Model complexes for the carboxylate–histidine–metal triad systems in metalloenzymes. Synthesis, crystal structures and spectroscopic properties of $[M(Him)_2(O_2CMe)_2]$ (M = Zn^{II} or Co^{II}, Him = imidazole)

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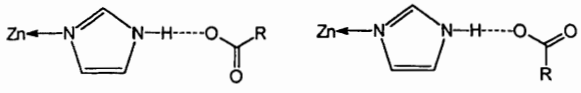
Two monomeric complexes $[M(Him)_2(O_2CMe)_2]$ (M = Zn^{II} **1** or Co^{II} **2**, Him = imidazole) have been synthesized and structurally characterised by X-ray analysis. The complexes are isostructural. In each structure the metal atom is co-ordinated by a pair of acetate groups and a pair of Him ligands in a distorted-tetrahedral N_2O_2 environment with M–O 1.965(3)–1.991(2) and 1.972(4)–2.013(4) Å, and M–N 1.996(2)–2.005(2) and 2.020(4)–2.030(5) Å for **1** and **2**, respectively. The solid-state structures of both complexes involve intermolecular N–H • • • O hydrogen bonds between the non-co-ordinated Him nitrogen atoms and the acetate oxygen atoms, with the acetate groups acting in both *syn* and *anti* modes, resulting in two types of carboxylate–imidazole–metal systems analogous to those found for metalloenzymes. The IR, Raman and ^{13}C NMR spectra of the complexes have been recorded and discussed in relation to the crystal structures.

The structure and function of metalloenzymes may be modulated by hydrogen bonding–ligand–metal interaction.[1–4] Such interactions may orient the ligands and may also enhance the electrostatic interaction between the metal ion and its ligands. Carbonic anhydrase II (CAII), a zinc enzyme, is a good example for dissecting this interaction. The structure of CAII from human blood has been determined by X-ray crystallography,[5] and shows that the zinc ion is co-ordinated by three imidazole (Him) groups of the histidine side chains and a hydroxide group to form a tetrahedral geometry. Each of the Him groups is involved in hydrogen bonding to a carboxylate oxygen of the adjacent amino acid residue. Two types of carboxylate–histidine–zinc triads have been found in CAII: the Zn–His-94–Glu-92 triad in the *syn* mode and Zn–His-119–Glu-117 in the *anti* mode (Scheme 1).[1,2] The hydrogen bonding between the carboxylate groups and the Him groups was considered to enhance the basicity of the histidine towards zinc, and this metal-binding motif was described as indirect carboxylate–zinc interaction across a bridging Him group.[6] Recently systematic studies on the relationship between the function and hydrogen bonding demonstrated that the activity was increased by the hydrogen bonding and was much decreased on removing it.[7] It is very interesting that carboxylate–histidine–zinc triad systems are frequently observed, and play important roles in the catalytic processes of more than 30 zinc enzymes.[2]

It is well known that cobalt(II) ion is frequently used to substitute for zinc ion in zinc proteins, and the cobalt(II)-substituted enzymes often show about as much catalytic activity as the native zinc enzymes.[8] This is a general characteristic since the co-ordination chemistry of cobalt(II) is very similar to that of zinc(II) and the two metal ions also show virtually identical ionic radii. The spectroscopic parameters obtained from various cobalt(II)-substituted enzymes have been treated in a phenomenological fashion and used to monitor changes occurring at the active site as a function of changes in various biochemical properties.

It is somewhat surprising that the structural information about model complexes containing the neutral imidazole ligand, which is a side chain of histidine, for the active sites in zinc enzymes or their cobalt(II)-substituted enzymes, is rather limited.[9] Our aim is to provide low-molecular-weight model complexes of zinc(II) and cobalt(II) ions containing the biologically relevant ligand imidazole for the triad interactions



Scheme 1 Carboxylate–histidine–zinc triad system with the carboxylate group in the *syn* (*a*) and *anti* (*b*) modes

to help us to understand the relation between the structure and function. As a sequel work to our preliminary report of the crystal structure of the zinc complex,[10] we now describe the synthesis, crystal structures and, IR, Raman and NMR spectroscopic properties of $[M(Him)_2(O_2CMe)_2]$, (M = Zn^{II} **1** or Co^{II} **2**). They are the first models of the carboxylate–histidine–metal triad systems in the metalloenzymes.

