ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 12, pp. 787–791. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © Yu.V. Kokunov, V.V. Kovalev, Yu.E. Gorbunova, G.A. Razgonyaeva, 2015, published in Koordinatsionnaya Khimiya, 2015, Vol. 41, No. 12, pp. 718–722.

Supramolecular Ensemble of a Coordination Compound of CdI_2 with 2-Amino-4-Methylpyrimidine

Yu. V. Kokunov*, V. V. Kovalev, Yu. E. Gorbunova, and G. A. Razgonyaeva

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia

**e-mail: kokunov@igic.ras.ru*

Received May 28, 2015

Abstract—Coordination compound $[CdI_2(Ampym)_2]$ is synthesized by the reaction of 2-amino-4-methylpyrimidine (Ampym, $C_5H_7N_3$) with CdI_2 in an acetonitrile–ethanol (20 : 1) mixture, and its crystal structure is determined. The crystals are triclinic, space group $P\bar{1}$, $a = 6.241(1)$, $b = 11.929(1)$, $c = 12.259(1)$ Å, $\alpha = 81.78(1)°$, $\beta = 78.82(1)°$, $\gamma = 75.82(1)°$, $V = 863.6(2)$ Å^3, $\rho_{calcd} = 2.248$ g/cm^3, $Z = 2$. The cadmium atom has a tetrahedral coordination by two nitrogen atoms of crystallographically nonequivalent ligands L and two iodine atoms (Cd(1)–N_{av} 2.305(6), Cd(1)–I(1) 2.7093(8), and Cd(1)–I(2) 2.7235(7) Å). The angles at the Cd atom are 100.8(2)°–124.51(3)° (the maximum value corresponds to the ICdI angle). The planar rings N_2C_4 (±0.01 Å) of coordinated ligands L are arranged at an angle of 84.8° relatively to each other. The complexes are joined by hydrogen bonds N–H···N into zigzag supramolecular chains.

DOI: 10.1134/S1070328415120027

INTRODUCTION

Studies of the self-organization of organic and inorganic molecules and the subsequent preparation of solid crystalline substances became more urgent in the recent years for the synthesis of new compounds with a number of important physical and chemical properties. Metal ions, counterions, and ligands are the main factors determining the structure and dimensionality of the compound. Organic compounds containing two and more functional nitrogen atoms (bipyridine, phenazine, pyrazine, pyrimidine, and others) are often used as N-aromatic ligands. Pyrimidine and its substituted analogs allow one to synthesize both polynuclear compounds using their bridging properties and discrete monomeric complexes and are involved in hydrogen bonding [1–9].

Ligand 2-amino-4-methylpyrimidine (Ampym) can add to the metal ion using several modes: as a monodentate ligand due to the amino group or one pyrimidine nitrogen atom, as a bridging ligand (N atoms of the amino group and pyrimidine ring, two N atoms of the heterocycle), as a chelating ligand (N atoms of the heterocycle and NH_2 group), or as a tridentate ligand [6]. In addition, as said above, Ampym can participate in hydrogen bonds to form supramolecular ensembles. The syntheses of coordination compounds of $AgReO_4$, $AgCH_3SO_3$, $CoCl_2$, and $Cd(NO_3)_2$ with Ampym are described [2, 8]. In these compounds, the latter is coordinated by the pyrimidine nitrogen atom through the monodentate mode.

In this work, we obtained the coordination compound $[CdI_2(Ampym)_2]$ (**I**) and determined its structure.

EXPERIMENTAL

The initial reagents were CdI_2 (reagent grade) and 2-amino-4-methylpyrimidine (Aldrich) taken in a ratio of 1 : 2.

Synthesis of compound I. A weighed sample of CdI_2 (0.4280 g, 1.17 mmol) was dissolved in an acetonitrile–ethanol (20 : 1) mixture (4 mL). A weighed sample of Ampym (0.2551 g, 2.34 mol) was dissolved in 6 mL of the same solvents with stirring and heating for 10 min at ~40°C. After mixing the solutions, a solid phase immediately precipitated as nontransparent plate-like crystals, which were recrystallized from the same mixture of solvents. In a day, the precipitated transparent prismatic crystals were separated from the solution, dried in air, and examined by elemental analysis, IR spectroscopy, and X-ray diffraction analysis.

For $C_{10}H_{14}N_6I_2Cd$			
anal. calcd., %:	C, 20.48;	N, 14.33;	H, 2.39.
Found, %:	C, 20.51;	N, 13.84;	H, 2.47.

IR spectra were recorded on a Nexus FT-IR spectrometer (Nicolet) using the attenuated total reflectance (ATR) technique in a range of 550–4000 cm^{-1}.

