Crystal structure of diaquabis[*N*-2-aminophenyl-5-methylpyrazol-yl acetamido]zinc(II) diperchlorate, $C_{24}H_{34}N_8O_4Zn(ClO_4)_2$

K. Chkirate^I, R. Regragui^I, E. M. Essassi^I and M. Pierrot^{*II}^I Université Mohamed V, Faculté des Sciences, Laboratoire de Chimie Organique Hétérocyclique, Rabat, Morocco^{II} Centre Scientifique Saint-Jérôme, LBS-UMR 6517, F-13397 Marseille Cedex 20, France

Received July 11, 2001, CCDC-No. 1267702

Abstract

$C_{24}H_{34}Cl_2N_8O_{12}Zn$, monoclinic, $P12_1/c1$ (No. 14), $a = 15.7901(6)$ Å, $b = 11.5163(4)$ Å, $c = 20.1992(6)$ Å, $\beta = 154.373(3)^\circ$, $V = 1588.8$ Å³, $Z = 2$, $R_{gt}(F) = 0.050$, $wR_{ref}(F^2) = 0.074$, $T = 298$ K.

Source of material

$1.25 \cdot 10^{-4}$ mol of $Zn(ClO_4)_2$ dissolved in 2.5 ml of ethanol was added to a solution of 5 ml of methanol containing $2.5 \cdot 10^{-4}$ mol of *N*-(2-aminophenyl)-5-methylpyrazol-3-yl acetamide. The mixture is slightly warmed and then left at room temperature. After a few days some yellow crystals are observed in the mother liquor.

Discussion

Pyrazolic derivatives are known as chelating agents for some alkali or alkaline-earth metals as well as for transition metals [1,2]. But our interest carried to this class of compounds is due to their remarkable properties as catalysts [3], their biological activities [4] or antitumoral actions [5]. In the course of our research in this field we were interested in the synthesis of a zinc complex with *N*-(2-aminophenyl)-5-methylpyrazol-3-yl acetamide ligand obtained by the action of hydrazine on 4-acetylpyridine-1,5-benzodiazepin-2-one [6].

The zinc atom, located on a symmetry center, is linked to two ligand molecules which are symmetry related. The octahedral coordination of the zinc is slightly distorted. The equatorial plane is composed of one nitrogen atom N2 ($d(Zn-N2) = 2.005(2)$ Å),

one oxygen atom O11 ($d(Zn-O11) = 2.090(2)$ Å), and their symmetry related atoms. The water molecules are in axial positions ($d(Zn-O10) = 2.217(2)$ Å) and the octahedral angles range between $86.227(4)^\circ$ for O10–Zn–N2, $87.685(4)^\circ$ for N2–Zn–O11 and $90.869(4)^\circ$ for O11–Zn–O10. The equatorial plane and the pyrazole ring are almost coplanar (dihedral angle: $16.7(2)^\circ$) while the phenyl ring C10–C11–C12–C13–C14–C15 is at $41.6(3)^\circ$ of the former plane. The oxygen atoms of the perchlorate counterions are fully disordered: the 4 oxygen atoms have been located over 15 crystallographic sites with an occupancy ranging from 0.5 to 0.1. The water molecule is linked to the perchlorate ions via an hydrogen bond to oxygen atoms O13 (occupancy: 0.5), O12 (occupancy: 0.4) and O23 (occupancy: 0.1).

Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.15 × 0.20 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	9.90 cm ⁻¹
Diffraction, scan mode:	Kappa CCD, 90 exposures, $\Delta\phi = 2^\circ$
$2\theta_{max}$:	50.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11389, 3023
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 3 \sigma(I_{obs})$, 2699
$N(param)_{refined}$:	238
Programs:	SIR92 [7], maXus [8], ORTEP-II [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
O(12)	4e	0.40	0.1326(2)	0.0735(1)	0.3766(2)	0.0627(4)
O(13)	4e	0.50	0.1422(2)	0.0333(1)	0.3623(1)	0.0573(3)
O(14)	4e	0.40	0.1962(3)	0.0385(2)	0.3062(2)	0.0715(5)
O(15)	4e	0.10	0.0884(9)	0.1555(6)	0.2018(7)	0.070(2)
O(16)	4e	0.20	0.2849(5)	0.0645(2)	0.3650(4)	0.0435(6)
O(17)	4e	0.30	0.3581(3)	0.1729(2)	0.4707(2)	0.0556(6)
O(18)	4e	0.20	0.2144(6)	0.2265(2)	0.3959(4)	0.0675(8)
O(19)	4e	0.30	-0.0269(4)	0.1822(2)	0.1989(3)	0.0668(7)
O(20)	4e	0.20	-0.0158(5)	0.1354(3)	0.1643(4)	0.0784(9)
O(21)	4e	0.20	0.0491(5)	0.2251(2)	0.2607(4)	0.0550(7)
O(22)	4e	0.40	0.3124(3)	0.2076(1)	0.4496(2)	0.0447(4)
O(23)	4e	0.10	0.1110(6)	0.0069(4)	0.2976(5)	0.108(1)
O(24)	4e	0.30	0.0089(4)	0.1921(2)	0.1998(3)	0.0626(6)
O(25)	4e	0.20	0.1512(5)	0.0866(3)	0.2504(4)	0.0644(8)
O(26)	4e	0.20	0.3660(7)	0.1002(4)	0.4480(6)	0.053(1)
H(1)	4e		0.6269	0.5291	0.7345	0.0575
H(8)	4e		0.6613	0.1089	0.5340	0.0582
H(12)	4e		0.3421	0.0027	0.2775	0.0690
H(13)	4e		0.1433	-0.0331	0.0451	0.0694
H(14)	4e		0.1450	0.0972	-0.0420	0.0694

* Correspondence author

(e-mail: marcel.pierrot@VMESA12.u-3mrs.fr)

Table 2. Continued..

Atom	Site	Occ.	x	y	z	U _{iso}
H(15)	4e		0.3242	0.2695	0.0910	0.0731
H(4A)	4e		0.7947	0.2244	0.8517	0.0587
H(4B)	4e		0.9841	0.2872	0.9600	0.0587
H(6A)	4e		0.8763	0.2653	0.7446	0.0617
H(6B)	4e		0.7630	0.1653	0.7008	0.0617
H(9A)	4e		0.5612	0.3777	0.3097	0.0749

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(9B)	4e		0.6812	0.3398	0.4568	0.0749
H(10A)	4e		0.1059	0.4803	0.2864	0.0715
H(10B)	4e		0.2092	0.3724	0.3606	0.0715
H(16A)	4e		0.8081	0.4894	0.9654	0.0792
H(16B)	4e		1.0028	0.4190	1.0939	0.0792
H(16C)	4e		0.8132	0.3565	0.9856	0.0792