Experimental

Physical measurements

The C, H and N microanalyses were carried out on a Perkin-Elmer 240Q elemental analyser. Fourier-transform IR spectra were recorded (KBr pellets) with a Bruker IFS-66 spectrometer, Raman spectra of complex **1** with a Bruker RFS-100 spectrometer (excited at 1064 nm) and those of **2** with a Renishan 3000 spectrometer (excited at 623.8 nm) and ^{13}C NMR spectra on a JEOL-400 spectrometer in the solid state using adamantane as an external standard (all chemical shifts given relative to $SiMe_4$).

Syntheses

$[Zn(Him)_2(O_2CMe)_2]$ 1. To an aqueous ethanol solution (1 : 2 v/v, 15 cm^3) containing $Zn(O_2CMe)_2 \cdot 2H_2O$ (0.22 g, 1.0 mmol) was added imidazole (0.136 g, 2.0 mmol). The resulting mixture was adjusted to pH ≈6 with dilute acetic acid and then stirred at 50 °C for 20 min. The colourless crystalline product was collected after slow evaporation at room temperature for about a week. The yield was 0.27 g, 84% (Found: C, 37.2; H, 4.5; N, 17.7. Calc. for $C_{10}H_{14}N_4O_4Zn$: C, 37.5; H, 4.4; N, 17.5%).

$[Co(Him)_2(O_2CMe)_2]$ 2. Imidazole (0.136 g, 2.0 mmol) in methanol (5 cm^3) was added to a methanol solution (10 cm^3) containing $Co(O_2CMe)_2 \cdot 4H_2O$ (0.249 g, 1.0 mmol). The purple

solution was stirred at room temperature for 3 h, then filtered. The purple crystalline product was obtained by diffusion of diethyl ether into the filtrate. The yield was 0.16 g, 51% (Found: C, 38.2; H, 4.3; N, 17.8. Calc. for $C_{10}H_{14}CoN_4O_4$: C, 38.3; H, 4.5; N, 17.9%).

Crystallography

A summary of selected crystallographic data for complexes **1** and **2** is given in Table 1. Data collections were carried out on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα (λ = 0.710 69 Å) radiation at 292 K. For both complexes, determination of the crystal class, orientation matrix, and cell dimensions was performed according to established procedures; the intensity data were collected using the ω–2θ scan (5.0° min^{-1}) mode.[11] Two standard reflections were monitored after every 200 data measurements, showing only small random variations (< 1.5%). The data were processed with the NRCVAX program package.[12]

Most of the non-hydrogen atoms in complexes **1** and **2** were located by direct methods with the SHELXS 86 program package[13] and subsequent Fourier syntheses were used to derive the remainder. All were refined anisotropically. Hydrogen atoms of the ligands were generated geometrically (C–H 0.96 Å), assigned isotropic thermal parameters, allowed to ride on their parent carbon atoms and included in the final stage of full-matrix least-squares refinement using SHELX 76 (based on F) and SHELXL 93 (based on F^2) for **1** and **2**, respectively.[14] Bond lengths and angles are listed in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/136.

Results and Discussion

Crystal structures

As shown in Fig. 1, the crystal structure of complex **1** consists of discrete $[Zn(Him)_2(O_2CMe)_2]$ molecules. The Zn atom is co-ordinated by a pair of monodentate Him ligands and a pair of *syn* monodentate acetate groups, forming a distorted-tetrahedral N_2O_2 geometry, where the most distorted bond angle is O(1)–Zn–N(1) at 96.0(1)°. The two Zn–N bond distances are virtually identical [1.996(2) and 2.005(2) Å], comparable with those of $[Zn(Him)_2(ClO_4)_2]$ (1.999 Å)[16] and $[Zn(Him)_2Cl_2]$ (1.995 and 2.020 Å),[17] but significantly shorter than those of $[Zn(Him)_6Cl_2]\cdot 4H_2O$ (2.204 Å).[18,19] Thus the Zn–N (Him) bond distance in an octahedral co-ordination geometry is much longer than those in a tetrahedral co-ordination geometry. The Zn–O bond distances (1.965–1.991 Å) are consistent with those of $[Zn(H_2NCONH_2)_2(O_2CMe)_2]$ [1.970(2) and 1.995(2) Å],[20] in which the zinc ion is tetrahedrally co-ordinated with the acetate groups acting in the monodentate mode. Moreover, the Zn–O bond lengths in complex **1** are slightly longer than those of polymeric $[Zn(O_2CMe)_2]$ [1.914(11)–1.955(11) Å],[21] in which each zinc ion is in a slightly distorted tetrahedral environment with the acetate groups in bidentate bridging mode. On the other hand, these bond lengths associated with tetrahedral co-ordination are distinctly shorter than those of $[Zn(O_2CMe)_2(H_2O)_2]$ (2.18 and 2.17 Å),[22] in which the zinc ion is six-co-ordinate and the acetate groups act as bidentate chelating ligands. Noteworthy is the fact that Zn–O(3) [1.991(2) Å] is slightly longer than Zn–O(1) [1.965(3) Å] in complex **1**, which may be attributed to the hydrogen bonding between the co-ordinated acetate O(3) atom and the non-co-ordinated nitrogen atom N(4) of a Him group from an adjacent molecule [O(3b)···N(4) 2.783(5) Å]. The hydrogen bonding can also affect the electron delocalisation in the acetate group,

