

Inorganica Chimica Acta 260 (1997) 145-150



The crystal and molecular structures of dichlorobis(5,7-diphenyl-1,2,4-triazolo[1,5- α]pyrimidine)zinc(II) (1) and dichlorobis(5,7-diphenyl-1,2,4-triazolo[1,5- α]pyrimidine)cobalt(II) (2)

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Received 23 July 1996; accepted 22 October 1996

Abstract

The synthesis and structural studies of the new ligand 5,7-diphenyl-1,2,4-triazolo[1,5- α]pyrimidine (dp.p), which can be considered as an analog of purine, and its complexes are described. Complexes were characterised by spectral measurements (IR, NMR, UV-Vis). In addition X-ray structural analysis was performed. Crystals of [Zn(C₁₇H₁₂N₄)₂Cl₂] (1) revealed the following parameters: M_r =680.9; monoclinic C2/c; a = 17.777(4); b = 18.738(4); c = 12.759(3) Å; $\beta = 133.04(3)^\circ$; V = 3106.3(12) Å³; Z = 4; Dx = 1.456 Mg m⁻³; Mo K $\alpha \lambda = 0.71069$ Å; $\mu = 1.019$ mm⁻¹; F(000) = 1392; T = 293 K; R = 3.74% for 2188 observed reflections. [Co(C₁₇H₁₂N₄)₂Cl₂] (2); $M_r = 674.4$; monoclinic C2/c; a = 17.791(4); b = 18.773(4); c = 12.780(3) Å; $\beta = 132.89(3)^\circ$; V = 3127.3(12) Å³; Z = 4; Dx = 1.432 Mg m⁻³; Mo K $\alpha \lambda = 0.71069$ Å; $\mu = 0.756$ mm⁻¹; F(000) = 1380; T = 293 K; R = 5.22% for 1630 observed reflections.

Keywords: Crystal structures; Zinc complexes; Purine analog complexes

1. Introduction

Purine analogs obtained from diketones and 3-amino-1,2,4-triazole are interesting objects of studies owing to their possible different ways of binding with metal ions [1-5] and applications for pharmaceutical and agrochemical purposes [6,7]. In the reported X-ray structures of dimethyltriazolopyrimidine (dmtp), analogs of dptp, the N(3) monodentate coordination of dmtp was found. Complexes with dmtp form monomers [5], dimers [2] or polymers [1] depending on the central ion and anions. Nevertheless, there are complexes which appeared to be multinuclear depending on the 5,7substituents and the type of central ion [8]. New purine analogs with bulky substituents and strong electron-acceptor properties such as phenyl groups gave opportunity to study the influence of the electronic and steric factors on the coordination properties of the ligand and structural effects in complexes. The purpose of the present work is to describe the molecular structure of the new Zn(II) and Co(II) complexes with 5,7-diphenyl-1,2,4-triazolo[1,5- α] pyrimidine.

2. Experimental

2.1. Materials

The metal salts for the complex preparations were reagent grade and used without further purification. Dptp was prepared from reagent grade 3-amino-1,2,4,-triazole and dibenzoylmethane which were purchased from Aldrich.

2.2. Ligand preparation

Diphenyltriazolopyrimidine (5,7-diphenyl-triazolopyrimidine, dptp) was synthesised from dibenzoylmethane (0.0104 mol) which was dissolved in EtOH and added to 3amino-1,2,4-triazole (0.0104 mol), the reaction mixture was heated to boiling, and after all ethanol had been evaporated, 20 ml of 10% HCl was added. The reaction temperature was increased when the evolution of gases had ceased and kept at 170°C for 2 h. After cooling a brown precipitate was formed which was poured out on cold ethanol. The crude material was recrystallized from hot ethanol with a small amount of Norite. White crystals from ethanol have m.p. 156–157°C, yield 30% (on amino-1,2,4-triazole). IR spectra revealed no

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bands from C=O groups in the region $1400-1600 \text{ cm}^{-1}$, only bands characteristic for the pyrimidine ring vibrations were present. *Anal.* Calc. for C₁₇H₁₂N₄: C, 75.0; H, 4.4; N, 20.5. Found: C, 74.8; H, 4.3; N, 20.3%. ¹H NMR spectrum shows the following peaks: H(2) 7.60 (s); H(6) 8.51(s) ppm and two multiplets centered at 7.63 ppm (3H) and 8.35 (2H) from phenyl rings. ¹⁵N resonances were observed at N(1)-110.1; N(4)-120.2; N(3)-150.2; N(8)-158.6 ppm.

