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Rare example of structurally characterized mononuclear N-heterocyclic carbene containing zinc carboxylate

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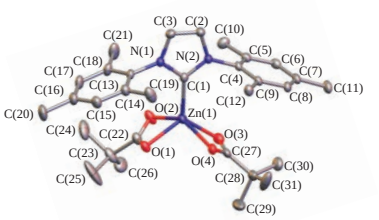
An adduct of Zn^{II} pivalate with N-heterocyclic carbene 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene has been prepared and characterized by X-ray diffraction analysis, NMR spectroscopy and DFT calculations. The compound preserves mononuclear structure in solution and does not switch the coordination mode from normal to abnormal.

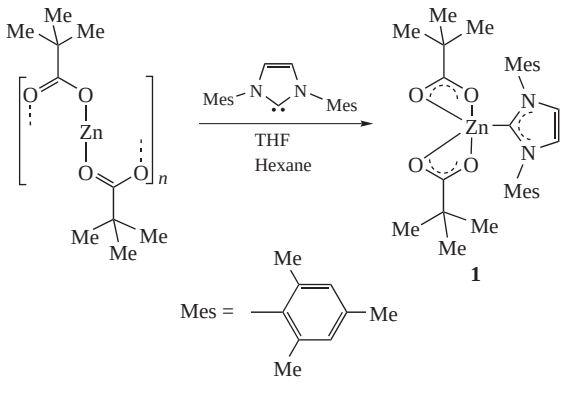


Keywords: N-heterocyclic carbenes, carboxylate complexes, zinc(II), DFT calculations, X-ray crystallography.

Organometallic complexes containing N-heterocyclic carbenes (NHCs) are well-known catalysts.[1–6] The NHC complexes of 3d metals can be considered as inexpensive analogs of noble metal catalysts.[7–10] In particular, Zn^{II} is a strong Lewis acid site, which exhibits catalytic activity in hydrogenation, amination and alkylation reactions[11–13] and promising reactivity toward industrially important substrates.[14,15] Surprisingly, only two structurally characterized NHC-containing Zn^{II} carboxylates, namely $[Zn(O_2CC_5Me_5)(C_6F_5)(IBu^t)]$ (IBu^t is 1,3-di-*tert*-butylimidazol-2-ylidene) and $[Zn_2(O_2CCH_2Ph)_4(IMes)_2]$ (IMes is 1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene), have been described.[8,9]

In this work, we performed the reaction between polymeric zinc(II) pivalate $[Zn(O_2CCMe_3)_2]_n$[16] and IMes in THF followed by crystallization, which resulted in the mononuclear complex $[Zn(O_2CCMe_3)_2(IMes)]$ **1** (Scheme 1, for the procedure details see Online Supplementary Materials). According to a quantum-chemical evaluation, the formation of this product causes an energy gain (more than 25 kcal mol^{-1}, see Online Supplementary Materials), which is consistent with strong σ-donor NHC properties.

Single crystals suitable for X-ray diffraction analysis† were isolated by the gradual cooling of a saturated solution of **1** in boiling hexane to room temperature. According to the X-ray diffraction data, the Zn^{2+} ion coordinates a carbon atom of the IMes moiety [1.995(2) Å] and four oxygen atoms of the two carboxylate groups [2.0164(19)–2.2344(19) Å]. The resulting ZnO_4C coordination environment resembles a trigonal bipyramid (TBPY-5) or, alternatively, a square pyramid (SPY-5), as quantified by continuous shape measures.[17] These measures show how close the shape of



Scheme 1

† *Crystal data for* **1**. $C_{31}H_{42}N_2O_4Zn$ (M = 572.09), monoclinic, space group $P2_1/c$, at 120 K: a = 21.095(3), b = 13.5329(16) and c = 21.295(3) Å, β = 147.382(7)°, V = 3277.0(10) $Å^3$, Z = 4, d_{calc} = 1.160 g cm^{-3}, μ(MoKα) = = 13.02 cm^{-1}, F(000) = 1216. Intensities of 44103 reflections were measured on a Bruker APEX2 CCD diffractometer [λ(CuKα) = 1.54178 Å, ω-scans, 2θ < 135°], and 5857 independent reflections (R_{int} = 0.1110) were used in the further refinement. Using Olex2,[18] the structure was solved with the ShelXT[19] structure solution program using Intrinsic phasing and refined with the olex2.refine[20] refinement package using Gauss–Newton minimization. Positions of hydrogen atoms were calculated and refined in the isotropic approximation using the riding model. The refinement converged to wR_2 = 0.1262 and GOF = 1.0398 for all the independent reflections [R_1 = 0.0481 was calculated against F for 4796 observed reflections with $I > 2\sigma(I)$].