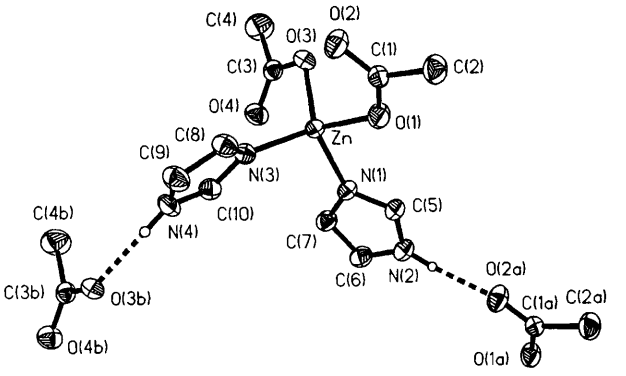


Fig. 1 An ORTEP[15] view (35% probability) of the molecular structure of complex **1** with the hydrogen bonding and atom-numbering scheme

Table 1 Crystallographic data for complexes **1** and **2***

Complex	**1**	**2**
Formula	$C_{10}H_{14}N_4O_4Zn$	$C_{10}H_{14}CoN_4O_4$
M	319.6	313.2
a/Å	7.732(2)	7.837(1)
b/Å	8.068(2)	8.083(1)
c/Å	11.338(3)	11.253(2)
α/°	92.32(2)	92.68(1)
β/°	99.77(2)	99.64(1)
γ/°	96.31(3)	95.98(1)
U/Å	691.5(5)	697.5(2)
D_c/Mg m^{-3}	1.535	1.491
μ/cm^{-1}	7.9	12.45
F(000)	328	322
Crystal size/mm	0.28 × 0.30 × 0.40	0.30 × 0.40 × 0.40
θ Range/°	1.4–25	1.3–26
Reflections collected	2154	2212
Unique data with $I > 2\sigma(I)$	2132	2024
Goodness of fit on F^2	1.062	1.158
Final $R1$ ($wR2$)	0.040 (0.052)	0.0525 (0.162)

* Details in common: triclinic, space group $P\bar{1}$; Z = 2; 172 parameters. $w = 1/\sigma^2(F) + 0.0002F^2$ and $w = 1/\sigma^2(F_o^2) + (0.0684P)^2 + 1.1184P$ where $P = (F_o^2 + 2F_c^2)/3$.

which can be reflected in its geometry. The C(3)–O(3) bond distance [1.284(4) Å] is longer than that of C(1)–O(1) [1.268(4) Å], and the bond angle O(3)–C(3)–O(4) [120.9(3)°] is smaller than that of O(1)–C(1)–O(2) [124.0(3)°].

Complex **2** is isostructural to **1**. The co-ordination sphere of the cobalt(II) ion is also a distorted tetrahedral N_2O_2, with the bond angles similar to those in **1**, as shown in Table 2. The Co–N [2.030(5) and 2.020(4) Å] and Co–O [2.013(4) and 1.972(4) Å] bond distances are only slightly longer than the corresponding Zn–N and Zn–O bonds of complex **1**. This observation is certainly consistent with the fact that cobalt(II) ions substitute for zinc(II) ions in several enzymes with retention of biological activity. The Co–N bond distances of complex **2** are comparable with those of tetrahedral $[Co(Him)_4]^{2+}$ (1.99 Å),[23] but significantly shorter than those of octahedral $[Co(Him)_6]^{2+}$ (2.17 Å).[24] These also indicate that the Co–N (Him) bond distances in a tetrahedral co-ordination geometry are significantly shorter than those in an octahedral one.

