Polish J. Chem., **75**, 1367–1370 (2001) **COMMUNICATION**

Synthesis and Structure of Zinc Complex of 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5*

by J.-L. Wang, X. Zhang, M. Yu and F.-M. Miao

College of Chemical and Life, Tianjin Normal University, Tianjin 300074, P. R. China
E-mail: wangjinling43@eyou.com

(Received November 28th, 2000; revised manuscript February 19th, 2001)

4-Benzoyl-5-pyrazolone is an enolizable β-diketone, which has been extensively researched [1]. Since 1959, 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (PMBP) was synthesized using a new method and its chelate properties with several metals were studied [2]. The extraction for lanthanides, actinides and alkaline earth metals were mainly reported [3]. Moreover, its analgesic and fever allaying functions were found [4–5]. Relatively little structural information have been gathered on complexes of this type [6–9]. In order to study the relationship between the structure and performances, the syntheses and structure of the dimethyl formamide–bis(1-phenyl-3-methyl-4-benzoyl-5-one-O,O′)zinc has been investigated.

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol) and HPMBP (0.2 mmol) was dissolved in hot ethanol. After stirring and refluxed for 2 h, the mixture was cooled to room temperature and then filtered. Colorless crystals suitable for X-ray analysis were produced in DMF solution. Chemical analysis confirmed the composition. IR spectra in the region of 4000–400 cm^{-1} were determined with a KBr pellet on PE 1730 Infrared Spectrophotometer. Table 1 lists the infrared absorption frequencies for $Zn(PMBP)_2 \cdot$ 2DMF and PMBP. The shift of the $\nu_{C=O}$ absorption band occurs from 1637–1505 cm^{-1} in the HPMBP to 1609–1497 cm^{-1} in the Zn-complex. The absence of the broad absorption band, due to $\nu_{OH\cdots O}$ in the spectra, suggests that the Zn atom is coordinated with the oxygen atoms [10].

Table 1. The infrared absorption frequencies of PMBP and $Zn(PMBP)_2 \cdot 2DMF$.

Frequencies (cm^{-1})	$\nu_{C=O}$	$\nu_{OH\cdots O}$	ν_{Zn-O}
PMBP	1637, 1505	2600	
Zn-complex	1609, 1497		460, 420

---

*Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC -151958. (CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

A colorless single crystal with dimensions of 0.22 × 0.14 × 0.18 mm was selected for the X-ray analysis and mounted on a Smart-1000 CCD diffractometer with a graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). A total of 4435 independent reflections were collected in the range of $2.14 \leq \theta \leq 25.02°$ by ω scan technique at 293 K, in which 2592 reflections with $I \geq 2\sigma(I)$ were observed. The SADABS absorption correction was applied. The crystal data as follows: monoclinic, $P2_1/n$, $a = 10.139(7)$, $b = 9.435(7)$, $c = 19.024(15)$ Å, $\beta = 90.60(1)°$, $Z = 2$, $D_{calc} = 1.398$ g · cm^{-3}, $\mu = 0.732$ mm^{-1}, $F(000) = 800$, final $R_1 = 0.0314$ and $wR_2 = 0.0937$ ($w = 1/[\sigma^2(F_o)^2 + (0.14079P)^2 + 0.3033P]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$, $\Delta/\sigma_{max} = 0.004$, GOF = 0.980. The maximum and minimum peaks in the final difference Fourier map were 0.460 and –0.274 e·Å^{-3}, respectively. All calculations were performed on a PC computer using SHELXL-97 program [11–12] incorporated in WinGX system [13]. The structure was solved by Patterson and Fourier methods. The remaining non-hydrogen atoms were located from the subsequent Fourier difference syntheses. The hydrogen atoms were located theoretically, refined and fixed isotropic thermal parameters. During the final cycles of the refinements, anisotropical thermal parameters were assigned to all the non-hydrogen atoms. An ORTEP view of the molecules and the numbering scheme are shown in Fig 1. The selected bond lengths and bond angles are listed in Table 2. The crystal structure indicates that the Zn complex is six-coordinated to form a

