(Pyrazolylborato)zinc−Aldehyde Complexes

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The zinc hydroxide complex $Tp^{Cum,Me}Zn–OH$ [**1**, $Tp^{Cum,Me}$ = tris(3-cumenyl-5-methylpyrazolyl)borate] reacts with trichloroacetaldehyde and pentafluorobenzaldehyde to form the complexes $Tp^{Cum,Me}Zn–O(CHOH)R$, containing the aldehyde ligands as the deprotonated aldehyde hydrates. **1** and 2-formylphenol, 2,6-diformylphenol and 2-formylthiophenol undergo condensation with the formation of the corresponding phenolate and thiophenolate complexes, in which one formyl group of each is coordinated to the zinc center as part of a six-membered chelate ring. The aldehyde–hydrate and aldehyde–phenolate bonding modes, which were confirmed by three structure determinations, represent two new kinds of aldehyde attachment to transition metal centers.

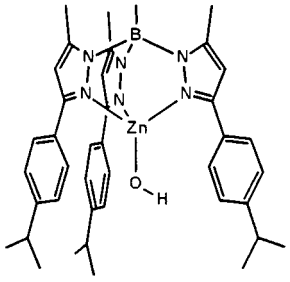
Introduction

Aldehyde functions belong to the standard functions of preparative organic chemistry, and metal salts are frequently used to increase their reactivity by Lewis acid activation.[1,2] For mechanistic considerations and for improving the knowledge about their basic coordination chemistry, it is therefore worthwhile to gain information on the bonding interactions between metal ions and the aldehyde CO functions. Due to the fact that aldehydes are very poor donor ligands, the number of isolated and structurally characterized aldehyde complexes is limited. Prior to our own work, only nine structures of such complexes with monodentate *O*-coordinated aldehyde ligands have been reported.[3]

Zinc salts, specifically zinc chloride, are among the most common activators for the reactivity of organic carbonyl functions. This holds for preparative organic chemistry,[1,2] as well as for enzymatic reactions: Two prominent representatives of the alcohol dehydrogenase class of enzymes, horse liver alcohol dehydrogenase (LADH, converting alcohols to aldehydes)[5,6] and yeast alcohol dehydrogenase (YADH, converting aldehydes to alcohols),[7,8] are zinc enzymes. All this provides ample motivation to study the coordination chemistry of zinc with alcohol and aldehyde ligands and to find out about the zinc-mediated reactivity of the corresponding substrates.

As we began our work in the preparative and structural chemistry of zinc−aldehyde complexes, only a small handful of these complexes had been described and only three structures reported.[3,9] We contributed several dozen compounds, including structural models for the alcohol dehydrogenases, and determined their structures.[4,9−12] Our findings underlined the general statement that monodentate aldehydes are very weak donors, and can be attached to zinc ions only in the absence of nitrogen or even weak oxygen donors, and that the combination with nitrogen donors is possible only when the aldehyde function forms a favorable chelate ligand together with them. Thus, one important bonding type, i.e. the monodentate attachment of an aldehyde molecule to a zinc ion in a "natural" environment, that is one with N and O or S donors, is still unknown.

We had experienced that encapsulating tris(pyrazolyl)borate (Tp) ligands are good mimics for a protein-like environment for zinc ions, thus allowing for the synthesis of structural models and mechanistic investigations of enzyme-like situations.[13] Moreover, the counterparts of the aldehydes in LADH or YADH reactivity, the alcohols, had already been attached to zinc ions together with the Tp ligands.[14−18] We therefore hoped that in a suitable TpZn environment, aldehydes might be induced to bind to the zinc center with their C=O functions. In order to ensure maximum protection of the substrates, we chose $Tp^{Cum,Me}$ as the Tp ligand with the most spacious substituents, and we used $Tp^{Cum,Me}Zn−OH$ (**1**),[19] bearing OH as a good leaving group,[13,20] as the reagent for the aldehyde substrates.