CCDC 1962238 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

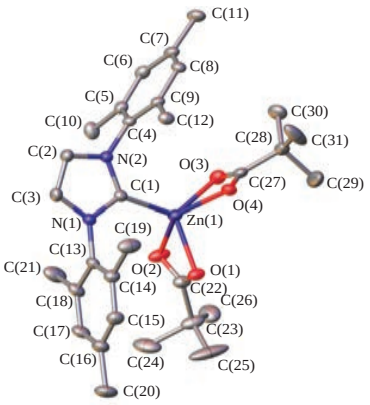


Figure 1 General view of complex **1** in the representation of atoms *via* thermal ellipsoids at a 30% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Zn(1)–O(1) 2.0290(17), Zn(1)–O(2) 2.2309(19), Zn(1)–O(3) 2.0164(19), Zn(1)–O(4) 2.2344(19), Zn(1)–C(1) 1.995(2), O(1)–C(22) 1.262(3), O(2)–C(22) 1.258(3), O(3)–C(27) 1.268(3), O(4)–C(27) 1.253(3); selected bond angles (°): O(2)–Zn(1)–O(1) 61.44(7), O(3)–Zn(1)–O(1) 111.19(8), O(3)–Zn(1)–O(2) 98.93(8), O(4)–Zn(1)–O(1) 95.77(7), O(4)–Zn(1)–O(2) 143.94(7), O(4)–Zn(1)–O(3) 61.58(7), C(1)–Zn(1)–O(1) 124.79(9), C(1)–Zn(1)–O(2) 108.96(9), C(1)–Zn(1)–O(3) 123.95(8), C(1)–Zn(1)–O(4) 107.03(8).

the coordination polyhedron of the metal ion fits an ideal polyhedron, *e.g.*, it should be zero for an ideal TBPY-5 or a SPY-5. The corresponding symmetry measures S(TBPY-5) and S(SPY-5) for **1** are 5.083 and 5.589, respectively. For comparison, an ideal pentagon (PP-5) produces a value of 31.292, which is very far from the true shape of the coordination polyhedron of the Zn^{2+} ion in **1**. The IMes ligand has an expected molecular geometry with the mesityl substituents rotated from the N-heterocyclic carbene plane due to the steric bulk of their methyl groups; the angles between these two aromatic fragments are 89.703(14) and 89.981(14)°. These methyl groups can also be responsible for the lack of stacking interactions between the mesityl substituents of the neighboring molecules of complex **1**; these are held together only by weak intermolecular interactions.

If the molecular structure of **1** is preserved in a toluene-d_8 solution, four individual signals are expected in the ^{1}H NMR spectrum due to the symmetry reasons. Indeed, we detected signals for imidazole C^4, C^5 protons (Figure 2) and *tert*-butyl protons (Figure S1). However, the region of the mesityl group protons shows several signals, which indicate some solution dynamics of these molecular parts. To prove the persistence of intact complex **1** in the toluene solution, we used DOSY NMR spectroscopy. According to the DOSY spectrum of **1** (Figure S2), all recorded signals show the same diffusion coefficient of 7.2×10^{-6} cm^2 s^{-1}, meaning that all these protons belong to the same molecule. Moreover, a rough estimation of the molecular size by the Einstein–Stokes equation (1) with the assumption of a spherical shape leads to a size of 10.1 Å, which is consistent with a molecular volume of 819.3 Å^3 estimated from the X-ray diffraction data. Therefore, we can conclude that the mononuclear structure of **1** is preserved in a toluene solution, but some dynamics of mesityl fragments (probably, hindered rotation around the N–C bond) is observed.

$$D = kT/6\pi\eta r, \quad (1)$$

where D is the diffusion coefficient, k is the Boltzmann constant, T is temperature, η is solution viscosity, and r is hydrodynamic radius.

The NMR spectra at temperatures to 360 K (Figure S3) reveal only slight variations in the range of mesityl group protons; thus, no irreversible transformation (such as isomerization in abnormal carbene complex) occurs at least up to 360 K.

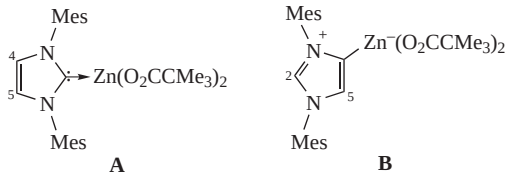


Figure 2 Probable isomers of complex **1**.

As for the isomerization, two major coordination modes are known for carbene derivatives of imidazole, namely, *via* the C(2) and C(4) atoms of an azole ring (Scheme 2), named normal and abnormal, respectively.[21–25] The abnormal coordination is favored for overcrowded coordination cores, inasmuch as only one bulky NR group of the carbene is situated adjacent to the metal. On the other hand, since the carbenic center is supported by a single adjacent heteroatom, the electronic structure of the ligand is modified to significantly enhance its donor properties. As a result, the properties such as catalytic performance of the complexes with abnormally coordinated NHCs can be tuned. Even though the presence of an abnormal isomer of complex **1** in solution has been ruled out by temperature-dependent NMR spectroscopy, we decided to shed more light on this eventual possibility. For this purpose, we performed a DFT B3LYP/Def2TZVP *in silico* study of the abnormalization process. The calculated bond lengths of structure **A** (see Figure 2), in which coordination of zinc(II) pivalate occurs by a normal type, are consistent with the X-ray diffraction data (Figure S4). The energy preference of **A**, as compared to the abnormal isomer **B**, is 8.5 kcal mol^{-1} (6.4 kcal mol^{-1} with consideration for nonspecific solvation (SMD; solvent, hexane) (Table S1). Therefore, the molecule of **1** exists as isomer **A** in agreement with the experimental results.

Thus, we have isolated mononuclear [$Zn(O_2CCMe_3)_2$(IMes)], a rare example of structurally characterized mononuclear zinc carboxylate containing an NHC ligand. The compound preserves mononuclear structure in solution and does not switch the coordination mode from normal (thermodynamically preferred) to abnormal. This is consistent with the results of DFT calculations.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.010.

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