The First Stable Aldehyde and Ketone Complexes of Zinc: the Structure of $[Zn(SeC_6H_2Bu^t{}_3)_2(p\text{-}O{=}CHC_6H_4OMe)]_2$

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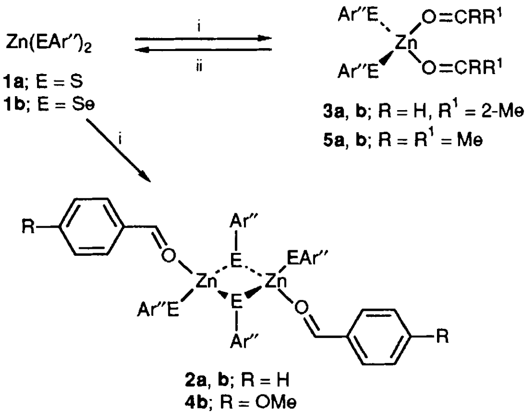
The reaction of $Zn(EC_6H_2Bu^t{}_3)_2$ (E = S or Se) with organic carbonyl compounds gives the first isolable aldehyde and ketone complexes of zinc as models for transient metal-substrate complexes in metalloenzymes such as liver alcohol dehydrogenase.

Zinc plays an important structural as well as catalytic role in many metalloenzymes and is frequently found coordinated to two or more sulphur ligands, with the additional coordination sites in the tetrahedral coordination sphere being taken up usually by nitrogen or oxygen donors.[1] Attempts have been made to construct suitable models for the different coordination environments of group 12 metals in metalloproteins, and bulky thiolato ligands have proved particularly useful for this purpose.[2] It is known from crystallographic data that the catalytically active site in horse liver alcohol dehydrogenase consists of zinc coordinated to one histidine-N and two cysteine-S atoms and one labile water ligand[3] and is thought to function by binding the alcohol or aldehyde substrate to the Lewis acidic zinc centre prior to electron transfer.[4] The interaction of zinc(II) with aldehydes was probed by resonance Raman and UV–VIS spectroscopy using aromatic aldehydes as chromophores. Significant red-shifts were found as the result of aldehyde coordination although the position of Zn^{2+}



Scheme 1 *Reagents and conditions*: i, aldehyde or ketone, 10 equiv., light petroleum, room temp.; ii, PhCN, 1 equiv. Ar″ = 2,4,6-C$_6$H$_2$Bu^t$_3$

in the Irving–Williams series did not allow the isolation of any aldehyde complexes.[5] We now report the synthesis and structural characterisation of the first stable chalcogenolato complexes of zinc with aldehyde of ketone ligands.

Treatment of a suspension of colourless Zn(EAr″)$_2$ **1** (Ar″ = 2,4,6-C$_6$H$_2$Bu^t$_3$; **a**, E = S, **b**, E = Se)[6] in hexane at room temperature with *ca.* 10 equiv. of an aromatic aldehyde RC$_6$H$_4$CHO (R = H, 2-OMe, 4-OMe) leads to an immediate colour change to yellow-orange and formation of a clear solution from which the product complexes precipitate. Recrystallisation of the crude products from light petroleum (R = OMe) or toluene (R = H) gives the complexes **2a, b** (R = H), **3a, b** (R = 2-OMe) and **4b** (R = 4-OMe) respectively as yellow (E = S) or orange (E = Se) crystals (Scheme 1).† The S-complex **4a** could not be obtained crystalline. Whereas the aldehyde-free complexes **1a, b** and their cadmium analogues show fluxionality and establish monomer–dimer solution equilibria,[7] the NMR spectrum of the 1:1 complex **4b** indicates that the compound maintains a dimeric structure in chloroform solution, as well as in the crystal (see below). It is probable that the benzaldehyde complexes **2**, which also have 1:1 stoichiometry, possess a similar dimeric structure, although in this case NMR was unable to distinguish between terminal and bridging chalcogenolato ligands, even at −55 °C. Because of the incorporation of various amounts of toluene of crystallisation, satisfactory elemental analyses of **2** could not be obtained.