$Tp^{Cum,Me}Zn$-OH (1)

Results and Discussion

Complexes of Hydrated Aldehydes

Treatment of **1** with simple aliphatic or aromatic aldehydes in nonprotic solvents did not produce any noticeable

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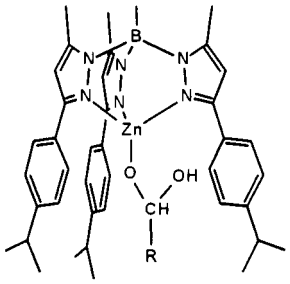
effects in the ^{1}H NMR spectra, and the reagents remained unchanged after removal of the solvent. However, aldehydes with electronegative substituents did react with **1**. Trichloroacetaldehyde and pentafluorobenzaldehyde were converted into complexes **2** and **3**. This conversion is accompanied by a shift of the ν(OH) band in the IR spectra to 3532 (**2**) and 3597 (**3**) cm^{-1}, and a shift of the OH resonance in the NMR spectra to δ = 4.10 (in $CDCl_3$) in both cases.



2: R = CCl_3 **3**: R = C_6F_5

Compounds **2** and **3** are α-hydroxyalkoxide complexes, i.e. they can be derived from the hydrated aldehydes. This could be verified for **2** by the synthesis from **1** and trichloroacetaldehyde hydrate (chloral hydrate). These hydrates, just like the aliphatic alcohols with electronegative substituents,[17] are sufficiently acidic to react with **1** by condensation. The direct formation of **2** and **3** under anhydrous conditions, however, is not a condensation reaction. It results from a nucleophilic attack of the Zn−OH function at the aldehyde carbon atom, followed by a concerted process of Zn−O(aldehyde) bond formation and Zn−O(OH) bond breaking. We have elucidated a trajectory for this type of reactions of TpZn−OH complexes by kinetic, structural and theoretical investigations.[20,21] In specific cases it corresponds to the initial stage of aldehyde hydration which is catalyzed as an abiotic process by zinc enzymes like carbonic anhydrase,[22] and which has been modeled for the catalytic hydration of acetaldehyde with zinc complexes of macrocyclic ligands.[23,24,25] The encapsulation provided by the Tp ligand and the uncharged nature of **2** and **3** renders these complexes stable and inert enough to be isolable as images of catalytic intermediates. This has been observed many times before for such images in the form of TpZn−X complexes.[13]

The structure determination of **2** (Figure 1) identifies the complex as belonging to the basic class of TpZn−OX complexes with monodentate OX ligands. There is little distortion of the threefold symmetry of the TpZn unit [O−Zn−N 120.9-124.6(1)°, N−Zn−N 91.1-96.9(1)°, Zn−O roughly on the threefold symmetry axis], and the Zn····O(OH) distance of 3.37 Å is outside the bonding range. The Zn−O bond length is as short as those in other TpZn−OR and TpZn−OH complexes,[14,17,18,19] and the bending angle Zn−O−C is at the lower end of its range.[17,18]

