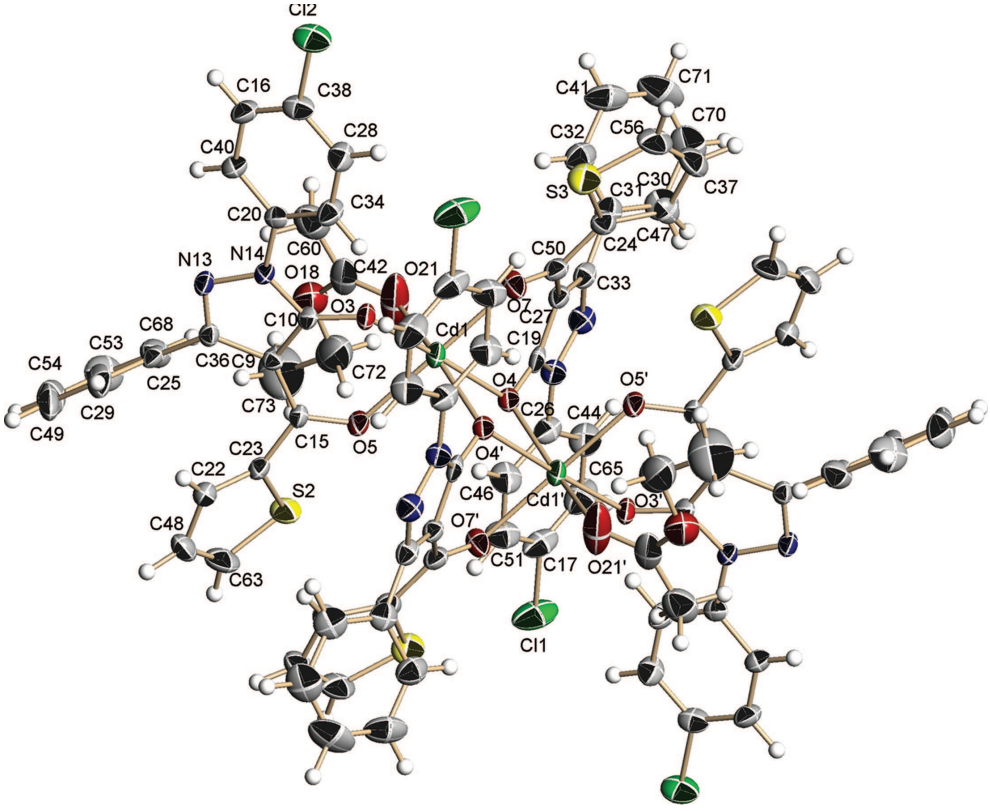
Yong-Jie Ding*, Chun-Xiang Zhao, Si-Shi Hu, Peng-Hui Wang, Chen-Cheng Ye, Hua-Li Jia and Guang-Ying Chen

Crystal structure of bis(μ$_2$-1-(4-chlorophenyl)-3-phenyl-4-thenoyl-1*H*-pyrazol-5-olato-κ^3*O*,*O′*:*O′*)-bis-(1-(4-chlorophenyl)-3-phenyl-4-thenoyl-1*H*-pyrazol-5-olato-κ^2*O*,*O*)-bis(ethyl acetate-κ*O*)dicadmium(II), $C_{88}H_{64}Cl_4N_8O_{12}S_4Cd_2$



https://doi.org/10.1515/ncrs-2018-0482
Received November 5, 2018; accepted January 12, 2019; available online February 5, 2019

Abstract

$C_{88}H_{64}Cl_4N_8O_{12}S_4Cd_2$, monoclinic, $P2_1/c$ (no. 14), $a = 13.5247(6)$ Å, $b = 15.3257(7)$ Å, $c = 20.6985(8)$ Å, $\beta = 101.8630(10)°$, $V = 4198.7(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0484$, $wR_{ref}(F^2) = 0.0967$, $T = 173(2)$ K.