2.3. Preparation of complexes

Dptp (0.006 mol) was dissolved upon heating in EtOH, followed by the addition of $CoCl_2 \cdot 6H_2O$ (0.003 mol) in ethanol. The reaction mixture was stirred for 15 min, during which a blue precipitate of $CoCl_2(dptp)_2$ appeared, which was filtered, washed with ethanol and dried on the air. Crystals suitable for X-ray analysis were isolated under slow evaporation from a water-methanol solution. The same method of synthesis was applied for $ZnCl_2(dptp)_2$ and crystals for X-ray analysis were obtained from water/methanol solution. Anal. 1: Calc. for $ZnCl_2(dptp)_2$: Zn, 9.6; C, 60.0; H, 3.55; N, 16.5; Cl, 10.4. Found: Zn, 9.8; C, 59.8; H, 3.6; N, 16.6; Cl, 10.2%. 2: Calc. for $CoCl_2(dptp)_2$: Co, 9.4; C, 60.6; H, 3.5; N, 16.6; Cl 10.5. Found: Co, 9.5; C, 60.4; H, 3.7; N, 16.5; Cl, 10.4%.

2.4. Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR, samples were in KBr discs for 4000-400 cm⁻¹ and in polyethylene discs for the 400–100 cm^{-1} range. UV–Vis spectra were taken on a Perkin-Elmer 330 spectrophotometer with MgO as a reference using the diffuse reflectance technique. NMR spectra were recorded on a Varian GEM 200-XL spectrometer, samples were dissolved in DMSO-d_c, with TMS as a standard and typical parameters for running ¹H and ¹³C spectra. Natural abundance ¹⁵N resonances at 20.27 MHz in 10 mm sample tubes were recorded only for dptp, because 1 does not dissolve sufficiently in DMSO. Chemical shifts were measured relative to CH₂NO₂, the dotp sample for running spectra was dissolved in DMSO-d₆, and the concentration was 0.5 M. Routinely the NOE suppressed spectra were recorded using a pulse angle of 30° and a delay time of 10 s. A typical spectral width was 20 000 Hz and satisfactory signal-to-noise ratios were received after ca. 2000 transients. For the ¹⁵N DEPT spectra the routine programme MULT = 0.5, $^{1}J(NH) = 90$ Hz pulse for 90° for ^{1}H and ^{15}N , with a recycle time 2 s was applied. C. H and N were determined by means of elemental semi-micro analysis, whereas Co and Zn were measured by complexometric titration with EDTA.

2.5. X-ray data collection of the complexes

Crystals of 1 were obtained from water-methanol solution. Data collected for $0.6 \times 0.3 \times 0.3$ mm colorless crystal on a Kuma KM-4 diffractometer with Mo K α radiation, $\lambda = 0.71069$ Å. A complex of $M_r = 680.9$ crystallized in the monoclinic space group C2/c; a = 17.777(4); b =18.738(4); c = 12.759(3) Å; $\beta = 133.04(3)^\circ$; V = 3106.3(12)Å³; Z = 4; Dx = 1.456 Mg m⁻³; 2918 reflections were col-

Table I

Summary of diffraction data collection, structure solution and refinement for $[Zn(C_{17}H_{12}N_4)_2Cl_2]$ (1) and $[Co(C_{17}H_{12}N_4)_2Cl_2]$ (2)