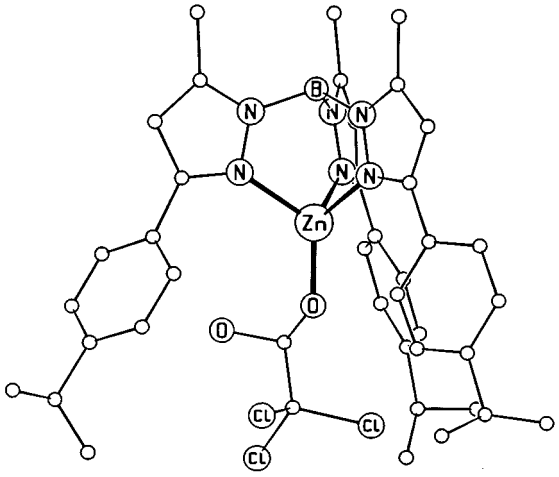


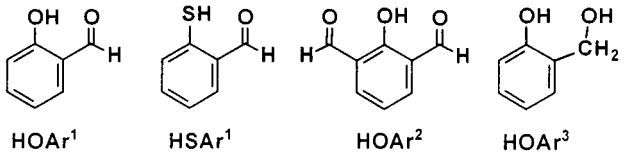
Figure 1. Molecular structure of complex **2**; selected bond lengths [Å] and angles [°]: Zn−O 1.865(2), Zn−N 2.063(3), 2.036(3), 2.040(3), C−O(Zn) 1.364(5), C−O(OH) 1.395(5), Zn−O−C 125.5(2)

In terms of a mechanistic discussion the structure of **2** corresponds to the completion of the first step of catalytic aldehyde hydration, i.e. the complete breaking of the old Zn−O bond and the complete formation of the new Zn−O bond. There are no other α-hydroxyalkoxide complexes of zinc available for comparison, but the situation resembles that in zinc carboxylate complexes. The structures of the latter[26] display a smooth transition from symmetrically bidentate to purely monodentate coordination of the carboxylate ligand, thereby outlining a simple trajectory for the reaction discussed here, namely the hydration of an aldehyde. Thus, there is good evidence that this reaction proceeds by the four-center mechanism which also applies to all other hydrolytic reactions of the TpZn−OH complexes.[20] This mechanism might be verified here by ^{17}O labeling studies. However, this would be doomed to be futile, as Parkin[27] showed that the lability and mobility of these systems lead to rapid ^{17}O scrambling over all possible positions.

Complexes of 2-Formylphenols

We had observed previously[17] that TpZn−phenolates, unlike simple TpZn−alkoxides, are easy to isolate and are stable against hydrolysis. In the course of these studies we had found IR-spectroscopic evidence for chelating aldehyde coordination in the TpZn complex of $HOAr^2$. Subsequent studies[20] then showed that, other than what was originally thought, five-coordinate zinc ions in TpZn complexes are not uncommon and CO coordination to zinc ions as part of five- or six-membered chelate rings is possible in TpZn complexes of e.g. hydroxamates, β-hydroxy ketonates or β-diketonates.[15,28] We therefore extended our investigations of the TpZn−phenolate complexes to those of phenolates with carbonyl-containing functional groups in the β-positions. We found evidence for aldehyde coordination with the formyl-substituted phenols $HOAr^1$ and $HOAr^2$, as well as with the thiophenol $HSAr^1$. The 2-hydroxymethylphenol

($HOAr^3$) was included in this investigation for comparative purposes.



$HOAr^1$ $HSAr^1$ $HOAr^2$ $HOAr^3$

We have already described the preparation of complexes **6** and **7**, derived from $HOAr^2$ and $HOAr^3$.[17] The new complexes **4** and **5** were formed in reasonable yields from **1** and the corresponding phenol in dichloromethane. Two significant pieces of evidence point to the zinc−aldehyde coordination in **4**−**6**, firstly a shift of −15 to −20 cm^{-1} for the aldehyde bands in the IR spectra of **4** (1655 cm^{-1}), **5** (1651 cm^{-1}) and **6** (1648 cm^{-1}) in comparison with those of the free aldehydes; and secondly a shift of more than −2 ppm for the aldehyde proton in the NMR spectra (see Experimental Section). In comparison, the ^1H NMR resonances of the OCH_2 groups of the ligand $HOAr^3$ appear virtually unchanged in its complex **7**.