The most interesting finding in the crystal structures of complexes **1** and **2** is the carboxylate–imidazole–metal systems, which strikingly resemble the triad systems in zinc(II)- and cobalt(II)-substituted enzymes. Both of the non-co-ordinated nitrogen atoms of the Him ligands in **1** and **2** participate in donor intermolecular hydrogen bonding with carboxylate groups from adjacent molecules: N(2)···O(2a) and N(4)···O(3b) are 2.724(5) and 2.783(5) and 2.717(6) and 2.800(5) Å for complexes **1** and **2**, respectively, comparable to the average value (2.8 Å) found in zinc enzymes.[2] It is noteworthy

Table 2 Bond lengths (Å) and angles (°) for complexes **1** (M = Zn) and **2** (M = Co)

	1	2		1	2
M–O(1)	1.965(3)	1.972(4)	M–O(3)	1.991(2)	2.013(4)
M–N(1)	2.005(2)	2.020(4)	M–N(3)	1.996(2)	2.030(5)
O(1)–C(1)	1.268(4)	1.274(6)	O(2)–C(1)	1.223(4)	1.226(7)
C(1)–C(2)	1.505(5)	1.497(8)	O(4)–C(3)	1.236(4)	1.241(6)
O(3)–C(3)	1.284(4)	1.266(7)	C(3)–C(4)	1.487(5)	1.489(8)
N(1)–C(5)	1.318(4)	1.318(7)	N(1)–C(7)	1.372(4)	1.384(6)
N(2)–C(5)	1.330(4)	1.342(7)	N(2)–C(6)	1.369(5)	1.368(8)
C(6)–C(7)	1.351(4)	1.345(8)	N(3)–C(8)	1.384(4)	1.319(7)
N(3)–C(10)	1.318(4)	1.371(7)	N(4)–C(9)	1.369(5)	1.321(8)
N(4)–C(10)	1.324(4)	1.379(8)	C(8)–C(9)	1.345(5)	1.352(8)
O(1)–M–O(3)	105.1(1)	105.1(2)	O(1)–M–N(1)	96.0(1)	94.3(2)
O(3)–M–N(1)	118.2(1)	119.5(2)	O(1)–M–N(3)	113.6(1)	111.6(2)
O(3)–M–N(3)	113.1(1)	115.5(2)	N(1)–M–N(3)	109.8(1)	108.6(2)
M–O(1)–C(1)	120.9(2)	119.2(4)	O(1)–C(1)–O(2)	124.0(3)	124.4(5)
O(1)–C(1)–C(2)	115.7(3)	120.6(5)	O(2)–C(1)–C(2)	120.2(3)	114.9(5)
M–O(3)–C(3)	107.3(2)	102.1(3)	O(4)–C(3)–O(3)	120.9(3)	120.5(5)
O(4)–C(3)–C(4)	122.1(3)	121.3(5)	O(3)–C(3)–C(4)	117.0(3)	118.2(5)
M–N(1)–C(5)	122.6(2)	105.2(4)	M–N(1)–C(7)	131.2(2)	123.2(4)
C(5)–N(1)–C(7)	106.1(2)	131.5(4)	C(5)–N(2)–C(6)	107.8(3)	106.3(5)
N(1)–C(5)–N(2)	110.9(3)	112.0(5)	N(2)–C(6)–C(7)	106.1(3)	107.4(5)
N(1)–C(7)–C(6)	109.2(3)	109.0(5)	M–N(3)–C(8)	129.2(2)	105.3(5)
M–N(3)–C(10)	124.4(2)	124.7(4)	C(8)–N(3)–C(10)	105.8(2)	129.5(3)
C(9)–N(4)–C(10)	108.1(3)	108.1(5)	N(3)–C(8)–C(9)	108.9(3)	110.2(5)
N(4)–C(9)–C(8)	106.2(3)	105.0(5)	N(3)–C(10)–N(4)	110.9(3)	111.4(5)
Hydrogen bonding					
N(2) · · · O(2a)	2.724(5)	2.717(6)	N(4) · · · O(3b)	2.783(5)	2.800(5)
C(5)–N(2) · · · O(2a)	113.6(3)	114.7(4)	C(6)–N(2) · · · O(2a)	138.3(3)	138.6(3)
C(10)–N(4) · · · O(3b)	112.7(3)	122.6(4)	C(9)–N(4) · · · O(3b)	128.7(3)	128.8(4)

Symmetry codes: a $x, 1 + y, z$; b $-1 + x, y, z$.

that the two carboxylate groups behave differently in their hydrogen bonding: the acetate defined by O(1), O(2), C(1) and C(2) utilises the pendant O(2) atom in hydrogen bonding with the carboxylate group in the *syn* mode, while the other acetate group uses the co-ordinated O(3) atom and hence acts in the *anti* mode, as in Fig. 1. Thus the crystal structures of complexes **1** and **2** comprise the two types of carboxylate–imidazole–metal triad systems (Scheme 1) found in zinc enzymes,[2] which are well exemplified by CAII.[6]

The other structural details of the triad systems in complex **1** also compare favourably with those of the zinc enzymes. The oxygen atoms involved in hydrogen bonding are almost coplanar with the corresponding Him groups (deviations *ca.* 0.3 Å). Likewise, the zinc atom is virtually coplanar with both Him moieties within *ca.* 0.2 Å. Hence the structure mimics the head-on and in-plane interactions of the Him groups with zinc and carboxylate groups in the biological triad systems.[5] Since complex **2** is isostructural to **1**, the ligation and the hydrogen bonding are very similar, showing very similar triad systems.