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Zn(1)	2b	0.5000(8)	0.5000(4)	0.5000(6)	0.04341(6)	0.02851(5)	0.03303(6)	0.00914(5)	0.03450(6)	0.00707(4)
Cl(2)	4e	0.16334(3)	0.12432(1)	0.32866(2)	0.04704(9)	0.03218(8)	0.0531(1)	-0.00086(7)	0.0448(1)	0.00010(7)
O(10)	4e	0.24214(7)	0.45208(4)	0.37904(6)	0.0463(3)	0.0488(3)	0.0596(3)	0.0031(2)	0.0470(3)	0.0055(2)
O(11)	4e	0.48512(6)	0.34200(3)	0.43897(5)	0.0462(3)	0.0299(2)	0.0366(3)	0.0099(2)	0.0371(2)	0.0067(2)
N(1)	4e	0.69350(8)	0.46037(4)	0.76746(6)	0.0427(3)	0.0342(3)	0.0356(3)	0.0026(2)	0.0357(3)	0.0007(2)
N(2)	4e	0.66075(7)	0.41874(4)	0.68225(6)	0.0417(3)	0.0331(3)	0.0328(3)	0.0050(2)	0.0341(3)	0.0035(2)
N(8)	4e	0.58450(8)	0.16962(4)	0.47026(6)	0.0473(3)	0.0272(2)	0.0401(3)	0.0098(2)	0.0396(3)	0.0071(2)
N(9)	4e	0.54937(9)	0.34394(5)	0.34252(7)	0.0605(4)	0.0423(3)	0.0621(4)	-0.0049(3)	0.0572(4)	-0.0001(3)
C(3)	4e	0.75370(9)	0.31731(5)	0.74452(7)	0.0318(3)	0.0307(3)	0.0275(3)	0.0037(2)	0.0261(3)	0.0044(2)
C(4)	4e	0.84602(9)	0.29517(5)	0.86977(7)	0.0389(4)	0.0408(3)	0.0367(4)	0.0000(3)	0.0336(3)	0.0037(3)
C(5)	4e	0.80484(9)	0.38780(5)	0.88143(7)	0.0387(3)	0.0423(3)	0.0328(4)	-0.0031(3)	0.0325(3)	-0.0001(3)
C(6)	4e	0.7596(1)	0.24567(5)	0.68686(7)	0.0474(4)	0.0399(3)	0.0381(4)	0.0154(3)	0.0384(4)	0.0113(3)
C(7)	4e	0.59568(9)	0.25716(5)	0.52143(7)	0.0382(3)	0.0265(3)	0.0375(4)	0.0010(2)	0.0349(3)	0.0010(2)
C(10)	4e	0.44551(9)	0.23927(5)	0.26682(7)	0.0395(3)	0.0370(3)	0.0422(4)	0.0066(3)	0.0375(3)	0.0046(3)
C(11)	4e	0.45177(9)	0.15835(5)	0.32269(7)	0.0367(3)	0.0307(3)	0.0364(4)	0.0054(2)	0.0334(3)	0.0020(2)
C(12)	4e	0.3390(1)	0.05748(5)	0.23941(8)	0.0547(4)	0.0352(3)	0.0572(5)	-0.0029(3)	0.0519(4)	-0.0059(3)
C(13)	4e	0.2237(1)	0.03514(6)	0.10383(9)	0.0464(4)	0.0506(4)	0.0513(5)	-0.0041(3)	0.0430(4)	-0.0143(3)
C(14)	4e	0.2204(1)	0.11352(7)	0.05008(8)	0.0456(4)	0.0644(5)	0.0382(4)	0.0133(4)	0.0361(4)	0.0024(3)
C(15)	4e	0.3282(1)	0.21412(6)	0.12933(8)	0.0556(4)	0.0549(4)	0.0489(5)	0.0165(3)	0.0482(4)	0.0134(3)
C(16)	4e	0.8628(1)	0.41579(6)	0.99165(9)	0.0634(5)	0.0653(5)	0.0489(5)	-0.0074(4)	0.0523(5)	-0.0051(3)

References

- Ramdani, A.; Tarrago, G.: Polypyrazolic macrocycles-11. A study of their complexing properties with alkali cations. *Tetrahedron* **37** (1981) 991-1000.
- Tarrago, G.; Zidane, I.; Marzin, C.; Tep, A.: Synthesis and ionophores properties of a syama, H.; Ema, T.; Nomura, A.; Yoshida, T.; Ogoshi, H.: Complexation of new tetrapyrazolic macrocycles. *Tetrahedron* **44** (1988) 91-100.
- Mizutani, T.: Kon-induced catalysis in zinc insertion into cationic porphyrine. *Chem. Letters* **10** (1995) 941-942.
- Rodriguezarguelles, M. C.; Ferrari, N. M.; Fava, G. G.; Pelizzi, C.; Tarasconi, P.; Albertini, R.; Dallaglio, P. P.; Lunghi, P.; Pinelli, S.: 2,6-Diacetylpyridine bis (thiosemicarbazones) zinc complexes-synthesis, structure and biological activity. *J. Inorg. Biochem.* **58** (1995) 157-175.
- Chen, C. H.; Wu, Z. S.; Yen, Z. H.: Synthesis, characterization and anticancer activity of Copper(II), Nickel(II) and Zinc(II) complexes derived from L-arginine. *Synthesis and reactivity in inorganic and metal-organic chemistry* **23** (1993) 1725-1733.
- Essassi, E. M.; El Abbassi, M.; Fifi, J.; Djerrari, B.: L'acide déhydroacétique, précurseur de synthèse de benzodiazépines. *Tetrahedron Lett.* **30** (1989) 7069-7070.
- Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M.: Sir92 - A program for automatic solution of crystal structures by direct methods. *J. Appl. Crystallogr.* **27** (1994) 435.
- Mackay, S.; Gilmore, C. J.; Edwards, C.; Stewart, N.; Shankland, K.: *maXus*. Computer Program for the Solution and Refinement of Crystal Structures. Nonius, The Netherlands 1999, MacScience, Japan & The University of Glasgow, UK 1999.
- Johnson, C. K.: ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA 1976. ORTEP-II/maXus.