$Tp^{Cum,Me}Zn\text{-}OAr^1$ **4** $Tp^{Cum,Me}Zn\text{-}SAr^1$ **5**

$Tp^{Cum,Me}Zn\text{-}OAr^2$ **6** $Tp^{Cum,Me}Zn\text{-}OAr^3$ **7**

The structures of complexes **4**, **6** and **7** were determined, see Figure 2 and 3 and Table 1. Complex **7** can be compared with **2** or the other phenolate and alkoxide complexes[17,18] having a symmetrical coordination of the Tp ligand, a roughly trigonal symmetry of the TpZn−O unit, a rather short Zn−O bond, and a distinctly noncoordinating CH_2OH unit. Complexes **4** and **6**, on the other hand, are quite similar, having one aldehyde function attached as a fifth donor to the zinc center, and containing the aldehyde−phenolate ligand as part of a six-membered chelate ring.

The coordination geometry of the zinc center in **4** and **6** is very close to trigonal bipyramidal, as seen by the nearly linear O2−Zn−N1 arrangement. In agreement with this, the Zn−N bond lengths differ significantly and the Zn−O1 line is bent away from the Zn−B line defining a trigonal axis of the Tp ligand. The Zn−O2 bond is 0.27 (**4**) and 0.19 (**6**) Å longer than the Zn−O1 bond. This is because of two reasons, the Zn−O(aldehyde) interaction is weaker than the Zn−O(phenolate) interaction, and Zn−O2 defines the axial direction of the trigonal bipyramid. The O1−C bond lengths are typical for zinc phenolates,[17,29] the O2−C bond lengths are characteristically short and almost unchanged in comparison with those in free aldehydes.[10−12]

There is a considerable variation in the Zn−O(aldehyde) bond lengths, mostly due to changes in coordination numbers and geometries around the zinc center.[4,10−12] Five-coordinated zinc complexes of pyridine-2-carbaldehydes[11] have the closest geometrical relation to **4** and **6**; but their Zn−O distances vary extensively. It can be stated, however, that for complexes in which nitrogen donors compete with aldehyde ligands, **4** and **6** are among those that have the

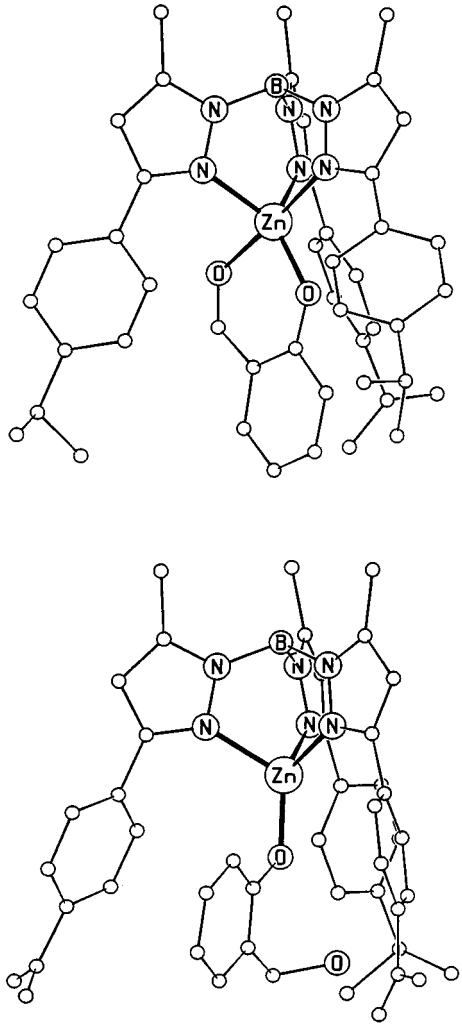


Figure 2. Comparison of the structures of **4** (top) and **7** (bottom)

