Xin-E. Duan, Yu-Hang Wang, Sheng-Di Bai*, Hong-Bo Tong and Bin-Shen Liu

Crystal structure of tetrakis[(Z)-(2-(1-(furan-2-yl)-2-methylpropylidene)-1-phenylhydrazin-1-ido- κ^2N,N')] zirconium(IV), $C_{56}H_{60}N_8O_4Zr$

Table 1: Data collection and handling.

Crystal:	Orange needle
Size:	0.40 × 0.20 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.26 mm ⁻¹
Diffraction, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	30.6°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	70,340, 16418, 0.096
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 8010
$N(\text{param})_{\text{refined}}$:	631
Programs:	Bruker [1], SHELX [2]

the list of the atoms including atomic coordinates and displacement parameters.

<https://doi.org/10.1515/ncrs-2020-0571>

Received November 4, 2020; accepted December 4, 2020;

published online December 18, 2020

Abstract

$C_{56}H_{60}N_8O_4Zr$, monoclinic, $C2/c$ (no. 15), $a = 24.665(4)$ Å, $b = 18.836(3)$ Å, $c = 25.425(6)$ Å, $\beta = 114.364(4)^\circ$, $V = 10760(4)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0550$, $wR_{\text{ref}}(F^2) = 0.1239$, $T = 296(2)$ K.

CCDC no.: 1959080

One of the two crystallographically independent complexes of the title crystal structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains

Source of material

To a stirred solution of compound (Z)-1-(furan-2-yl)-2-methyl-propylidene)-2-phenylhydrazone (1.016 g, 4.45 mmol) in diethyl ether (about 30 mL) at 0 °C, lithium diisopropylamide (0.477 g, 4.45 mmol) was added in small portions to form an orange solution. The solution was slowly warmed to room temperature and kept stirring for about 10 h. To the obtained solution, anhydrous $ZrCl_4$ (0.259 g, 1.12 mmol) was added in small portions at –78 °C. The resulting orange-red mixture was slowly warmed to room temperature and stirred overnight. 12-crown-4 (0.784 g, 4.45 mmol) being purified by potassium mirrors *in vacuo* before use was added dropwise at 0 °C. The resulting orange solution was slowly warmed to room temperature and stirred overnight. The obtained mixture was filtered and concentrated *in vacuo* to ca. 20 mL and left at room temperature to give needle orange crystals of the title zirconium complex.

Experimental details

Hydrogen atoms were positioned geometrically ($C-H = 0.93-0.98$ Å). The U_{iso} values were set to 1.2 U_{eq} of the parent atoms.

*Corresponding author: Sheng-Di Bai, Institute of Applied Chemistry, Shanxi University, Taiyuan 030006, P. R. China, E-mail: duanxe@sxu.edu.cn

Xin-E. Duan, Yu-Hang Wang and Bin-Shen Liu, School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, P. R. China. <https://orcid.org/0000-0002-3911-6073> (X.-E. Duan)