X-ray diffraction analysis. An experimental material for crystals **I** was obtained on an Enraf-Nonius CAD-4 automated diffractometer. The structure was

Table 1. Main crystallographic data and experimental characteristics for structure **I**

Parameter	Value
FW	584.5
Color, habitus	Colorless block
Crystal size, mm	0.30 × 0.23 × 0.10
Crystal system, space group	Triclinic, $P\bar{1}$
Parameter of bonds:	
a, Å	6.241(1)
b, Å	11.929(1)
c, Å	12.259(1)
α, deg	81.78(1)
β, deg	78.82(1)
γ, deg	75.82(1)
V, Å^3	863.6(2)
Z	2
ρ_{calcd}, g/cm^3	2.248
μ_{Mo}, mm^{-1}	4.836
F(000)	540
Temperature, K	293(2)
Radiation (λ, Å)	MoK_α (0.71073), graphite monochromator
Scan mode	ω
θ Range, deg	2.33–29.97
Index ranges	$-8 \le h \le 4$, $-16 \le k \le 16$, $-17 \le l \le 17$
Total number of reflections/independent (R_{int})	6809/4980 (0.0398)
Completeness to θ = 29.97, %	99.2
Number of reflections with $I \ge 2\sigma(I)$	2991
Number of refined parameters	173
Goodness-of-fit for F^2	0.979
R_1, wR_2 ($I \ge 2\sigma(I)$)	0.0657, 0.1671
R_1, wR_2 (all data)	0.1135, 0.1976
Residual electron density (max/min), *e*/Å^3	2.742/–2.968

solved by a direct method and refined by least squares in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [10]. Positions of hydrogen atoms were calculated geometrically and included into refinement in the riding model. The main crystallographic data and experimental characteristics for structure **I** are presented in Table 1. The geometric parameters of hydrogen bonds are given in Table 2.

RESULTS AND DISCUSSION

The most significant vibration frequencies of the free Ampym molecule and coordination compound **I** observed in the IR spectra are presented in Table 3. In the IR spectrum of compound **I**, the bands of antisymmetrical and symmetrical stretching vibrations of theNH_2 group are not shifted to the low-frequency range compared to similar bands in the spectrum of the free molecule. For the coordination of primary amine with the metal through the nitrogen atom of the amino group, a similar shift can attain 100 cm^{-1}. For the earlier studied Ag(I) compounds with the dianiline derivatives, the low-frequency shift in the spectra was 60–80 cm^{-1} due to ligand binding through the amino group [3, 11]. Therefore, in compound **I** Ampym is coordinated only through the nitrogen atoms of the heterocycle. It is substantial that the ν_s(N–H) band at 3143 cm^{-1} in the spectrum of free Ampym is noticeably split in the spectrum of compound **I** (into two components at 3114–3144 cm^{-1}). The ν_{as}(N–H) band of the free ligand at 3303 cm^{-1} in the spectrum of compound **I** is shifted to the high-frequency range and is split into three bands at 3385, 3357, and 3318 cm^{-1}. In our opinion, the latter is related to different hydrogen bonds in the complex that are formed by the protons of the amino group of Ampym, which is shown in Fig. 1. Substantial changes in the ν(C=N) and ν(C=C) stretching vibrations of free Ampym (1561 and 1470 cm^{-1}, respectively) are observed in the spectrum of complex **I**. The former appear as two intense bands at 1592 and 1554 cm^{-1}, and the ν(C=C) band is split into two maxima at 1476 and 1462 cm^{-1}. We believe that these changes are related to the nonequivalent character of the N atoms of the heterocycle in the

Table 2. Geometric parameters of hydrogen bonds in structure **I**

Bond A–H···B	Distance, Å			Angle AHB, deg	Position of atom B
	A···B	A–H	H···B		
N(2)–H(2*A*)···I(1)	3.735(7)	0.86	2.89	169	*x*, *y*, *z*
N(2)–H(2*B*)···N(3)	3.038(8)	0.86	2.18	175	$-x$, $-y+1$, $-z+1$
N(5)–H(5*D*)···N(6)	3.022(9)	0.86	2.20	161	$-x$, $-y$, $-z$
N(5)–H(5*E*)···I(2)	3.580(6)	0.86	2.72	178	*x*, *y*, *z*

complex caused by the monodentate coordination mode of the organic ligand. Similar changes in the IR spectra were also observed for the earlier structurally studied complexes of Ag(I), Cd(II), and Co(II) with Ampym in which the latter exhibited the monodentate properties [2, 3]. The $\delta(NH_2)$ band at 1648 cm^{-1} and δ(CH) of the heterocycle at 786 cm^{-1} shifted to the low-frequency range by 11 and 8 cm^{-1}, respectively, compared to the spectrum of Ampym can be distinguished among the bending vibrations observed in the spectrum of compound **I**. A more significant change for this type of vibrations is observed in the spectrum of compound **I** in a range of 900–650 cm^{-1}. For the most part of primary amines, this change is characterized by the appearance of a broad band due to external bending vibrations of the NH_2 group. This range is poorly studied but interesting, because its shape and position depend noticeably on the formation of hydrogen bonds. The spectrum of Ampym exhibits a broad intense band split into three components with maxima at 629, 617, and 599 cm^{-1}, which can be assigned to the considered type of vibrations. In the spectrum of compound **I**, this band with a less pronounced splitting is shifted to 691 cm^{-1}, indicating that hydrogen bonds involving the NH_2 group exist in the complex.