Compound	$[Zn(C_{17}H_{12}N_4)_2Cl_2] (1)$	$[C_0(C_{17}H_{12}N_4)_2Cl_2]$ (2)
Empirical formula	$C_{34}H_{24}Cl_2N_8Zn$	C34H24Cl2N8C0
Crystal size (mm)	0.6×0.3×0.3	0.15×0.2×0.4
Space group	C2/c	C2/c
a (Å)	17.777(4)	17.791(4)
Ь (Å)	18.738(4)	18.773(4)
c (Å)	12.759(3)	12.780(3)
β(°)	133.04(3)	132.89(3)
V (Å ³)	3106.3(12)	3127.3(12)
Z	4	4
F(000)	1392	1380
Formula weight	680.9	674,4
Absorption coefficient (mm ⁻¹)	1.019	0.756
Diffractometer used	KM-4	Syntex P21
Radiation	Mo Kα λ=0.71073	Mo K α $\lambda = 0.71073$
20 range	2.0-50.0°	1.0-48.0°
Scan type	20-0	2 0 0
Index ranges	$-21 \le h \le 15, 0 \le k \le 22, 0 \le l \le 15$	$0 \le h \le 20, 0 \le k \le 21, -14 \le l \le 10$
Reflections collected	2918	2331
Independent reflections	2758 ($R_{int} = 1.17\%$)	$2304 (R_{int} = 2.78\%)$
Observed reflections	2188 $(F \ge 2.0\sigma(F))$	$1630 (F \ge 2.0\sigma(F))$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$	$w^{-1} = \sigma^2(F) + 0.0000F^2$
Final R indices (obs. data)	R = 3.74%, $wR = 3.64%$	R = 5.22%, $wR = 4.41%$
R indices (all data)	R = 5.46%, wR = 3.67%	R = 11.08%, w $R = 4.47%$
Coodness-of-fit	3.32	2.68
Largest and mean Δ / σ	0.135, 0.007	0.063, 0.004
Largest difference peak (e Å-3)	0.37	0.33
Largest difference hole (e Å $^{-3}$)	- 0.30	-0.31

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lected for the 2θ range $2.0-50.0^\circ$ using a $2\theta-\theta$ scan with a variable speed; index ranges $-21 \le h \le 15$, $0 \le k \le 22$, $0 \le l \le 15$. 2758 reflections were independent, $R_{int} = 1.17\%$. No absorption correction was applied. Two standard reflections were measured every 98 reflections, and did not reveal any significant intensity variations. The structure was solved by the Patterson method using Siemens SHELXTL PLUS [9]. Hydrogen atom positions were calculated from geometry and used as riding atoms with fixed isotronic U in the refinement. Least-squares refinement with statistical weights $w = \sigma^{-2}(F)$ resulted in R(F) = 3.74%, wR = 3.64%. S=3.32. Largest and mean Δ/σ values for the final refinement were 0.135 and 0.007, respectively. Largest positive and negative peaks on a difference map were 0.37 and $-0.30 \text{ e} \text{ Å}^{-3}$, respectively. Crystals of 2 were obtained from water-methanol solution. Data collected for 0.15×0.2×0.4 mm dark blue crystal on a Kuma KM-4 diffractometer with Mo K α radiation, $\lambda = 0.71069$ Å. A complex of $M_{\rm c} = 674.4$ crystallized in the monoclinic space group $C2/c; a = 17.791(4); b = 18.773(4); c = 12.780(3) \text{ Å}; \beta =$ $132.89(3)^{\circ}$; V = 3127.3(12) Å³; Z = 4; Dx = 1.432 Mg m⁻³; 2331 reflections were collected for the 2θ range 1.0-48.0° using a $2\theta - \theta$ scan with a variable speed; index ranges $0 \le h \le 20, \ 0 \le k \le 21, \ -14 \le l \le 10.$ 2304 reflections were independent, $R_{int} = 2.78\%$. No absorption correction applied. Two standard reflections were measured every 98 reflections, and did not reveal any significant intensity variations. The structure was solved by the Patterson method using Siemens SHELXTL PLUS [9]. Hydrogen atom positions were cal-