Hong-Bo Tong, Institute of Applied Chemistry, Shanxi University, Taiyuan 030006, P. R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Zr1	0.500000	0.17470 (2)	0.250000	0.03224 (9)
Zr2	0.500000	0.67922 (2)	0.250000	0.03385 (9)
N1	0.52980 (10)	0.18741 (11)	0.17758 (9)	0.0435 (5)
N2	0.53430 (10)	0.24986 (11)	0.20820 (9)	0.0413 (5)
N3	0.41006 (10)	0.16241 (11)	0.17578 (9)	0.0447 (5)
N4	0.43023 (9)	0.09892 (11)	0.20547 (8)	0.0389 (5)
N5	0.54316 (9)	0.66672 (11)	0.18745 (9)	0.0413 (5)
N6	0.51822 (10)	0.60330 (11)	0.19563 (9)	0.0425 (5)
N7	0.40382 (9)	0.69189 (11)	0.18546 (9)	0.0409 (5)
N8	0.43674 (9)	0.75353 (11)	0.19318 (9)	0.0416 (5)
O1	0.55364 (10)	0.22939 (11)	0.05076 (9)	0.0662 (6)
O2	0.28033 (9)	0.12933 (12)	0.04402 (9)	0.0730 (6)
O3	0.63582 (12)	0.63439 (16)	0.11076 (11)	0.0942 (8)
C36	0.31193 (14)	0.81302 (17)	0.15305 (14)	0.0606 (8)
H36	0.346723	0.835529	0.177685	0.073*
C1	0.53193 (13)	0.18085 (14)	0.12788 (11)	0.0483 (7)
C2	0.53586 (12)	0.24132 (15)	0.09449 (11)	0.0464 (7)
C3	0.52078 (14)	0.30992 (15)	0.09359 (13)	0.0585 (8)
H3	0.507725	0.332050	0.118959	0.070*
C4	0.52840 (15)	0.34225 (17)	0.04708 (14)	0.0689 (9)
H4	0.520509	0.389302	0.035308	0.083*
C5	0.54893 (16)	0.29258 (19)	0.02357 (14)	0.0760 (10)
H5	0.558867	0.299885	−0.007546	0.091*
C6	0.58358 (12)	0.29530 (14)	0.22295 (11)	0.0417 (6)
C7	0.63447 (13)	0.28073 (18)	0.21406 (13)	0.0604 (8)
H7	0.637616	0.238340	0.196776	0.072*
C8	0.68063 (15)	0.3300 (2)	0.23117 (17)	0.0822 (11)
H8	0.714347	0.320263	0.224701	0.099*
C9	0.67746 (16)	0.3919 (2)	0.25711 (18)	0.0893 (12)
H9	0.708750	0.424154	0.268362	0.107*
C10	0.62814 (16)	0.40634 (18)	0.26653 (16)	0.0780 (11)
H10	0.625630	0.448678	0.284211	0.094*
C11	0.58199 (13)	0.35844 (15)	0.24994 (13)	0.0564 (8)
H11	0.548788	0.368835	0.257094	0.068*
C12	0.36610 (12)	0.17108 (14)	0.12603 (11)	0.0488 (7)
C13	0.33175 (12)	0.11240 (15)	0.09133 (11)	0.0498 (7)
C14	0.34106 (14)	0.04212 (16)	0.09146 (12)	0.0608 (8)
H14	0.372513	0.016965	0.118810	0.073*
C15	0.29401 (16)	0.01343 (19)	0.04215 (14)	0.0748 (10)
H15	0.288597	−0.033905	0.030741	0.090*
C16	0.25958 (16)	0.0673 (2)	0.01582 (15)	0.0829 (11)
H16	0.225157	0.063279	−0.018046	0.099*
C17	0.39298 (11)	0.05715 (13)	0.22201 (10)	0.0397 (6)
C18	0.33540 (13)	0.07451 (17)	0.21402 (12)	0.0576 (8)
H18	0.318332	0.116711	0.195658	0.069*
C19	0.30321 (14)	0.0290 (2)	0.23338 (15)	0.0751 (10)
H19	0.264485	0.040836	0.227364	0.090*
C20	0.32739 (16)	−0.0324 (2)	0.26092 (16)	0.0783 (10)
H20	0.305468	−0.062281	0.273898	0.094*
C21	0.38413 (15)	−0.05014 (17)	0.26948 (15)	0.0696 (9)
H21	0.400820	−0.092229	0.288327	0.084*
C22	0.41681 (12)	−0.00601 (14)	0.25035 (12)	0.0510 (7)
H22	0.455406	−0.018708	0.256507	0.061*
C23	0.58014 (12)	0.67519 (14)	0.16374 (11)	0.0455 (6)
C24	0.60391 (13)	0.61686 (18)	0.14235 (12)	0.0553 (8)