Discrete complexes $[Cd(Ampym)_2I_2]$ are formed in structure **I** (Fig. 2). The cadmium atom has a tetrahedral coordination with two nitrogen atoms of the crystallographically nonequivalent Ampym ligands and two iodine atoms (Cd(1)–N_{av} 2.305(6), Cd(1)–I(1) 2.7093(8), and Cd(1)–I(2) 2.7235(7) Å; the angles at the Cd atom range from 100.8(2)° to 124.51(3)°, and the maximum value corresponds to the ICdI angle). The planar rings N_2C_4 (±0.01 Å) of coordinated ligands L are arranged at an angle of 84.8° relatively to each other. The complexes are bound by hydrogen bonds N–H···N into zigzag supramolecular chains extended along the [001] direction (Fig. 1, Table 2). Note that both the nitrogen atoms of the adjacent heterocycle and the iodine atoms are proton acceptors in the hydrogen bond of each amino group of Ampym (Fig. 3). The crystals of compound **I** are isostructural to the earlier studied crystals of $[Co(Ampym)_2Cl_2]$ [3].

Table 3. Vibration frequencies (cm^{-1}) in the IR spectra of free Ampym and $CdI_2(Ampym)_2$

Frequency assignment	Ampym	$CdI_2(Ampym)_2$
ν_{asym}(N–H)	3303	3385, 3357, 3318
ν_{sym}(N–H)	3143	3144, 3114
ν(C=N)	1561	1592, 1554
ν(C=C)	1470	1475, 1462
δ(NH)	1659	1645
δ(CH) of heterocycle	796	788
External bending vibrations of NH_2 group	629, 617, 599	691

We have previously studied the structures of two silver compounds with 2-amino-4-methylpyrimidine and weakly coordinating anions $[Ag(Ampym)_2(ReO_4)]$ (**II**) and $[Ag(Ampym)_2(CH_3SO_3)]$ (**III**) [2]. In both cases, discrete cationic complexes $[Ag(Ampym)_2]^+$ with the nearly linear coordination of the Ag^+ cation are formed. The complexes in compound **II** interact due to the hydrogen bonds N–H···N with the formation of supramolecular zigzag chains $\left[Ag(Ampym)_2\right]^+_\infty$, joined by the hydrogen bonds N–H···O into 2D supramolecular layers, where the atoms of $O(ReO_4)^-$ are proton acceptors. In compound **III**, the methanesulfonate anion participates in

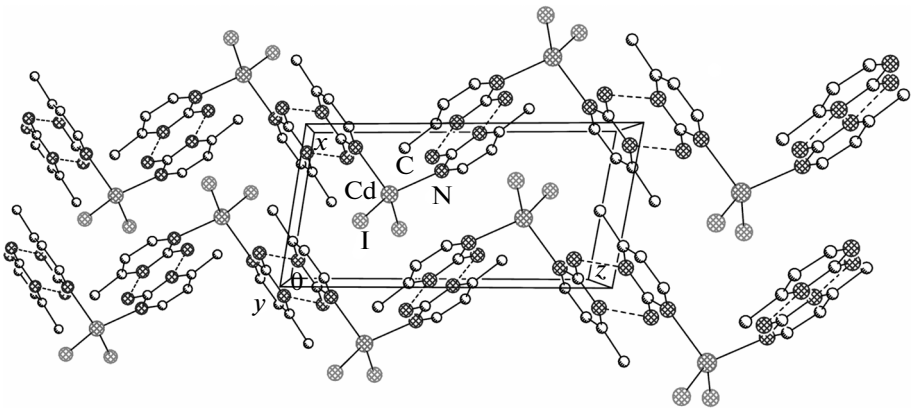

Fig. 1. General view of structure **I** along the [010] direction: zigzag supramolecular chains $[Cd(Ampym)_2]^+$ extended along the [001] direction.