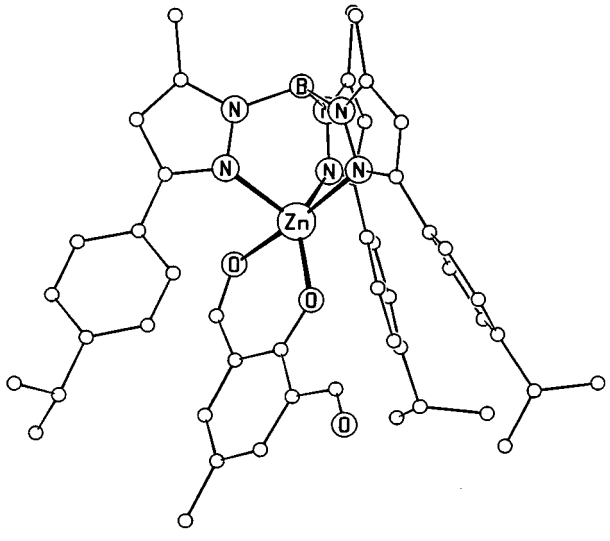


Figure 3. Molecular structure of **6**

Table 1. Structural comparison of **4**, **6** and **7** [Å, °]

	4	**6**	**7**
Zn−N1	2.213(2)	2.159(3)	2.011(3)
Zn−N2	2.038(2)	2.059(3)	2.044(3)
Zn−N3	2.046(2)	2.046(3)	2.053(3)
Zn−O1	1.904(2)	1.921(2)	1.859(2)
Zn−O2	2.173(2)	2.210(3)	4.473(2)
O1−C	1.302(3)	1.305(4)	1.346(4)
O2−C	1.230(3)	1.225(5)	1.437(7)
O1−Zn−N1	93.4(1)	100.7(1)	124.1(1)
O1−Zn−N2	136.3(1)	136.2(1)	125.6(1)
O1−Zn−N3	128.1(1)	123.2(1)	119.8(1)
O1−Zn−O2	87.9(1)	86.7(1)	−
O2−Zn−N1	177.5(1)	171.9(1)	−
Zn−O1−C	132.2(2)	131.9(2)	123.1(2)
Zn−O2−C	123.8(2)	124.0(3)	−

shortest, i.e. strongest, Zn−O(aldehyde) interactions. In this respect **4** and **6** resemble the TpZn−β-diketonate complexes[17,28] which also have six-membered chelate rings and short Zn−O bonds. Apparently, in a TpZn(X)(Y) environment the six-membered chelate ring is a more strain-free alternative for the attachment of X and Y to the zinc ion than the common five-membered chelate ring. This has helped to create stable Zn−O(aldehyde) ligation inside the TpZn pocket, which yields the significant information that zinc−aldehyde interactions can be strong enough to overcome the reluctance of the encapsulated TpZn−X complexes to increase the coordination number of the zinc ion from four to five.

Conclusions

This work has provided two new bonding modes of aldehydes to zinc ions, the attachment as anions of the aldehyde hydrates and the attachment as part of bidentate O,O donors forming six-membered chelate rings. Unlike in the previous examples, the aldehydes under these conditions can form stable zinc complexes even in the presence of several good nitrogen donors. It is likely that the protection offered by the encapsulating pyrazolylborate ligands and the uncharged molecular nature of the complexes have helped to make them accessible.

The structures of the aldehyde complexes yield two pieces of information in terms of catalytic or enzymatic aldehyde interconversions. Firstly, they support a consistent mechanistic picture of the nucleophilic attack at carbonyl functions, exemplified here by aldehyde hydration. Secondly, they visualize the increase of the coordination number of the zinc ion from four to five, even when the weakly coordinating aldehydes are the fifth ligands. For the processes during the action of the LADH or YADH enzymes, this means that a coligand, cosubstrate or reagent may be present at the zinc ion during the catalytic turnover.

Experimental Section

The general working and measuring conditions were as in ref. [30] Reagents, except for **1**,[19] $HSAr^1$ [31] and $HOAr^2$,[32] were obtained commercially.