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C25	0.60695 (14)	0.54687 (18)	0.15206 (15)	0.0674 (9)
H25	0.589619	0.522174	0.172852	0.081*
C26	0.6416 (2)	0.5174 (3)	0.1247 (2)	0.1044 (16)
H26	0.650886	0.469743	0.123396	0.125*
C27	0.6579 (2)	0.5708 (3)	0.1015 (2)	0.1170 (18)
H27	0.681574	0.566310	0.081248	0.140*
C28	0.48383 (11)	0.55982 (13)	0.14923 (11)	0.0402 (6)
C29	0.46253 (13)	0.49706 (14)	0.16197 (12)	0.0498 (7)
H29	0.471485	0.485776	0.200279	0.060*
C30	0.42829 (14)	0.45098 (15)	0.11891 (14)	0.0620 (8)
H30	0.414727	0.409039	0.128611	0.074*
C31	0.41408 (14)	0.46611 (18)	0.06238 (14)	0.0679 (9)
H31	0.391581	0.434565	0.033460	0.081*
C32	0.43362 (15)	0.52871 (19)	0.04901 (13)	0.0745 (10)
H32	0.423405	0.539989	0.010468	0.089*
C33	0.46833 (13)	0.57577 (16)	0.09161 (12)	0.0605 (8)
H33	0.481167	0.617953	0.081500	0.073*
C34	0.34654 (12)	0.68464 (14)	0.16096 (11)	0.0467 (7)
C35	0.30607 (12)	0.74421 (18)	0.14008 (13)	0.0592 (8)
O4	0.24852 (12)	0.73059 (15)	0.10394 (15)	0.1404 (14)
C37	0.2208 (2)	0.7949 (4)	0.0954 (3)	0.167 (3)
H37	0.180547	0.801592	0.072279	0.200*
C38	0.2566 (2)	0.8457 (3)	0.1232 (2)	0.1115 (15)
H38	0.247494	0.893614	0.123219	0.134*
C39	0.43033 (11)	0.79833 (13)	0.14698 (11)	0.0403 (6)
C40	0.46342 (13)	0.86091 (14)	0.16025 (12)	0.0524 (7)
H40	0.487864	0.871102	0.198568	0.063*
C41	0.46065 (16)	0.90783 (16)	0.11786 (15)	0.0682 (9)
H41	0.483252	0.949177	0.127724	0.082*
C42	0.42469 (16)	0.89404 (18)	0.06099 (14)	0.0703 (9)
H42	0.422165	0.926266	0.032360	0.084*
C43	0.39274 (15)	0.83254 (18)	0.04704 (13)	0.0661 (9)
H43	0.368887	0.822813	0.008477	0.079*
C44	0.39496 (13)	0.78422 (15)	0.08889 (12)	0.0512 (7)
H44	0.372954	0.742471	0.078347	0.061*
C45	0.52680 (18)	0.10566 (16)	0.10485 (13)	0.0749 (11)
H45	0.517269	0.075287	0.131179	0.090*
C46	0.5859 (2)	0.0788 (2)	0.10621 (17)	0.1125 (17)
H46A	0.581813	0.029937	0.094548	0.169*
H46B	0.616331	0.083112	0.144686	0.169*
H46C	0.596534	0.106594	0.080256	0.169*
C47	0.4756 (2)	0.09755 (19)	0.04524 (16)	0.0989 (14)
H47A	0.439001	0.111337	0.047087	0.148*
H47B	0.472996	0.048939	0.033081	0.148*
H47C	0.482798	0.127289	0.018095	0.148*
C48	0.35463 (16)	0.24764 (16)	0.10509 (14)	0.0760 (11)
H48	0.387342	0.275835	0.132804	0.091*
C49	0.35653 (17)	0.25835 (19)	0.04675 (15)	0.0975 (14)
H49A	0.392803	0.238812	0.047527	0.146*
H49B	0.354844	0.308183	0.038280	0.146*
H49C	0.323154	0.234843	0.017507	0.146*
C50	0.29720 (19)	0.2758 (2)	0.10759 (17)	0.1083 (15)
H50A	0.263665	0.249984	0.080672	0.162*
H50B	0.292706	0.325301	0.097755	0.162*
H50C	0.299372	0.269651	0.145892	0.162*
C51	0.60012 (13)	0.75137 (16)	0.16298 (13)	0.0588 (8)

Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H51	0.583382	0.779142	0.185318	0.071*
C52	0.57570 (17)	0.7837 (2)	0.10306 (16)	0.0902 (12)
H52A	0.589875	0.757242	0.078997	0.135*
H52B	0.588767	0.832101	0.105485	0.135*
H52C	0.533002	0.782314	0.086745	0.135*
C53	0.66762 (15)	0.75982 (19)	0.19359 (16)	0.0862 (11)
H53A	0.685936	0.738018	0.170881	0.129*
H53B	0.681782	0.737379	0.230766	0.129*
H53C	0.677544	0.809382	0.198372	0.129*
C54	0.32428 (15)	0.60864 (17)	0.15849 (15)	0.0685 (9)
H54	0.359230	0.579720	0.180994	0.082*
C55	0.29930 (18)	0.5793 (2)	0.09761 (17)	0.1034 (14)
H55A	0.263566	0.604431	0.074304	0.155*
H55B	0.290421	0.529762	0.098411	0.155*
H55C	0.328070	0.585002	0.081541	0.155*
C56	0.2812 (2)	0.6001 (2)	0.1869 (2)	0.1130 (15)
H56A	0.299498	0.617002	0.225949	0.169*
H56B	0.271136	0.550815	0.186861	0.169*
H56C	0.245734	0.626931	0.165828	0.169*

Comment

Hydrazones and their corresponding complexes have gained considerable attention because of their wide applications [3, 4]. Some corresponding metal complexes have been reported and used as olefins polymerization pre-catalysts [5–9]. We have previously reported five 2-furyl-phenylhydrazonato ligands $[(C_4H_3O)CR=NNHPh]$, which differ from one another by their differently bulky alkyl substituents $[R = H, CH_3, CH_3CH_2, (CH_3)_2CH$ and $(CH_3)_3C]$ which were attached on an imine-carbon atom. Based on the X-ray crystallographic analyses and/or 1H – 1H NOESY spectra of the ligands as well as the corresponding zirconium complexes, we found that the alkyl groups provided the influential steric effect on the configuration of the ligands (*trans*- or *cis*-), the unique structures as well as the intra- and intermolecular hydrogen bonding interactions of the obtained zirconium complexes [8, 9]. In addition, their corresponding mononuclear or dinuclear zirconium complexes display moderate activities towards ethylene polymerization and produced an ultra-high molecular weight with narrow polydispersity [8, 9].