Table 2

Atomic fractional coordinates (×10⁴) and equivalent isotropic displacement parameters U_{co} (Å²×10³) for [Zn(C₁₇H₁₂N₄)₂Cl₂] (1)

	x	у	z	U _{eq}
Zn(1)	5000	1725(1)	2500	37(1)
Cl(1)	6077(1)	2353(1)	2523(1)	51(1)
N(1)	2489(2)	750(1)	- 1364(3)	44(2)
C(2)	3031(2)	1254(2)	-412(3)	46(2)
N(3)	4033(2)	1093(1)	754(2)	38(2)
C(3A)	4125(2)	420(2)	517(3)	32(2)
N(4)	4949(2)	3(1)	1325(2)	33(2)
C(5)	4828(2)	-660(2)	857(3)	33(2)
C(6)	3888(2)	- 897(2)	-472(3)	38(2)
C(7)	3047(2)	-459(2)	- 1305(3)	36(2)
N(8)	3190(2)	205(1)	- 757(2)	35(2)
C(51)	5725(2)	-1140(2)	1822(3)	39(2)
C(52)	6623(2)	-883(2)	3112(3)	50(2)
C(53)	7459(3)	-1332(2)	4056(4)	64(3)
C(54)	7418(3)	- 2028(2)	3715(4)	77(3)
C(55)	6548(3)	- 2287(2)	2434(5)	90(4)
C(56)	5698(3)	- 1849(2)	1503(4)	66(3)
C(71)	2029(2)	-664(2)	-2686(3)	44(2)
C(72)	1978(3)	-1014(2)	- 3691(4)	61(3)
C(73)	1023(3)	1237(2)	- 4976(4)	86(3)
C(74)	153(3)	-1119(2)	- 5218(5)	99(3)
C(75)	210(3)	-772(2)	- 4240(5)	89(4)
C(76)	1146(3)	-537(2)	- 2950(4)	64(3)

Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ii} tensor.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients U_{eq} ($\dot{A}^2 \times 10^3$) for [Co(C₁-H₁-N₄)-Cl₂] (2)

	x	y	z	U _{eq}
Co(1)	5000	1717(1)	2500	43(1)
CI(1)	6080(1)	2355(1)	2529(1)	58(1)
N(1)	2480(3)	746(2)	- 1367(4)	51(3)
C(2)	3034(4)	1256(3)	-412(5)	52(4)
N(3)	4031(3)	1095(2)	754(4)	42(3)
C(3A)	4117(3)	416(2)	507(5)	38(3)
N(4)	4943(3)	0(2)	1319(4)	39(3)
C(5)	4819(3)	-660(3)	852(5)	38(4)
C(6)	3871(3)	-900(3)	-483(5)	43(4)
C(7)	3036(4)	-461(3)	- 1311(5)	41(4)
N(8)	3178(3)	206(2)	-765(4)	41(3)
C(51)	5719(4)	~1145(3)	1811(5)	44(4)
C(52)	6615(4)	- 884(3)	3114(5)	53(4)
C(53)	7448(4)	-1334(3)	4039(6)	69(5)
C(54)	7400(5)	-2029(4)	3702(7)	81(6)
C(55)	6528(5)	-2286(3)	2436(7)	95(6)
C(56)	5691(4)	-1851(3)	1493(6)	72(5)
C(71)	2025(4)	-664(3)	-2690(5)	49(4)
C(72)	1968(4)	-1013(3)	- 3691(5)	61(4)
C(73)	1012(5)	- 1234(3)	-4972(6)	98(6)
C(74)	148(5)	-1117(4)	- 5227(8)	105(6)
C(75)	209(5)	-776(3)	-4228(8)	95(6)
C(76)	1144(4)	- 535(3)	- 2945(6)	70(5)

Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ii} tensor.

culated from geometry and used as riding atoms with fixed isotropic U in the refinement. Least-squares refinement with statistical weights $w = \sigma^{-2}(F)$ resulted in R(F) = 5.22%, wR = 4.41%, S = 2.68. Largest and mean Δ/σ values for final refinement were 0.063 and 0.004, respectively. Largest positive and negative peaks on a difference map were 0.33 and -0.31 e Å^{-3} , respectively. The atomic scattering factors were taken from the International Tables for Crystallography [10]. The data collection, structure solution and refinement process are summarized in Table 1. The atomic positions and isotropic thermal parameters for 1 and 2 are listed in Table 2 and Table 3, respectively. The selected bond lengths and angles are listed in Table 4. See also Section 7.