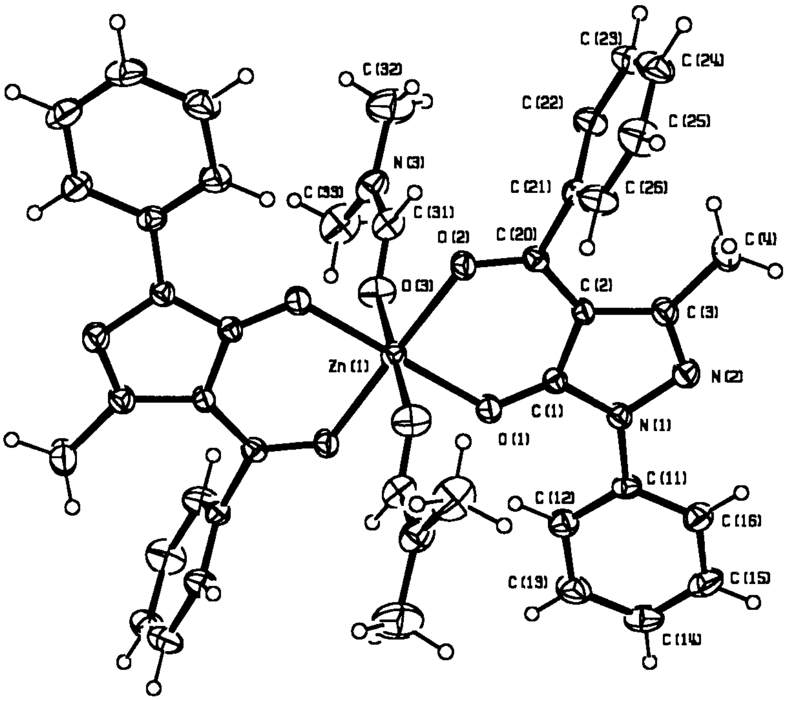

Figure 1. Perspective drawing of the $Zn(PMBP)_2 \cdot 2DMF$.

distorted octahedral structure, in which the Zn(1) atom lies on an inversion center and therefore is formed by two asymmetric units. The four oxygen atoms of O(1), O(2), O(1)^{i} and O(2)^{i} from two PMBP anions form an equatorial plane, while O(3) and O(3)^{i} (symmetry code i: 1 – x, 1 – y, 2 – z) from two DMF molecules occupy the apical positions. A similar coordination was also observed in the Sc (PMBP)$_3$ [14], (PMBP)$_2$ Sn (t-C$_4$H$_9$)$_2$ [15], UO$_2$ (PMBP)$_2$HMPA [16], (CH$_3$)$_2$(PMBP)$_2$ Sn(IV) [17] and Zn(MpO)$_2$(H$_2$O)$_2$ [18]. There are two sets of Zn–O bonds: 2.077 Å of Zn(1)–O(2) and Zn(1)–O(2)^{i} are longer than 2.042 Å of Zn(1)–O(1) and Zn(1)–O(1)^{i} . The shorter Zn–O bonds are adjacent to the longer C–O bonds. This feature was already observed elsewhere [19] and attributed to the asymmetry ring. The Zn(1) atom is located in the O–C–C–C–O plane and the O(3) and O(3)^{i} atoms are 2.142 Å out of this plane (plane equations is listed in the Table 3). The largest deviation from the O–C–C–C–O plane is O(1) –0.066 Å. The dihedral angle between the pyrazolone ring plane and its adjacent chelate ring plane is 2.35°, and 12.91° between the pyrazolone ring and the C(11)–C(16) phenyl rings, above three planes form a big conjugate system. But the dihedral angles between the C(21)–C(26) phenyl and the corresponding pyrazolone ring are 93.70° due to the steric hindrance. The crystal packing of Zn(PMBP)$_2$·2DMF is dominated by van der Waals forces.

Table 2. Selected bond lengths (Å) and angles (°).

Zn(1)–O(1)	2.042(2)	Zn(1)–O(2)	2.077(2)
Zn(1)–O(2)^{i}	2.077(2)	Zn(1)–O(3)	2.143(2)
Zn(1)–O(1)^{i}	2.042(2)	Zn(1)–O(3)^{i}	2.143(2)
O(1)–Zn(1)–O(1)^{i}	180.00	O(1)–Zn(1)–O(2)	90.88(10)
O(1)–Zn(1)–O(2)^{i}	89.12(10)	O(2)–Zn(1)–O(2)^{i}	180.00
O(1)–Zn(1)–O(3)	91.20(9)	O(1)–Zn(1)–O(3)^{i}	88.80(9)
O(2)–Zn(1)–O(3)	91.44(8)	O(2)–Zn(1)–O(3)^{i}	88.56(9)
C(1)–O(1)–Zn(1)	122.21(16)	C(20)–O(2)–Zn(1)	127.15(17)
C(31)–O(3)–Zn(1)	124.8(2)	N(2)–N(1)–C(11)	118.0(2)

Symmetry code i: 1 – x , 1 – y , 2 – z.