Spectroscopic properties

The IR spectra of complexes **1** and **2** exhibit a medium-intensity and broad band at 3439 and 3420 cm^{-1}, respectively. These bands can be assigned to ν(N–H), and the broadness is indicative of hydrogen bonding, in accord with the crystal structures. Two $\nu_{asym}(CO_2)$ (1607 and 1579 and 1593 and 1574 cm^{-1}) and two $\nu_{sym}(CO_2)$ (1419 and 1394 and 1419 and 1403 cm^{-1}) bands are observed for **1** and **2**, respectively, indicating that there are two different geometries of the acetate groups in each complex. These can be attributed to the existence of the two different types (*syn* and *anti*) of hydrogen bonds connecting the Him groups in the solid state. If the hydrogen bonding is considered as weak, the acetate groups can be regarded as two types of bridges, namely tri- and mono-atomic. Bands at 1607 and 1394, and 1593 and 1403 cm^{-1} are assigned to the stretching modes of the monoatomic acetate bridges, and those at 1579 and 1419, and 1574 and 1419 cm^{-1} to the triatomic acetate bridges in complexes **1** and **2**, respectively. Owing to the more asymmetrical bonding of the monoatomic carboxylate group, a large splitting (Δ = 213 in **1**, 190 cm^{-1} in **2**) of the CO_2 stretching frequencies is observed.[25]

The Raman spectrum of complex **1** shows four peaks for the metal–ligand bond-stretching modes in the range 450–210 cm^{-1}: those at 260w and 239m cm^{-1} can be assigned to ν(Zn–N), consistent with the assignment for $[Zn(Him)_2Cl_2]$ (250w, 239m, cm^{-1});[26] those at 297w and 283m cm^{-1} can be assigned to ν(Zn–O), in accord with those of $[Zn(O_2CMe)_2]$ (316m and 282m cm^{-1}).[27] For complex **2**, four medium-intensity peaks for the metal–ligand bond-stretching modes are also observed in the range 430–210 cm^{-1}. According to the assignments for $[Co(Him)_2Cl_2]$ (274 and 232 cm^{-1}) and $[Co(Him)_4]^{2+}$ (301 cm^{-1}) by resonance-Raman spectroscopy,[28] the peaks at 280 and 237 cm^{-1} can be assigned to ν(Co–N) and those at 318 and 304 cm^{-1} to ν(Co–O).

The ^{13}C NMR spectrum of complex **1** shows that the chemical shifts of the carboxylate carbon in the two acetate groups are equivalent (δ 179.2), but those of the methyl groups are different (δ 21.35, 20.18). This may be attributed to the shielding effect of the Him ligands. The methyl C(4) atom has a closer intermolecular contact with a Him group of the adjacent molecule, and it may therefore be shielded by the Him group. The closest atom–atom distance between the C(4) atom and the Him group is *ca.* 3.6 Å, while that between the methyl C(2) atom and the adjacent Him group is *ca.* 3.8 Å. Hence the chemical shifts at δ 20.18 and 21.35 may presumably be assigned to C(4) and C(2) atoms, respectively. This assignment is also in accord with the fact that the C(3)–C(4) bond [1.478(5) Å] is shorter than C(1)–C(2) [1.505(5) Å]. The chemical shifts of the two Him groups are different. There are three pairs of signals at δ 140.83 and 138.50, 128.88 and 128.49, and 118.49 and 116.93,

corresponding to two Him groups. The chemical shifts in low field (δ 140.83 and 138.50) may be assigned to C(5) and C(10). Those of C(8) and C(9), or C(6) and C(7), are identical in solution due to tautomerisation, but distinguishable in the solid state. The signals at δ 128.88 and 128.49 may be assigned to C(7) and C(8), and the remainder to C(6) and C(9), because the distances C(8)–N(3) and C(7)–N(1) are slightly longer than those of C(9)–N(4) and C(6)–N(2).

Acknowledgements

This work was supported by a research grant from National Natural Science Foundation of China and a grant from the State Education Commission of China.

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Received 4*th March* 1996; *Paper* 6/01538G