3. Results and discussion

Both complexes are isomorphous. The complex molecules with the numbering scheme are shown on Figs. 1 and 2.

3.1. Description of the molecular structures

3.1.1. $[Zn(C_{17}H_{12}N_4)_2Cl_2](1)$

The Zn(II) ion is located on a crystallographic twofold axis; therefore the complex molecule reveals the diad symmetry. The coordination sphere of a Zn(II) is a distorted tetrahedron, with Zn–Cl and Zn–N distances of 2.232(1) and 2.022(2) Å, respectively. The Cl–Zn–Cl angle is 116.3(1)°,

N(3)-Zn-N(3) is 108.4(1)°, while two N-Zn-Cl angles are 102.5(1) and 113.6(1)°, respectively.

The phenyl substituents were found to be slightly disordered. An attempt to define a model for the disorder including

Table 4

Selected bond lengths (Å) and bond angles (°) for $[Zn(C_{17}H_{12}N_4)_2Cl_2]$ (1) and $[Co(C_{17}H_{17}N_4)_2Cl_2]$ (2)

1		2	
Zn(1)-Cl(1)	2.232(1)	Co(1)-Cl(1)	2.243(2)
Zn(1)-N(3)	2.022(2)	Co(1)-N(3)	2.020(3)
Zn(1)-Cl(1A)	2.232(1)	Co(1)-Cl(1A)	2.243(2)
Zn(1)-N(3A)	2.022(2)	Co(1)-N(3A)	2.020(3)
N(1)-C(2)	1.303(4)	N(1)-C(2)	1.319(6)
N(1)-N(8)	1.371(4)	N(1)-N(8)	1.365(6)
C(2)-N(3)	1.364(3)	C(2)-N(3)	1.364(5)
N(3)-C(3A)	1.333(4)	N(3)-C(3A)	1.346(6)
C(3A)-N(4)	1.327(4)	C(3A)-N(4)	1.330(6)
C(3A)-N(8)	1.371(3)	C(3A)-N(8)	1.376(5)
N(4)-C(5)	1.331(4)	N(4)-C(5)	1.327(6)
C(5)-C(6)	1.413(3)	C(5)-C(6)	1.429(5)
C(5)-C(51)	1.478(4)	C(5)-C(51)	1.491(6)
C(6)-C(7)	1.367(4)	C(6)-C(7)	1.365(6)
C(7)-N(8)	1.364(4)	C(7)-N(8)	1.371(6)
C(7)-C(71)	1.475(3)	C(7)-C(71)	1.474(5)
Cl(1)-Zn(1)-N(3)	113.6(1)	Cl(1)-Co(1)-N(3)	113.9(2)
Cl(1)-Zn(1)-Cl(1A)	116.3(1)	Cl(1)-Co(1)-Cl(1A)	115.5(1)
N(3)-Zn(1)-Cl(1A)	102.5(1)	N(3)-Co(1)-Cl(1A)	102.3(1)
Cl(1)-Zn(1)-N(3A)	102.5(1)	Ci(1)-Co(1)-N(3A)	102.3(1)
N(3)-Zn(1)-N(3A)	108.4(1)	N(3)-Co(1)-N(3A)	109.3(2)
Cl(1A)-Zn(1)-N(3A)	113.6(1)	CI(1A)-Co(1)-N(3A)	113.9(2)
N(1)-C(2)-N(3)	116.2(3)	N(1)-C(2)-N(3)	116.5(5)
Zn(1)-N(3)-C(2)	124.6(2)	Co(1)-N(3)-C(2)	125.1(4)
Zn(1)-N(3)-C(3A)	131.3(2)	Co(1)-N(3)-C(3A)	131.2(2)
N(4)-C(5)-C(51)	116.2(2)	N(4)-C 5)-C(51)	116.4(3)
C(6)-C(5)-C(51)	121.9(3)	C(6)- (5)-C(51)	121.6(4)
C(6)-C(7)-C(71)	124.9(3)	C(6)-C(7)-C(71)	124.8(4)
N(8)-C(7)-C(71)	119.9(3)	N(8)C(7)C(71)	119.8(4)
C(5)-C(51)-C(52)	119.5(3)	C(5)-C(51)-C(52)	118.8(5)
C(5)-C(51)-C(56)	122.6(2)	C(5)-C(51)-C(56)	122.8(4)
C(52)-C(51)-C(56)	117.9(3)	C(52)-C(51)-C(56)	118.3(4)
C(7)-C(71)-C(72)	118.7(4)	C(7)-C(71)-C(72)	119.4(6)
C(7)-C(71)-C(76)	120.6(4)	C(7)-C(71)-C(76)	120.0(6)
C(72)-C(71)-C(76)	120.6(3)	C(72)C(71)C(76)	120.5(5)