CCDC no.: 1877059

***Corresponding author: Yong-Jie Ding,** College of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou, P.R. China, e-mail: yongjieding@163.com
Chun-Xiang Zhao, Si-Shi Hu, Peng-Hui Wang, Chen-Cheng Ye, Hua-Li Jia and Guang-Ying Chen: College of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou, P.R. China

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.37 × 0.37 × 0.30 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.80 mm^{-1}
Diffractometer, scan mode:	CCD, φ and ω
θ_{max}, completeness:	25.4°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	33670, 7740, 0.089
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5090
$N(param)_{refined}$:	534
Programs:	Bruker [1], SHELX [2], Diamond [3], WinGX/ORTEP [4], Mercury [5]

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Open Access. © 2019 Yong-Jie Ding et al., published by De Gruyter. This work is licensed under the Creative Commons Attribution 4.0 Public License.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Cd1	0.04296(2)	0.06277(2)	0.072283(15)	0.03198(10)
S2	0.25452(9)	−0.19214(8)	0.17554(6)	0.0396(3)
S3	−0.20907(10)	0.30191(9)	0.00257(7)	0.0526(4)
Cl1	−0.14977(13)	−0.47997(9)	0.04873(7)	0.0658(4)
Cl2	0.17279(10)	0.59167(8)	0.18583(7)	0.0517(3)
O3	0.1581(2)	0.16232(18)	0.10580(13)	0.0306(7)
O4	−0.0714(2)	−0.04239(17)	0.03245(12)	0.0261(7)
O5	0.1664(2)	−0.02989(18)	0.11437(14)	0.0335(7)
O7	−0.0903(2)	0.14795(19)	0.03598(14)	0.0353(8)
C9	0.2657(3)	0.0691(3)	0.18782(18)	0.0216(9)
C10	0.2230(3)	0.1476(3)	0.15858(19)	0.0237(9)
N11	−0.3038(3)	−0.0687(3)	0.08077(16)	0.0343(9)
N12	−0.2152(3)	−0.0988(2)	0.06357(16)	0.0299(9)
N13	0.3332(2)	0.1814(2)	0.25533(15)	0.0261(8)
N14	0.2678(2)	0.2139(2)	0.19949(15)	0.0241(8)
C15	0.2445(3)	−0.0153(3)	0.15880(19)	0.0236(9)
C16	0.2454(3)	0.4433(3)	0.2493(2)	0.0339(10)
H16	0.2620	0.4782	0.2879	0.041*
C17	−0.1693(4)	−0.3679(3)	0.0535(2)	0.0451(13)
O18	0.0619(3)	−0.0113(3)	0.27698(19)	0.0610(10)
C19	−0.1582(3)	−0.0312(3)	0.04824(18)	0.0271(10)
C20	0.2445(3)	0.3041(3)	0.19552(19)	0.0242(9)
O21	−0.0018(3)	0.0429(4)	0.17766(18)	0.0887(16)
C22	0.4126(3)	−0.0963(3)	0.19579(19)	0.0313(11)
H22	0.4566	−0.0475	0.1992	0.038*
C23	0.3100(3)	−0.0905(3)	0.17888(19)	0.0258(10)
C24	−0.2549(3)	0.1974(3)	0.00438(19)	0.0293(9)
C25	0.3902(3)	0.0408(3)	0.30155(19)	0.0268(10)
C26	−0.1978(3)	−0.1900(3)	0.06113(19)	0.0338(11)
C27	−0.2140(3)	0.0460(3)	0.05203(19)	0.0258(10)
C28	0.1764(3)	0.4305(3)	0.1334(2)	0.0367(11)
H28	0.1443	0.4567	0.0929	0.044*
C29	0.4954(3)	0.0412(3)	0.3160(2)	0.0454(13)
H29	0.5316	0.0783	0.2923	0.055*
C30	−0.4827(3)	0.0431(3)	0.0770(2)	0.0432(13)
H30	−0.4984	−0.0129	0.0579	0.052*
C31	−0.3827(3)	0.0707(3)	0.09326(19)	0.0335(11)
C32	−0.3605(4)	0.1496(3)	0.1252(2)	0.0433(13)
H32	−0.2922	0.1674	0.1389	0.052*
C33	−0.3019(3)	0.0172(3)	0.07395(19)	0.0283(10)
C34	0.1996(3)	0.3426(3)	0.1357(2)	0.0350(11)
H34	0.1850	0.3084	0.0966	0.042*
C36	0.3327(3)	0.0964(3)	0.24769(18)	0.0232(9)
C37	−0.3946(4)	0.2766(3)	−0.0470(2)	0.0444(12)
H37	−0.4626	0.2882	−0.0681	0.053*
C38	0.2001(3)	0.4801(3)	0.1899(2)	0.0349(11)
C40	0.2666(3)	0.3551(3)	0.2521(2)	0.0289(10)
H40	0.2965	0.3291	0.2931	0.035*
C41	−0.4370(5)	0.2026(4)	0.1373(2)	0.0568(15)
H41	−0.4212	0.2571	0.1587	0.068*
C42	0.0398(3)	0.0542(5)	0.2350(3)	0.0562(17)
C44	−0.2790(4)	−0.2468(3)	0.0578(2)	0.0458(13)
H44	−0.3446	−0.2247	0.0580	0.055*
C46	−0.1019(4)	−0.2229(3)	0.0615(2)	0.0425(12)
H46	−0.0460	−0.1843	0.0648	0.051*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C47	−0.3592(3)	0.1911(3)	−0.02666(18)	0.0289(10)
H47	−0.3983	0.1391	−0.0327	0.035*
C48	0.4461(3)	−0.1837(3)	0.2077(2)	0.0418(13)
H48	0.5151	−0.2002	0.2198	0.050*
C49	0.5473(4)	−0.0131(4)	0.3653(3)	0.0595(17)
H49	0.6191	−0.0141	0.3745	0.071*
C50	−0.1820(3)	0.1293(3)	0.03216(19)	0.0291(10)
C51	−0.0881(4)	−0.3123(3)	0.0571(2)	0.0441(13)
H51	−0.0230	−0.3351	0.0566	0.053*
C53	0.3921(5)	−0.0647(4)	0.3870(2)	0.0617(16)
H53	0.3564	−0.1006	0.4120	0.074*
C54	0.4959(5)	−0.0647(4)	0.4005(3)	0.0657(17)
H54	0.5319	−0.1009	0.4346	0.079*
C56	−0.3238(4)	0.3392(4)	−0.0339(2)	0.0522(14)
H56	−0.3374	0.3990	−0.0444	0.063*
C60	0.0720(4)	0.1405(4)	0.2659(3)	0.0605(16)
H60A	0.0636	0.1856	0.2316	0.091*
H60B	0.1431	0.1375	0.2884	0.091*
H60C	0.0304	0.1551	0.2979	0.091*
C63	0.3687(4)	−0.2405(3)	0.1998(2)	0.0480(13)
H63	0.3773	−0.3015	0.2071	0.058*
C65	−0.2633(4)	−0.3361(3)	0.0541(2)	0.0514(14)
H65	−0.3183	−0.3753	0.0521	0.062*
C68	0.3395(4)	−0.0121(3)	0.3368(2)	0.0424(12)
H68	0.2678	−0.0130	0.3268	0.051*
C70	−0.5592(4)	0.0971(5)	0.0884(3)	0.0607(17)
H70	−0.6277	0.0791	0.0755	0.073*
C71	−0.5362(5)	0.1769(5)	0.1183(3)	0.0694(19)
H71	−0.5888	0.2142	0.1259	0.083*
C72	0.0371(4)	−0.1017(5)	0.2547(3)	0.082(2)
H72A	0.0647	−0.1149	0.2150	0.099*
H72B	−0.0370	−0.1104	0.2439	0.099*
C73	0.0851(6)	−0.1599(5)	0.3114(4)	0.111(3)
H73A	0.1563	−0.1440	0.3262	0.167*
H73B	0.0802	−0.2209	0.2969	0.167*
H73C	0.0498	−0.1526	0.3480	0.167*