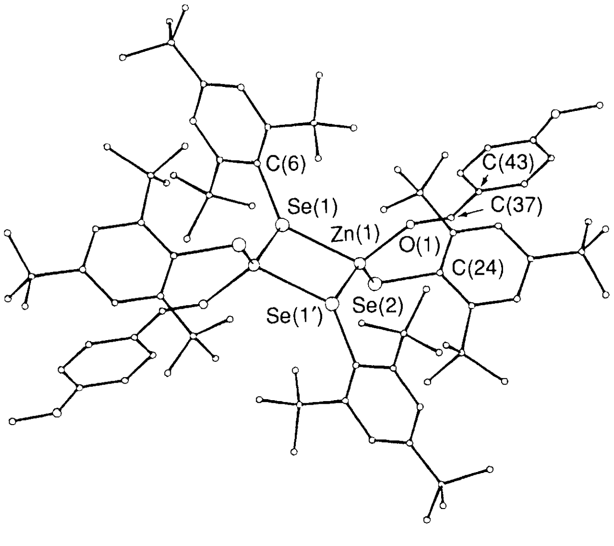


Fig. 1 Molecular structure of **4b**. Selected bond lengths (Å) and angles (°): Zn(1)–Se(1) 2.552(4), Zn(1)–Se(2) 2.345(3), Zn(1)–Se(1′) 2.453(4), Zn(1)–O(1) 2.059(7), C(6)–Se(1) 1.974(6), C(24)–Se(2) 1.965(6), C(37)–O(1) 1.242(10), C(37)–C(43) 1.440(9); Se(2)–Zn(1)–Se(1) 111.1(1), Se(1)–Zn(1)–Se(1′) 80.8(4), Zn(1)–Se(1)–Zn(1′) 99.2(2), Se(2)–Zn(1)–Se(1′) 135.6(5), O(1)–Zn(1)–Se(1) 111.3(2), O(1)–Zn(1)–Se(2) 114.4(3), O(1)–Zn(1)–Se(1′) 98.7(4), C(6)–Se(1)–Zn(1) 135.6(1), C(6)–Se(1)–Zn(1′) 116.1(5), Zn(1)–O(1)–C(37) 133.5(4).

The reaction of **1a, b** with acetone gives the bis(acetone) complexes **5a** and **5b** as colourless crystals. Similar complexes with acetophenone are formed in solution but could not be isolated.

Whereas for cationic rhenium complexes an equilibrium between σ- and π-co-ordinated aldehyde has recently been established,[8] the carbonyl ligands in the complexes reported here are η^1 coordinated in all cases. A limited number of aldehyde complexes of transition metals is known, the majority of which contain the carbonyl ligand side-on (η^2) bonded; this holds true in particular for formaldehyde compounds.[9] Bis(aldehyde) metal complexes such as **3** have to our knowledge not been reported, and it is interesting to note that in **3** the coordination of a second aldehyde molecule is favoured over the binding to a potentially chelating *ortho*-OMe substituent within the same ligand, in spite of the steric crowding in the complex imposed by the bulky aryl groups. The η^1 coordination mode is indicated by the IR spectra: Complexation of carbonyl compounds to zinc reduces the ν(C=O) stretching frequencies by 30 cm^{-1} in the case of the acetone complexes **5**, and by *ca.* 50 cm^{-1} for **2–4**, compared to the free ligands, whereas η^2 bonding results in much greater low-frequency shifts.[8,9] These shifts to lower frequency are typical of aldehyde coordination to Lewis acids but are less than those observed for the adducts of stronger Lewis acids such as BF$_3$ or aluminium phenoxides.[10]

The coordination of aldehyde ligands is easily reversible in solution unless an excess of aldehyde is present. For example,