Fig. 1. The ORTEP drawing of the $[Zn(C_{17}H_{12}N_4)_2Cl_2]$ molecule (1) with the atom numbering scheme. Ellipsoids correspond to 30% probability.



Fig. 2. The ORTEP drawing of the $[Co(C_{17}H_{12}N_4)_2Cl_2]$ molecule (2) with the atom numbering scheme. Ellipsoids correspond to 30% probability.

the rotation around the single bonds failed. Consequently in the final refinement the atoms of both phenyl rings were refined anisotropically in a single substituent orientation. The dynamics of the structure is revealed, however, in the anisotropy of the U_{ij} thermal parameters (see deposited material), with the most pronounced effect observed for the ring atoms distant from the single bonds to the triazolopyrimidine system. This suggests the model for the disorder should account not only for rotation around the single bond, but also for some tilt from this bond line.

The phenyl rings of the ligand reveal the shortest bonds around C(54) and C(74) atoms. The shortening of these bonds could be considered to be a result of a triazolopyrimidine substituent effect. However, the structure dynamics contributes significantly to the geometry distortion, and the precise analysis of the phenyl ring geometry would require low temperature experimental data.

Two phenyl substituents of a triazolopyrimidine system are oriented differently with respect to the central ring system. The steric effects around the C(7) atom result in a rotation of the phenyl substituent around the single C(7)-C(71)bond, the dihedral angle between best planes being 127.1°. In contrast, the less crowded environment of C(5) results in a dihedral angle of 5.5° between the best planes calculated for both ring systems. The Zn(II) ion deviates from the ligand triazolopyrimidine-phenyl best plane by 0.23 Å, compared with the mean value of 0.009 Å for atoms defining the plane. The deviation of phenyl ring C(51) atom from the triazolopyrimidine best plane by 0.13 Å is also statistically significant. In contrast, the deviation of C(71) from this plane is found to be 0.005 Å, smaller than the mean deviation value.

3.1.2. $[Co(C_{17}H_{12}N_4)_2Cl_2](2)$

The central ion is positioned on a diad, similar to the Zn(II) ion in complex 1. Analogous to 1, the molecule of the Co(II) complex reveals twofold symmetry.

There is no statistically significant difference in the ligand geometry, compared with that found in a Zn(II) complex 1.



Fig. 3. The perspective view of two complex molecules in $[Co(C_{17}-H_{12}N_4)_2Cl_2]$ (2). The extensive stacking interactions between two ligand molecules (similar to those found in $[Zn(C_{17}H_{12}N_4)_2Cl_2]$) enforce the planarity of C(5) bound phenyl ring. The C(7) phenyl substituent penetrates the space available between the Cl and dpt pigands of the adjacent molecule and is twisted with respect to the triazolpyrimidine ring system.

Also the rotation of the phenyl rings around the bridging single bonds is similar in both complexes: the C(5)-bound ring forms a dihedral angle of 5.8°, while the dihedral angle between C(7) bound phenyl substituent and the best plane of a triazolopyrimidine system is 132.0°. The deviation of the central Co(II) ion from the best plane of ligand core is 0.24 Å, compared with mean value of 0.008 Å for the ring system atoms defining the plane (deposited material). The deviations of the phenyl C(51) and C(71) atoms from the best plane of triazolopyrimidine by 0.021 and -0.020 Å are found to be statistically significant.