Source of material

The title compound was prepared by the reported procedure [6, 7]. A mixture of a 20 mL of a solution of 1-(4-chlorophenyl)-3-phenyl-1*H*-pyrazol-5(4*H*)-one (HCPTP) (2 mmol, 0.762 g) in anhydrous ethanol and 10 mL ethanolic solution of $Cd(Ac)_2 \cdot 2H_2O$ (1 mmol, 0.227 g) was refluxed for 2 h at 75 °C. After filtration, the light yellow powder was dried in vacuo to constant weight. Yellow single crystals were obtained by evaporating slowly the solvent from the ethyl acetate solution at room temperature after several days (yield: 72%).

Experimental details

All non-hydrogen atoms were refined anisotropically and the H-atoms were positioned with idealized geometry and refined

using a riding model. The structure was solved by direct methods with the SHELXS program.

Comment

The acylpyrazolones are an interesting class of β-diketones, containing a pyrazolyl moiety used as a chelating arm. Their metal complexes have been found to display catalytic performance, biological activity and enhanced luminescence [8–12]. Herein we report the new crystal structure of a complex of HCPTP containing Cd(II). The title crystal structure is built by the $C_{88}H_{64}Cl_4N_8O_{12}S_4Cd_2$ molecules, in which all bond lengths and angles are in normal ranges [13].