In the previous paper, we have reported that the reaction of the lithium *cis*-1-(furan-2-yl-2-methyl-propylidene)-2-phenylhydrazonide with anhydrous $ZrCl_4$ afforded corresponding dinuclear zirconium complexes with a lithium adduct [9]. With the expectation to remove the lithium adduct, herein, the reaction of lithium *cis*-1-(furan-2-yl-2-methyl-propylidene)-2-phenylhydrazonide with $ZrCl_4$ in

2:1 ligand/metal ratio was carried out in the presence of 12-crown-4 in diethyl ether and the title mononuclear zirconium complex was obtained. It was suggested that the addition of 12-crown-4 caused the elimination of LiCl through the strong complexation of the lithium cation, resulting in the formation of the title zirconium complex and $[Li(12-crown-4)]Cl$ [10].

For the title crystal structure, there are two similar crystallographically independent target complexes (each located on a twofold axis) and the figure illustrates one. The zirconium centers are octa coordinated by a distorted square antiprism and coordinated with four monoanionic ligands. The bond lengths of $Zr-N_a$ [N_a = phenylamido nitrogen atom, from 2.254(2) Å to 2.259(2) Å] and $Zr-N_i$ [N_i = imine nitrogen, from 2.143(2) Å to 2.162(2) Å] are respectively longer than that in dinuclear zirconium complex of the same ligand [9]; and the bite N_a-Zr-N_i angles [from 36.67(7)° to 36.68(7)°] are a little bit smaller than those in the dinuclear zirconium complex of the same ligand [9]. These should have resulted from the steric crowding of four bidentate chelating ligands.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The Natural Science Foundation of Shanxi Province (2015011015), the Key Research and Development Projects in Shanxi Province (201803D121040), Shanxi Province Foundation for Returnees (2017-027), the Shanxi Key Laboratory of Functional Molecules and Students Research Training of Shanxi University (2020018334).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. *SMART. (Version 5.0) and SAINT (Version 6.02)*; Bruker AXS Inc.: Madison, WI, 2000.
2. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
3. Shakdofa M. M. E., Shtaiwi M. H., Morsy N., Abdel-rassel T. M. A. Metal complexes of hydrazones and their biological, analytical and catalytic applications: a review. *Main Group Chem.* 2014, *13*, 187–218.
4. Belskaya N. P., Dehaen W., Bakulev V. A. Synthesis and properties of hydrazones bearing amide, thioamide and amidine functions. *Arkivoc* 2010, *i*, 275–332.
5. Britovsek G. J. P., Gibson V. C., Kimberley B. S., Mastroianni S., Redshaw C., Solan G. A., White A. J. P., Williams D. J. Bis(imino)

- pyridyliron and cobalt complexes: the effect of nitrogen substituents on ethylene oligomerisation and polymerization. *J. Chem. Soc. Dalton Trans.* 2001, 1639–1644. <https://doi.org/10.1039/b101173l>.
6. Tabernero V., Cuenca T., Herdtweck E. Hydrazonide titanium derivatives synthesis, characterization and catalytic activity in olefin polymerization. molecular structure of $[Ti(\eta^5-C_5H_4SiMe_3)Cl(\mu-N_2CPh_2)]_2$. *J. Organomet. Chem.* 2002, 663, 173–182.
 7. Hou J. X., Sun W. H., Zhang D. H., Chen L. Y., Li W., Zhao D. F., Song H. B. Preparation and characterization of acylhydrazone nickel(II) complexes and their catalytic behavior in vinyl polymerization of norbornene and oligomerization of ethylene. *J. Mol. Catal. A Chem.* 2005, 231, 221–233.
 8. Duan X. E., Xing Q. F., Dong Z. M., Chao J. B., Bai S. D., Liu D. S., Sun W. H. Trichlorozirconium 2-hydrazonides: synthesis, characterization and their catalytic behavior toward ethylene polymerization. *Chin. J. Polym. Sci.* 2016, 34, 390–398.
 9. Duan X. E., Yuan B., Li R., Vignesh A., Bariashir C., Li Z. L., Bai S. D., Ma Y. P., Chao J. B., Tong H. B., Sun W. H. Alkyl substituents triggered an unexpected formation of mono- and dinuclear zirconium hydrazonate complexes: synthesis, characterization and their catalytic behavior toward ethylene polymerization. *Appl. Organomet. Chem.* 2020, 34, e5586.
 10. Zauliczny M., Grubba R., Ponikiewski Ł., Pikies J. Phosphanylphosphido and phosphanylphosphinidene complexes of zirconium(IV) supported by bidentate *N,N* ligands. *Polyhedron* 2017, 123, 353–360.