Complex 2: A solution of **1** (500 mg, 0.72 mmol) in 30 mL of dichloromethane and 40 mL of acetonitrile was treated with freshly distilled trichloroacetaldehyde (531 mg, 528 μL, 3.60 mmol) and stirred for 20 h. After concentrating to 30 mL in vacuo, the solution was left standing at −4 °C for several weeks. 341 mg (49%) of **2** was precipitated as colorless crystals, m.p. 178 °C, which were washed with a few mL of petroleum ether. − $C_{41}H_{48}BCl_3N_6O_2Zn{\cdot}2CH_3CN{\cdot}2H_2O$ (839.4 + 82.1 + 36.0): calcd. C 56.44, H 6.10, N 11.70; found C 56.47, H 5.68, N 10.44. − ^{1}H NMR ($CDCl_3$): δ = 1.18 (d, *J* = 6.9 Hz, 18 H, *i*Pr), 1.55 (s, 4 H, H_2O), 1.98 (s, 6 H, CH_3CN), 2.45 [s, 9 H, Me(pz)], 2.83 (sept, *J* = 6.9 Hz, 3 H, *i*Pr), 4.00 [s, 1 H, CH (aldehyde)], 6.11 [s, 3 H, H (pz)], 7.22 (d, *J* = 8.2 Hz, 6 H, Ph), 7.55 (d, *J* = 8.2 Hz, 6 H, Ph).

Complex 3: 1 (200 mg, 0.29 mmol) and C_6F_5CHO (569 mg, 2.90 mmol) in 40 mL of dichloromethane were stirred for 20 h. The solvent was removed in vacuo and the residue washed with a few mL of acetonitrile. Recrystallization from acetonitrile/dichloromethane (3:1) yielded 86 mg (33%) of **3** as colorless crystals, m.p. 225 °C. − $C_{46}H_{48}BF_5N_6O_2Zn$ (888.1): calcd. C 62.21, H 5.45, N 9.46; found C 61.15, H 5.90, N 10.15. − ^{1}H NMR ($CDCl_3$): δ = 1.23 (d, *J* = 6.9 Hz, 18 H, *i*Pr), 2.53 [s, 9 H, Me (pz)], 2.91 (sept, *J* = 6.9 Hz, 3 H, *i*Pr), 4.09 [s, 1 H, CH (aldehyde)], 6.19 [s, 3 H, H (pz)], 7.29 (d, *J* = 8.2 Hz, 6 H, Ph), 7.64 (d, *J* = 8.2 Hz, 6 H, Ph).

Complex 4: 1 (200 mg, 0.29 mmol) and $HOAr^1$ (35 mg, 0.31 μL, 0.29 mmol) in 30 mL of dichloromethane were stirred for 4 h. The solvent was removed in vacuo and the residue dissolved in 20 mL of acetone. Slow concentration over several weeks yielded 179 mg (53%) of **4** as yellow crystals, m.p. 181 °C. − $C_{46}H_{51}BN_6O_2Zn$ (796.2): calcd. C 69.40, H 6.46, N 10.56; found C 68.37, H 6.40, N 10.46. − ^{1}H NMR ($CDCl_3$): δ = 1.16 (d, *J* = 6.9 Hz, 18 H, *i*Pr), 2.58 [s, 9 H, Me (pz)], 2.78 (sept, *J* = 6.9 Hz, 3 H, *i*Pr), 6.21 [s, 3 H, H(pz)], 6.41 (t, *J* = 7.8 Hz, 1 H, OPh), 6.65 (d, *J* = 7.8 Hz, 1 H, OPh), 7.09 (d, *J* = 8.2 Hz, 6 H, Ph), 7.22 (m, 2 H, OPh), 7.54 (d, *J* = 8.2 Hz, 6 H, Ph), 7.87 [s, 1 H, CH (aldehyde)].