The structure of $Cd_2(CPTP)_4(CH_3COOC_2H_5)_2$ is a centrosymmetric dimer, each containing two six-co-ordinate cadmium atoms with Cd···Cd distance of 3.546 Å. The coordination of each Cd(II) is octahedral, coordinated by three oxygens of two acylpyrazolonate ligands, two oxygens of bridging bidentate one and one oxygen of ethyl acetate. As expected, the Cd—O(O4) distances, 2.269(3) Å, are longer than Cd—O(O3, O5), 2.189(3) and 2.228(3) Å. The distances Cd—O(ethyl acetate) are 2.400(4) Å.

Acknowledgements: The work was supported by the Natural Science Basic Research Project of Education Department of Henan Province (No. 17A150057) and the Scientific Innovation Fund Project of College of Chemistry and Chemical Engineering (ZKHYCX201902).

References

1. BRUKER. SAINT, APEX2 and SADABS. Bruker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System, Version 2.0f. Crystal Impact, Bonn, Germany.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
5. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A.: Mercury CSD2.0-new features for the visualization and investigation of crystal structures. J. Appl. Crystallogr. **41** (2008) 466–470.
6. Cingolani, A.; Marchetti, F.; Pettinari, C.; Pettinari, R.; Skelton, B. W.; Somers, N.; White, A. H.: Copper(I) monophosphine complexes with functionalized acylpyrazolonate ligands: syntheses of heterobimetallic Cu—Zn and Cu—Ru adducts. Polyhedron **25** (2006) 124–133.
7. Cingolani, A.; Marchetti, F.; Pettinari, C.; Pettinari, R.; Skelton, B. W.; White, A. H.: Silver coordination chemistry of a new versatile "Janus"-type N_2,O_2-bichelating donor, formation of an unprecedented supramolecular network of binuclear silver building locks containing a five-coordinate β-diketonate, and isolation of unexpected silver-tin-silver heterotrimetallic complexes from silver metathesis reactions. Inorg. Chem. Commun. **43** (2004) 4387–4399.
8. Begines, E.; Carrasco, C. J.; Montilla, F.; Alvarez, E.; Marchetti, F.; Pettinari, R.; Pettinari, C.; Galindo, A.: Oxidoperoxidomolybdenum(VI) complexes with acylpyrazolonate ligands: synthesis, structure and catalytic properties. Dalton Trans. **47** (2018) 197–208.
9. Jadejia, R. N.; Parihar, S.; Vyas, K.; Gupta, V. K.: Synthesis and crystal structure of a series of pyrazolone based Schiff base ligands and DNA binding studies of their copper complexes. J. Mol. Struct. **1013** (2012) 86–94.
10. Qin, J. C.; Cheng, X. Y.; Fang, R.; Wang, M. F.; Yang, Z. Y.; Li, T. R.; Li, Y.: Two Schiff-base fluorescent sensors for selective sensing of aluminum(III): experimental and computational studies. Spectrochim. Acta A **152** (2016) 352–357.
11. Hills, L.; Moyano, R.; Montilla, F.; Pastor, A.; Galindo, A.; Alvarez, E.; Marchetti, F.; Pettinari, C.: Dioxomolybdenum(VI) complexes with acylpyrazolonate ligands: synthesis, structures, and catalytic properties. Eur. J. Inorg. Chem. **19** (2013) 3352–3361.
12. Marchetti, F.; Pettinari, C.; Pettinari, R.: Acylpyrazolone ligands: synthesis, structures, metal coordination chemistry and applications. Coord. Chem. Rev. **249** (2005) 2909–2945.
13. Zhao, C.-X.; Ding, Y.-J.; Zhang, H.-Q.; Zhou, C.-Y.; Wang, Q.-Z.; Wang, X.; Zhao, H.; Chen, Y.-H.; Xie, J.-P.; Wang, Y.-S.: Crystal structure of bis-(1-(4-chlorophenyl)-3-phenyl-4-thenoyl-1*H*-pyrazol-5-olato-$\kappa^2 O,O'$)-(*N*,*N*-dimethylformamide)zinc(II), $C_{43}H_{31}Cl_2N_5O_5S_2Zn$. Z. Kristallogr. NCS **232** (2017) 553–555.