The disorder of the phenyl substituents found in both complexes is similar and is more pronounced for the phenyl substituent of C(7) position. This suggests the dynamics of both structures is related to the steric effects near the phenyl substituents and to intermolecular interactions in the crystal lattice. The differences in the phenyl ring orientation between planar C(5) and tilted C(7) substituents is almost identical in both complex structures. The non-planar binding of C(7)substituent could be related to the minimization of phenyl hydrogen interactions with N(1) and C(6)-H atoms of the triazolopyrimidine system.

There are extensive stacking interactions in both complex structures between planar phenyl-triazolopyrimidine ring systems of the molecules related by a center of symmetry. The interatomic distances between head-to-tail oriented rings range from 3.305 Å for $C(5) \cdots N(4) [1-x, -y, -z]$ to 3.348 Å for $C(51) \cdots C(3a) [1-x, -y, -z]$ in $[Zn(C_{17}H_{12}N_4)_2Cl_2]$ (1), while corresponding distances in $[Co(C_{17}H_{12}N_4)_2Cl_2]$ (2) vary from 3.318 to 3.451 Å. In the crystal lattice, the tilted C(71)-C(76) phenolic ring penetrates the space between the Cl and dptp ligands of the adjacent molecule (Fig. 3). In this orientation the repulsive interactions to the C(51)-C(56) ring of the adjacent mole-

cule are minimized, and only its H(55a) hydrogen is positioned above the center of the tilted ring. In the Zn complex it forms a series of contacts to all six ring carbon atoms ranging from C(73)...H(55a) [-1/2+x, -1/2-y, -1/2]2+z 2.763 Å to C(76)...H(55a) [-1/2+x, -1/2-y]-1/2+z] 3.042 Å. In the Co(II) complex there are only three such interactions to C(71), C(72) and C(73) atoms, the respective distances being 3.048, 2.905 and 2.935 Å. The twisted phenyl ring C(71)-C(76) forms some stacking interactions with similar ring of an adjacent molecule. In the Zn(II) complex 1 there is only one such contact $C(75) \cdots C(75) [-x, -y, -1-z] 3.273 \text{ Å}$, while in the Co complex 2 the corresponding distance is 3.306 Å. In this orientation the C(74)-H group of the twisted phenyl ring forms a contact to Cl(1) [0.5-x, -0.5+y, -0.5-z], the H…Cl and C…Cl distances being 2.880 and 3.584 Å in the Zn complex 1 and 2.903 and 3.594 Å in the Co complex 2 structure, respectively.

The C(2)-H(2a) group, positioned in the triazolopyrimidine ring between N(1) and N(3) bound to the central ion, seems to be polarized. In both complexes it forms an interaction to Cl(1), the H(2a)...Cl(1) [-1/2+x, 1/2-y]-1/2+z and C(2)...Cl(1) [-1/2+x, 1/2-y, -1/2]+z] distances being 2.806 and 3.649 Å in the Zn(II) complex 1, and 2.828 and 3.655 Å in the Co(II) complex 2. The H…Cl distance is shorter than the sum of the entity radii (ca. 3.0 Å) and therefore could be considered as a weak H-bond. The calculated angles C-H···Cl are 139(1) and 145(1)° for Zn(II) and Co(II) complexes, respectively. The contacts described fulfil the H...A distance criterion [11] and DH...A angular criterion by Jaskólski [12] for H-bonds. Similar interactions have been observed for histamine complexes with Cu(II) chloride and Co(III) carbonate chloride (13,14] and in the case of histidinium salt [15].

4. Electronic spectra

Ligand field spectra of $CoCl_2(dptp)_2$ revealed multiple absorptions in the near-infrared with maxima at 6150 cm⁻¹, 7580 cm⁻¹, 9150 cm⁻¹ and in the visible range at 16 740 cm⁻¹. The latter can be assigned as $\nu_3 = {}^{4}A_2 \rightarrow {}^{4}T_1$ (P) in tetrahedral field. Among them the near-infrared absorption at 7580 cm⁻¹ can be assigned to the transition $\nu_2 = {}^{4}A_2 \rightarrow {}^{4}T_1$ (F). The positions of the absorption bands clearly correspond to the tetrahedral symmetry of CoL₂Cl₂. The presence of three bands in the near-infrared range is typical of ligands which differ significantly in strength. In comparison with the Co(dmtp)₂Cl₂ spectrum [16] the bands in the complex discussed are shifted slightly (500 cm⁻¹) into the direction of higher wavenumbers. This can be explained by a stronger field from dptp.

