.987(1)	0.508(3)
S2A	−0.073(2)	−0.769(2)	0.787(2)
Cl1A	0.324(2)	−0.552(2)	0.558(3)
Cl2A	0.370(2)	−0.728(2)	0.929(3)
Cl3A	−0.094(1)	−0.390(1)	0.573(2)
Cl4A	−0.047(1)	−0.284(1)	0.866(2)
CdB	0.264(1)	−0.338(1)	0.033(1)
N1B	0.391(7)	−0.368(8)	−0.100(9)
N2B	0.494(7)	−0.215(7)	−0.039(8)
N3B	0.396(8)	−0.242(7)	0.150(8)
C1B	0.472(3)	−0.309(5)	−0.109(6)
C2B	0.388(3)	−0.463(3)	−0.178(3)
C3B	0.484(3)	−0.469(3)	−0.258(3)
C4B	0.476(5)	−0.200(5)	0.100(5)
C5B	0.499(2)	−0.122(2)	−0.121(5)
C6B	0.588(3)	−0.047(3)	−0.068(3)
C7B	0.648(3)	−0.070(5)	0.066(3)
C8B	0.382(5)	−0.228(2)	0.291(2)
C9B	0.403(8)	−0.132(5)	0.354(2)
C10B	0.384(4)	−0.118(5)	0.491(2)
C11B	0.345(8)	−0.199(2)	0.564(5)
C12B	0.324(7)	−0.294(2)	0.501(3)
C13B	0.342(7)	−0.309(4)	0.365(7)
S1B	0.562(3)	−0.356(3)	−0.212(1)
S2B	0.571(2)	−0.121(2)	0.191(2)
Cl1B	0.227(2)	−0.489(2)	0.152(3)
Cl2B	0.162(2)	−0.218(2)	−0.086(3)
Cl3B	0.411(2)	0.000(2)	0.566(3)
Cl4B	0.322(1)	−0.183(1)	0.732(2)

3.5 Description of the structure

The crystal structure of the [$CdCl_2$(TzTn)] complex is discussed next, although our interpretation needs to be treated with some caution since the crystallographic data were determined from powder diffractometry.

The X-ray diffraction study of the Cd^{II} complex showed the crystals to be made up of triclinic unit cells (space group $P\bar{1}$), each containing four $C_{13}H_{13}Cl_4CdN_3S_2$ molecules. Only two of these four molecules are independent and therefore form the asymmetric unit. Table 2 lists selected

Table 2 Selected bond lengths /Å and bond angles /° for the $[CdCl_2(TzTn)]$ complex.

Cd(A)-Cl(1A)	2.44(3)	Cd(A)-Cl(2A)	2.44(3)
Cd(A)-N(3A)	2.37(10)	Cd(A)-N(1A)	2.33(8)
S(2A)-C(4A)	1.80(6)	S(1A)-C(1A)	1.81(5)
N(2A)-C(1A)	1.45(10)	N(2A)-C(4A)	1.47(10)
C(8A)-N(3A)	1.47(13)	C(4A)-N(3A)	1.34(10)
C(1A)-N(1A)	1.34(11)	Cd(B)-Cl(1B)	2.45(3)
Cd(B)-Cl(2B)	2.45(3)	Cd(B)-N(3B)	2.37(9)
Cd(B)-N(1B)	2.33(10)	S(2B)-C(4B)	1.80(7)
S(1B)-C(1B)	1.81(7)	N(2B)-C(1B)	1.45(11)
N(2B)-C(4B)	1.46(10)	C(8B)-N(3B)	1.34(11)
C(4B)-N(3B)	1.34(12)	C(1B)-N(1B)	1.310(1)
Cl(1A)-Cd(A)-Cl(2A)	134.14(2)	Cl(1A)-Cd(A)-N(3A)	110.62(3)
Cl(2A)-Cd(A)-N(3A)	104.69(3)	Cl(1A)-Cd(A)-N(1A)	108.51(4)
Cl(2A)-Cd(A)-N(1A)	105.60(2)	N(3A)-Cd(A)-N(1A)	79.98(3)
C(4A)-N(2A)-C(1A)	122.22(5)	C(4A)-N(2A)-C(5A)	115.61(6)
S(2A)-C(4A)-N(2A)	112.29(6)	S(2A)-C(4A)-N(3A)	125.90(7)
N(2A)-C(4A)-N(3A)	121.81(7)	Cd(A)-N(3A)-C(4A)	127.17(6)
Cd(A)-N(3A)-C(8A)	112.66(5)	C(4A)-N(3A)-C(8A)	120.14(7)
Cd(A)-N(1A)-C(1A)	125.92(6)	Cd(A)-N(1A)-C(2A)	119.62(4)
C(1A)-N(1A)-C(2A)	114.37(5)	S(1A)-C(1A)-N(1A)	115.27(6)
S(1A)-C(1A)-N(2A)	119.40(4)	N(2A)-C(1A)-N(1A)	125.30(6)
Cl(1B)-Cd(B)-Cl(2B)	134.16(3)	Cl(1B)-Cd(B)-N(3B)	110.70(4)
Cl(2B)-Cd(B)-N(3B)	104.80(3)	Cl(1B)-Cd(B)-N(1B)	108.11(3)
Cl(2B)-Cd(B)-N(1B)	105.75(4)	N(3B)-Cd(B)-N(1B)	80.03(3)
C(4B)-N(2B)-C(1B)	122.39(4)	C(4B)-N(2B)-C(5B)	115.73(4)
S(2B)-C(4B)-N(2B)	112.69(4)	S(2B)-C(4B)-N(3B)	125.59(7)
N(2B)-C(4B)-N(3B)	121.72(4)	Cd(B)-N(3B)-C(4B)	127.16(6)
Cd(B)-N(3B)-C(8B)	112.57(3)	C(4B)-N(3B)-C(8B)	120.25(4)
Cd(B)-N(1B)-C(1B)	125.58(5)	Cd(B)-N(1B)-C(2B)	119.53(4)
C(1B)-N(1B)-C(2B)	114.79(6)	S(1B)-C(1B)-N(1B)	115.52(5)
S(1B)-C(1B)-N(2B)	119.15(4)	N(2B)-C(1B)-N(1B)	125.27(7)