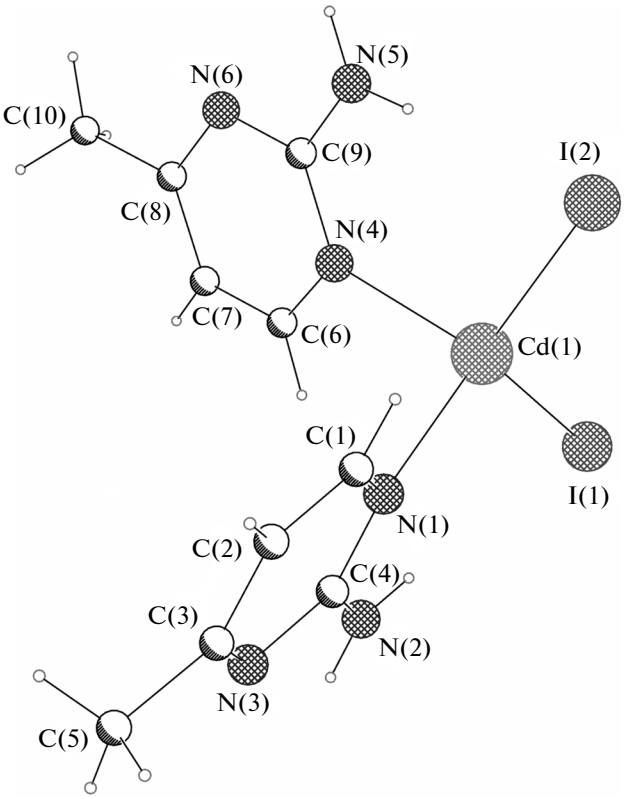

Fig. 2. Complex $[Cd(Ampym)_2I_2]$ in structure **I**.

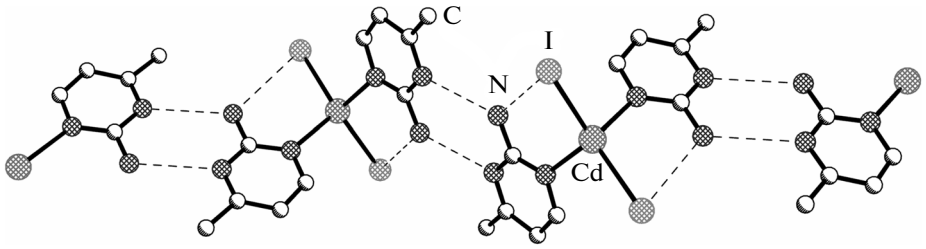

Fig. 3. Fragment of the $[Cd(Ampym)_2]^+$ chain: the cadmium complexes joined by the hydrogen bonds N–H···N.

the N–H···O hydrogen bond as a proton acceptor. As a result, supramolecular strips are formed.

In all syntheses mentioned, the presence of ligands with the NH_2 group and weakly coordinating anions favors the formation of strong hydrogen bonds N–H···N(O), resulting in diverse supramolecular architectures.

ACKNOWLEDGMENTS

This work was supported by the Federal Agency of Scientific Organizations.

REFERENCES

1. Kokunov, Yu.V., Gorbunova, Yu.E., et al., *Russ. J. Inorg. Chem.*, 2007, vol. 52, no. 10, p. 1530.
2. Kokunov, Yu.V., Gorbunova, Yu.E., Kovalev, V.V., et al., *Russ. J. Coord. Chem.*, 2013, vol. 39, no. 8, p. 565.
3. Kokunov, Yu.V., Gorbunova, Yu.E., Kovalev, V.V., et al., *Russ. J. Inorg. Chem.,* 2013, vol. 58, no. 10, p. 1187.
4. Kokunov, Yu.V., Gorbunova, Yu.E., and Kovalev, V.V., *Russ. J. Inorg. Chem.*, 2009, vol. 54, no. 12, p. 1909.
5. Sharma, C.V.K., Griffin, S.T., and Rogers, R.D., *Chem. Commun.* (Cambridge, UK), 1998, p. 215.

6. Jensen, P., Batten, S.R., Munbaraki, B., et al., *Chem. Commun.* (Cambridge, UK), 2000, p. 793.

7. Navarro, J.A.R., Barea, E., Galunclo, M.A., et al., *J. Solid State Chem.*, 2006, vol. 178, no. 8, p. 2436.

8. Wang, Y.-H., Chu, K.-L., Chen, H.-C., et al., *CrystEngComm*, 2006, vol. 8, p. 84.

9. Lee, J.-H.P., Lewis, B.D., Mendes, J.M., et al., *J. Coord. Chem.*, 2003, vol. 56, no. 16, p. 1425.

10. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.

11. Kokunov, Yu.V., Gorbunova, Yu.E., and Kovalev, V.V., *Russ. J. Inorg. Chem.*, 2012, vol. 57, no. 7, p. 953.

Translated by E. Yablonskaya