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† Satisfactory elemental analyses (except for **2**, see text). Selected physical data: Compound **2a**: IR ν_{max}/cm^{-1} (Nujol mull): 1640; ^{1}H NMR (90 MHz, CDCl$_3$): 1.20 (s, 18 H, *p*-Bu^t), 1.37 (s, 36 H, *o*-Bu^t), 2.30 (s, 3 H, toluene), 7.12–7.8 (m, 14 H, aryl-H of Ar″, PhCHO, toluene), 9.53 (s, 1 H, CHO). **2b**: IR ν_{max}/cm^{-1} (Nujol): 1640;; ^{1}H NMR (CDCl$_3$): 1.20 (s, 18 H, *p*-Bu^t), 1.53 (s, 36 H, *o*-Bu^t), 7.12–7.8 (m, 9 H, aryl), 9.62 (s, 1 H, CHO). **3a**: IR ν_{max}/cm^{-1} (Nujol): 1644; ^{1}H NMR (CDCl$_3$): 1.10 (s, 18 H, *p*-Bu^t), 1.45 (s, 36 H, *o*-Bu^t), 3.85 (s, 6 H, OMe), 6.8–7.7 (m, 12 H, aryl), 10.10 (s, 2 H, CHO); ^{13}C NMR (CDCl$_3$): Ar″: 31.33 (*p*-C*Me*$_3$), 31.98 (*o*-C*Me*$_3$), 34.65 (*p*-*C*Me$_3$), 38.0 (*o*-*C*Me$_3$), 122.02 (*m*-C), 146.50 (*p*-C), 152.88 (*o*-C); *o*-anisaldehyde: 55.68 (OMe), 111.66, 120.77, 128.85, 136.55, 190.90 (CHO). **3b**: IR ν_{max}/cm^{-1} (Nujol): 1642; ^{1}H NMR (CDCl$_3$): 1.08 (s, 18 H, *p*-Bu^t), 1.52 (s, 36 H, *o*-Bu^t), 3.78 (s, 6 H, OMe), 6.8–7.8 (m, 12 H, aryl), 10.08 (s, 2 H, CHO); ^{13}C NMR (CDCl$_3$): Ar″: 31.33 (*p*-C*Me*$_3$), 32.42 (*o*-C*Me*$_3$), 34.69 (*p*-*C*Me$_3$), 38.81 (*o*-*C*Me$_3$), 122.13 (*m*-C), 122.78 (*ipso*-C), 147.24 (*p*-C), 153.75 (*o*-C); *o*-anisaldehyde: 55.68 (OMe), 111.71, 120.83, 128.96, 136.66, 190.96 (CHO). **4b**: IR ν_{max}/cm^{-1} (Nujol): 1643; ^{1}H NMR (CDCl$_3$: Ar″: 1.08 (s, 9 H, *p*-Bu^t), 1.19 (s, 9 H, *p*-Bu^t), 1.53 (s, 18 H, *o*-Bu^t), 1.56 (s, 18 H, *o*-Bu^t), 7.22 (s, 2 H), 7.38 (s, 2 H); *p*-anisaldehyde: 3.83 (s, 3 H, OMe), 6.90 (d, 2 H, aryl, *J* 9 Hz), 7.64 (d, 2 H, aryl, *J* 9 Hz), 10.08 (s, 1 H, CHO); ^{13}C NMR (CDCl$_3$): Ar″: 31.38, 31.55 (*p*-C*Me*$_3$), 32.04, 32.31 (*o*-C*Me*$_3$), 33.38, 34.86 (*p*-*C*Me$_3$), 38.38, 38.98 (*o*-*C*Me$_3$), 121.90, 122.70 (*m*-C), 122.78 (*ipso*-C), 147.50 (*p*-C), 152.07, 154.24 (*o*-C); *o*-anisaldehyde: 55.63 (OMe), 114.31, 132.38, 191.72 (CHO). **5a**: IR ν_{max}/cm^{-1} (Nujol): 1685; ^{1}H NMR (CDCl$_3$): 1.20 (s, 18 H, *p*-Bu^t), 1.43 (s, 36 H, *o*-Bu^t), 2.00 (s, 12 H, OCMe$_2$), 7.7 (s, 4 H, aryl); ^{13}C NMR (CDCl$_3$): Ar″: 30.90 (*Me*$_2$CO), 31.55 (*p*-C*Me*$_3$), 32.09 (*o*-C*Me*$_3$), 34.58 (*p*-*C*Me$_3$), 38.22 (*o*-*C*Me$_3$), 121.53 (*m*-C), 145.02 (*p*-C), 152.88 (*o*-C), 219.22 (Me$_2$CO). **5b**: IR ν_{max}/cm^{-1} (Nujol): 1685; ^{1}H NMR (CDCl$_3$): 1.20 (s, 18 H, *p*-Bu^t), 1.49 (s, 36 H, *o*-Bu^t), 1.94 (s, 12 H, OCMe$_2$), 7.17 (s, 4 H, aryl); ^{13}C NMR (CDCl$_3$): Ar″: 30.92 (*Me*$_2$CO), 31.52 (*p*-C*Me*$_3$), 32.36 (*o*-C*Me*$_3$), 34.80 (*p*-*C*Me$_3$), 38.92 (*o*-*C*Me$_3$), 121.91 (*m*-C), 122.83 (*ipso*-C), 147.08 (*p*-C), 153.91 (*o*-C).

the reaction of **3a** with one equivalent of benzonitrile leads to the precipitation of **1a** instead of the formation of $Zn(SAr'')_2(OCHAr)(NCPh)$.

The crystal structure of **4b** was determined (Fig. 1).‡ The compound is dimeric, with two asymmetrically bridging selenolato ligands. Such an asymmetric bridging mode has previously been observed for three-coordinate chalcogenolato complexes of cadmium[6,7] and zinc[11] and appears to be a typical feature of these crowded molecules. Zinc is coordinated to three selenium atoms and one aldehyde ligand in a distorted tetrahedral manner. The Zn_2Se_2 ring is planar by symmetry. The aryl substituents of the aldehyde ligands are nearly co-planar to the C=O double bonds to allow conjugation with the arene ring. The C=O bond is slightly shorter than in $[CpRe(NO)(PPh_3)(p\text{-anisaldehyde})]^+$ (Cp = η-C_5H_5) [1.242(10) *vs.* 1.271(8) Å],[8] suggestive of a weaker metal–oxygen interaction in the case of zinc.

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‡ *Crystal data* for **4b**: $C_{88}H_{132}O_4Se_4Zn_2$, M = 1700.62, triclinic, space group $P\bar{1}$, a = 11.310(4), b = 12.921(8), c = 15.267(4) Å; α = 93.32(2), β = 92.40(1), γ = 100.87(2)°, V = 2184.18 Å^3, D_c = 1.294 g cm^{-3}, Z = 1. X-ray measurments were made using an Enraf-Nonius FAST TV area detector diffractometer and graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). Unit cell parameters and intensity data were obtained using the relevant procedures in the 'small molecule version' of the SADONL software.[12] Approximately one hemisphere of data was scanned ($1.5 < \theta < 27.0°$), leading to a total of 14 330 data of which 9715 were unique and 4108 observed [$F_o > 3\sigma(F_o)$]. The structure was solved by the heavy atom method and refined by full-matrix least squares. An absorption correction based on the DIFABS procedure[13] was applied. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were introduced in idealised positions. Final R = 0.043, R_g = 0.047 (w = 1). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallogrpahic Data Centre. See Notice to Authors, Issue 1.

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