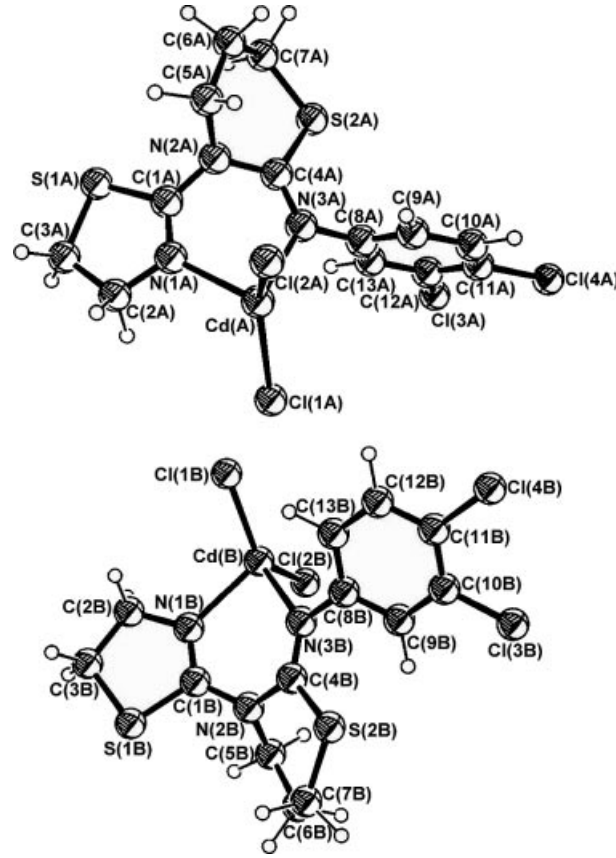


Figure 3 Molecular structure of $[CdCl_2(TzTn)]$ complex, showing the atom-numbering scheme. The thermal ellipsoids are drawn at a 50 % level.

bond lengths and angles, and Figure 3 shows a representation of the molecules forming the asymmetric unit.

According to the X-ray diffraction analysis, the bond lengths and angles as well as the rotation rate of the thiazoline ring with respect to the tetrahydro-1,3-thiazine ring are almost the same for the two independent molecules. However, the rotation between the 3,4-dichlorophenyl ring and the tetrahydro-1,3-thiazine fragment is clearly different in the two molecules [torsion angles of −77.1° for C(4A)-N(3A)-C(8A)-C(9A) and of 41.8° for C(4B)-N(3B)-C(8B)-C(9B)].

The Cd^{II} atom is bound to two chlorine atoms [Cd(A)-Cl(1A) = 2.44(3) Å and Cd(B)-Cl(1B) = 2.45(3) Å; Cd(A)-Cl(2A) = 2.44(3) Å and Cd(B)-Cl(2B) = 2.45(3) Å], one thiazoline nitrogen atom[Cd(A)-N(1A) = 2.33(8) Å and Cd(B)-N(1B) = 2.33(10) Å], and one imino nitrogen atom [Cd(A)-N(3A) = 2.37(10) Å and Cd(B)-N(3B) = 2.37(9) Å], in a distorted tetrahedral geometry.