Table 3. Plane equations.

Plane	Atoms in the plane (Å)						Atoms out of the plane (Å)		
1	Zn(1)	O(1)	C(1)	C(2)	C(20)	O(2)	N(1)	N(2)	C(3)
	0.014(1)	–0.066(2)	–0.003(1)	0.028(1)	–0.026(1)	0.002(1)	–0.049(1)	–0.026(1)	0.015(1)
2	C(1)	C(2)	C(3)	N(1)	N(2)		C(4)	C(11)	Zn(1)
	0.004(2)	–0.003(1)	0.001(1)	–0.004(1)	0.002(1)		0.024(1)	–0.067(2)	–0.028(1)
3	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)	N(1)	Zn(1)	
	0.005(1)	0.002(1)	–0.006(1)	0.004(1)	0.002(1)	–0.007(2)	0.060(2)	–0.814(3)	
4	C(21)	C(22)	C(23)	C(24)	C(25)	C(26)	Zn(1)		
	0.010(3)	–0.004(2)	–0.006(2)	0.008(2)	–0.002(1)	–0.008(1)	–1.277(5)		

Dihedral angles: Plane 1 – Plane 2: 2.35°, Plane 2 – Plane 3: 12.91°, Plane 2 – Plane 4: 93.70°.

Acknowledgments

This work was supported by the Foundation of Tianjin Scientific Committee (003601711).

REFERENCES

1. Jensen B.S., *Acta Chem. Scand.*, **13**, 1668 (1959).
2. Jensen B.S., *Acta Chem. Scand.*, **13**, 1890 (1959).
3. Peng Chun-Lin., *J. Chin. Anal. Chem.*, **13**, 1890 (1959).
4. Domag K.G., Behnisch R., Mietzsch F. and Schmidt H., *Naturwiss.*, **33**, 315 (1946).
5. Petering H.G., Buskirk H.H. and Underwood G.E., *Cancer Res.*, **64**, 367 (1964).
6. Jarvinen G.D., Zozulin A.J., Larson E.M. and Ryan R.R., *Acta Cryst.*, **C47**, 262 (1991).
7. Uhlemann E., Schilde U. and Weller F., *Z. Naturforsch. B*, **50**, 31 (1995).
8. Ryan R.R. and Jarvinen G.V., *Acta Cryst.*, **C43**, 1295 (1987).
9. Chen Ming In, Song Yuan, Gu Yi Dong and Jin Xiang Lin., *Fenz. Kex. Yu Huax. Yanjiu.*, 465 (1984).
10. Kawaguchi S., "Variety of coordination modes of ligands in metal complexes." Springer Verlag, Berlin, Chapter 5 (pp. 75), (1988).
11. Sheldrik G.M. SHELXS-97. Program for Crystal Structure Solution, University of Göttingen, Germany, chapter 13 (1997).
12. Sheldrik G.M. SHELXL-97. Program for Crystal Structure Refinement, University of Göttingen, Germany, chapter 11 (1997).
13. Farrugia L.J. WinGX – A Windows Program for Crystal Structure Analysis, University of Glasgow, Scotland, *J. Appl. Cryst.*, **32**, 837 (1999).
14. Zhang Yi, Li Biao Guo, Jin Tian Zhu, Huang Chun Hui, Xu Guang Xian, Han Yu Zheng and Li Pei Geng, *Acta Scient. Nat. Univ. Pekin*, **31**, 387 (1995).
15. Huang Chun Hui, Wang Ke Zhi, Xu Zhen Hua, Xu Guang Xian, Han Yu Zhen and Shi Ni Cheng, *Chem. J. Chin. Uni.*, **10**, 129 (1989).
16. Tong Yue Jin, Wei Jian Mei, Wang Jia Hu and Lin Yong Hua, *J. Fujian Norm. Univ.* (Nature Science), **11**, 53 (1995).
17. Bovio B., Cingolani A., Marchetti F. and Pettinari C., *J. Organomet. Chem.*, **458**, 39 (1993).
18. Barjesteh H., Chakrabarti J. and Charalambous J., *Polyhedron*, **15**, 1323 (1996).
19. Pettnari C., Rafaiani G., Lobbia G., Lorenzotti F., Bonati F and Bovio B., *J. Organomet. Chem.*, **405**, 75 (1991).