5. NMR spectra

¹H and ¹³C resonances of the phenyl ring in the Zn(II) complex are found at the same frequencies in comparison

with the observed in the free ligand spectrum. Only signals from H(2) and H(6) are shifted downfield upon complexation from 8.17 and 7.50 ppm in the free ligand to 8.16 and 8.73 ppm. The positions of the ¹³C signals from C(2) and C(6) in the spectrum of complex 1 appeared at 156.0 and 106.8 ppm (dptp:156.0, 106.9), C(3a) 155.8, C(5) 160.7, C(7) 147.5 and they do not differ from the free ligand signals. Coordination via N(3) does not affect the ¹³C spectrum of complex.

6. Infrared spectra analysis

Infrared spectra in the range $400-4000 \text{ cm}^{-1}$ of the free ligand and both complexes reveal no distinct differences what is obvious for the ligand with such low symmetry as dptp (C_s) . Only small shifts (not exceeding 10 cm⁻¹) in the range 1500–1600 cm⁻¹ for pyrazole and pyrimidine ring vibrations are noticed upon complexation.

The far-infrared spectra (400-100 cm⁻¹) of both salts present absorption bands from the metal-donor atom stretching vibrations. Because the local symmetry of the ligand atoms around the central ion is C_{2m} from group theory calculations we have to expect two symmetric (A1) M-Cl and M-N stretching vibration bands and two asymmetric M-Cl and M-N stretching vibrations bands of the type B₁ and B₂. Also five deformation vibrations bands of the angles Cl-M-Cl (A₁), Cl-M-N (A₁, B₁, B₂) and N-M-N (A₁) should be observed in the same region. In the range below 400 cm⁻¹ the spectrum of ZnCl₂(dptp)₂ exhibited a series of absorption bands which can be assigned to the following M-L bonds vibrations: $Zn-Cl_{as} = 325 \text{ cm}^{-1}$, $Zn-Cl_{s} = 299 \text{ cm}^{-1}$, Zn- $N_{as} = 270 \text{ cm}^{-1}$, Zn-N_s = 249 cm⁻¹, whereas for the CoCl₂- $(dptp)_2$ the following bands were found Co- $Cl_{as} =$ 337 cm^{-1} , Co-Cl_s = 303 cm⁻¹, Co-N_{as} = 276 cm⁻¹, Co-N_s = 245 cm⁻¹. Frequencies at which M-L stretching vibrations were found in the spectra of the complexes studied are in good agreement with Nakamoto's [17] studies of the isotopical shift observed in the transition metal complexes. Absorption bands are in the region proposed by other authors for tetrahedral MCl₂L₂ complexes, where L are N donor ligands of different amines [18,19]. The values found for M-L stretching vibrations are in good agreement with those reported for the dimethyltriazolopyrimidine complexes with transition metals [20], adenine [21,22] and adenosine complexes [23,24].

The deformation vibrations of the angles N–Zn–N and N– Co–N appeared at 209 and 222 cm⁻¹, which is in accordance with the extensive studies of Goldstein and Hughes [25] of the tetrahedral complexes of pyridine and deuterated pyridine. Bending vibrations of Cl–M–Cl angles in the spectra of both complexes can be tentatively assigned to the medium intensity bands in the range 190–195 cm⁻¹. Deformation bands of Cl–M–N angles most probably appeared below 150 cm^{-1} but it is difficult to assign them to the exact frequencies.

7. Supplementary material

Details of data collection and structure determination, complete lists of bond lengths and angles, anisotropic thermal parameters, hydrogen atom parameters, details of intermolecular contacts and best planes, as well as the structure factor tables are deposited with the Cambridge Structural Database as Supplementary Material.

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