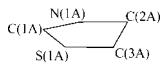
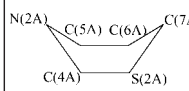
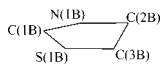
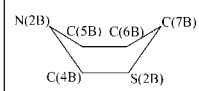
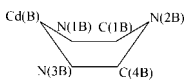
The Cd-Cl bond lengths in the $[CdCl_2(TnTz)]$ complex are slightly shorter than the average value [2.516(80) Å] for 45 tetrahedral Cd^{II} complexes with a Cd-Cl bond as calculated with the *CONQUEST* program [54] on the basis of the data from the *Cambridge Structural Database* (*CSD*) [55]. The Cd-N_{imine} bond distance is similar to the mean value [2.261(92) Å] calculated in the same way for 11 tetrahedral Cd^{II} complexes with a Cd-N_{imine} bond [55]. Finally, the Cd-$N_{thiazoline}$ bond distance is comparable to the values found for the following compounds: $[Cd(NO_3)_2(ATH)_2]$ [2.230(12) Å and 2.384(12) Å] [ATH is 2-acetyl-2-thiazoline- hydrazone] [24], $[CdCl_2(HzTz)]\cdot H_2O$ [2.241(2) Å] [HzTz is (2-thiazolin-2-yl)hydrazine] [25], $[CdCl\{(\mu\text{-}Cl)_2CdCl(\mu\text{-}Cl)\text{-}(\mu\text{-}PITT)Cd\}_2]_n$[2.271(2) Å] [PyTT is 2-(2-pyridyl)imino-N-(2-thiazolin-2-yl)thiazolidine] [26], $[Cd(NO_3)_2(PyTT)\text{-}(H_2O)]$ [2.351(2) Å] [26], $[Cd(NO_3)_2(TnInA)_2]$ [2.325(2) Å and 2.394(3) Å] [TnInA is 2-(indazol-1-yl)-2-thiazoline] [27], and $[Cd(NO_3)_2(TnInL)_2]$ [2.318(2) Å] [TnInL is 2-(indazol-2-yl)-2-thiazoline] [27].

The ligand-metal-ligand bite angles differ from the ideal value of 109.5°, varying between 79.98(3)° [N(3A)-Cd(A)-N(1A)] and 134.14(2)° [Cl(1A)-Cd(A)-Cl(2A)] in unit *A* and 80.03(3)° [N(3B)-Cd(B)-N(1B)] and 134.16(3)° [Cl(1B)-Cd(B)-Cl(2B)] in unit *B*. The dihedral angle formed by the Cl(1)-Cd-Cl(2) and N(1)-Cd-N(3) planes is 88.85° (in units *A* and *B*).

Table 3 gives the conformations and puckering parameters of the chelate and heterocycle rings calculated for the $[CdCl_2(TzTn)]$ complex according to the Cremer-Pople criterion [56]. It can be observed that the chelate rings and the six-membered heterocycle rings adopt a near-to-boat conformation, whereas the five-membered heterocycle rings are essentially planar.

Supplementary material. Crystallographic data for the structure of $[CdCl_2(TzTn)]$ have been deposited with the Cambridge Crystallo-

Table 3 Ring conformations and puckering parameters for the [$CdCl_2$(TzTn)] complex.

Unit	Ring conformation	Puckering parameters	Apex deviation from the mean plane (Å)	Maximum mean-plane deviation (Å)
A	 **Planar**	q = 0.023 Å	–	C(3A) = 0.014
	 **Boat**	Q = 0.690 Å θ = 94.9° ϕ = 302.0°	0.655 [N(2A)] 0.527 [C(7A)]	C(5A) = 0.015
	 **Boat**	Q = 0.556 Å θ = 81.4° ϕ = 357.5°	0.632 [Cd(A)] 0.377 [N(2A)]	C(1A) = 0.013
B	 **Planar**	q = 0.032 Å	–	C(3B) = 0.019
	 **Boat**	Q = 0.684 Å θ = 94.5° ϕ = 302.5°	0.645 [N(2B)] 0.528 [C(7B)]	C(5B) = 0.018
	 **Boat**	Q = 0.559 Å θ = 81.3° ϕ = 357.9°	0.636 [Cd(B)] 0.379 [N(2B)]	C(1B) = 0.010

graphic Data Centre (CCDC 642021 code). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: intcode +(1223)336-033; e-mail for inquiry: **fileserv@ccdc.cam.ac.uk**; e-mail for deposition: deposit@ccdc.cam.ac.uk).

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