Complex 5: 1 (200 mg, 0.29 mmol) and $HSAr^1$ (46 mg, 0.89 mmol) in 40 mL of dichloromethane were stirred for 4 h. The solvent was removed in vacuo and the residue dissolved in 30 mL of methanol/dichloromethane (4:1). Slow concentration over several weeks yielded 121 mg (49%) of **5** as yellow crystals, m.p. 217 °C. − $C_{46}H_{51}BN_6OSZn$ (812.2): calcd. C 68.02, H 6.33, N 10.35; found C 66.73, H 6.65, N 9.25. − ^{1}H NMR ($CDCl_3$): δ = 1.21 (d, *J* = 6.9 Hz, 18 H, *i*Pr), 2.51 [s, 9 H, Me(pz)], 2.81 (sept, *J* = 6.9 Hz, 3 H, *i*Pr), 6.19 [s, 3 H, H (pz)], 7.09 (d, *J* = 8.2 Hz, 6 H, Ph), 7.22 (m, 3 H, SPh), 7.49 (d, *J* = 8.2 Hz, 6 H, Ph), 7.64 (d, *J* = 8.4 Hz, 1 H, SPh), 7.95 [s, 1 H, CH (aldehyde)].

Structure Determinations:[33] The crystals were obtained directly from the reaction solutions and used without drying in vacuo. They were immersed in fluorinated polyether oil and immediately placed in the nitrogen stream of the diffractometer's cooling system. Diffraction data were recorded at ca. −100 °C using the ω/2θ technique with a Nonius CAD4 diffractometer fitted with a molybdenum tube (K_α, λ = 0.7107 Å) and a graphite monochromator and treated without absorption corrections. The structures were solved with direct methods and refined anisotropically with the SHELX program suite.[34] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5 times those of their attached atoms. Parameters were refined against F^2. The *R* values are defined as $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]\Sigma[w(F_o^2)^2]\}^{1/2}$. Drawings were produced with SCHAKAL.[34] Table 2 lists the crystallographic data.

Table 2. Crystallographic details

	2	**4**	**6**	**7**
Empirical formula	$C_{45}H_{58}BCl_3N_8O_4Zn$	$C_{46}H_{51}BN_6O_2Zn$	$C_{49}H_{55}BCl_2NO_3Zn$	$C_{46}H_{53}BN_6O_2Zn$
Molecular mass	957.5	796.2	923.1	798.2
Crystal size [mm]	0.5 × 0.4 × 0.3	0.6 × 0.5 × 0.4	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.3
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Z	2	2	4	2
a [Å]	12.270(2)	10.603(7)	12.233(1)	12.530(3)
b [Å]	14.140(3)	11.048(7)	23.234(5)	13.139(3)
c [Å]	16.730(3)	18.419(2)	17.270(3)	14.132(3)
α [°]	73.14(3)	95.760(6)	90	86.85(3)
β [°]	75.20(3)	99.770(6)	108.01(1)	68.29(3)
γ [°]	67.16(3)	91.650(5)	90	89.32(3)
V [Å^3]	2526.2(8)	2113.3(3)	4668.1(1)	2158.2(8)
d(calcd.) [gcm^{-3}]	1.65	1.25	1.31	1.23
μ(Mo-K_α) [mm^{-1}]	1.02	0.63	0.69	0.61
hkl range	h: −15 to 14 k: −17 to 17 l: −20 to 20	h: −13 to 13 k: −13 to 0 l: −22 to 22	h: 0 to 16 k: 0 to 32 l: −23 to 22	h: −15 to 14 k: −16 to 16 l: −17 to 0
Measured reflections	18708	8723	12903	8842
Independent reflections	9096	8271	12903	8479
Observed refl. [$I > 2\sigma(I)$]	6805	5743	8466	6132
Parameters	559	505	559	505
Refined reflections	9096	8271	12903	8479
R_1(obs.refl.)	0.059	0.042	0.075	0.054
wR_2(all refl.)	0.167	0.123	0.238	0.181
Residual electron density [e/Å^3]	+ 0.9 −0.5	+ 0.4 −0.3	+ 1.2 −1.1	+ 0.6 −0.3

Acknowledgments

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[33] Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144035 (**2**), -144036 (**4**), -144037 (**6**) and -144038 (**7**). Copies of the data can be obtained free of charge on applicaton to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]
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