

Transition metal complexes with pyrazole-derived ligands. XI. [Zn(μ -L)(HL)(OAc)]₂ (HL is 4-acetyl-3-amino-5-methylpyrazole)

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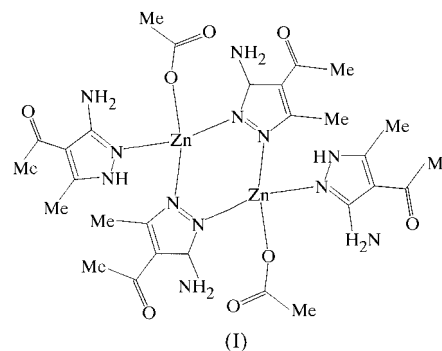
The title compound, bis(μ -4-acetyl-3-amino-5-methylpyrazolato-*N*¹:*N*²)bis[(acetato-*O*)(4-acetyl-3-amino-5-methylpyrazole-*N*²)zinc(II)], [Zn₂(C₆H₈N₃O)₂(C₂H₃O₂)₂(C₆H₉N₃O)₂], exists as a centrosymmetric binuclear molecule with two tetrahedrally coordinated Zn atoms bridged by two pyrazolate anions. The geometry of the terminal and bridging pyrazole ligands are slightly different as a consequence of their differing modes of coordination.

Comment

In previous work, we described the synthesis, physicochemical and structural characteristics of some transition metal complexes of Pt^{II} (Kukushkin *et al.*, 1992), Cu^{II}, Zn^{II} and Hg^{II} with HL (HL is 4-acetyl-3-amino-5-methylpyrazole), including the structure of the uncomplexed ligand (Hergold-Brundić *et al.*, 1991). It was observed that in the tetrahedral mononuclear complexes [MCl₂(HL)₂] (*M* = Cu^{II}, Hg^{II}) and [Zn(NO₃)₂(HL)₂], the HL ligand is coordinated as a neutral molecule through the *N*² atom, while in the square-planar binuclear complex [Pt₂Cl₂(μ -L)₂(dmsO)₂] (dmsO is dimethyl sulfoxide), the ligand exists in its bridging form coordinated *via* the *N*¹ and *N*² atoms. As an extension of this work, we report the synthesis and crystal structure of the title compound, (I).

As can be seen from the formula of the complex, the pyrazole ligand appears in two forms, as a neutral molecule and as an anion. The monoanionic form, obtained by deprotonation of *N*¹, makes formation of a dimeric molecule possible, where two Zn atoms are connected *via* the bridging pyrazolate ligand. It should be noted that the reaction of HL with Zn(NO₃)₂ in ethanol gives the complex [Zn(NO₃)₂(HL)₂], where this ligand appears in the neutral form. It is not

surprising that the reaction with Zn(OAc)₂ gives a complex with the pyrazolate anion, keeping in mind the well known proton-acceptor capability of the acetate group. It should be noted that other pyrazolate complexes are obtained in the presence of a strong base (MOH; Trofimenko, 1986). The already mentioned dimeric complex [Pt₂Cl₂(μ -L)₂(dmsO)₂] was obtained using an essentially different method, *i.e.* thermal conversion of solid [PtCl₂(HL)(dmsO)] with the abstraction of HCl.



The crystal structure of the title compound consists of discrete centrosymmetric molecules (Fig. 1) separated by normal van der Waals distances. The two Zn atoms are bridged by two pyrazolate anions and are separated by a non-bonded distance of 3.615 (1) Å, with two other coordination sites occupied by the *N*² atom from the neutral pyrazole ring and an O atom from the acetate group. The coordination geometry around zinc is a distorted tetrahedron with the angles ranging from 104.9 (1) (N2–Zn–N4) to 112.7 (1)° (O1–Zn–N2). The Zn–N bond distances involving the bridging ligand are shorter than that involving terminal pyrazole. The N–N distance in the bridging ligand of 1.394 (4) Å is slightly longer than in the terminal ligand of 1.383 (4) Å. In the free and coordinated HL ligand, this distance ranges from 1.373 (5) to 1.385 (2) Å. It is interesting to compare this result with the structures of [Zn₂(dmpz)₄(Hdmpz)₂] (Ehlert *et al.*, 1990; Hdmpz is 3,5-dimethylpyrazole) and [Ni(NO)₂(dmpz)₂] (Chong *et al.*, 1979). In the former compound, the N–N distances are 1.396 (5) and 1.375 (4) Å in the bidentate bridging and monodentate terminal ligands, respectively. In the latter compound, pyrazole appears as a bridging ligand only and the N–N distance is 1.463 (4) Å. Besides the bidentate bridging of pyrazolate ligands observed in the above-mentioned complexes, there has also been a report on a bidentate chelating pyrazolate ligand (Cosgriff & Deacon, 1998).

The geometry of both types of pyrazole rings is comparable to that found in the complexes of Cu, Zn, Hg and Pt with the same ligand. A comparison of bond lengths in the neutral and anionic ligand shows that in the latter, the difference between the bond lengths in the pyrazole ring is smaller, which is an indication of a greater degree of π -delocalization. A characteristic short bond (C5–N3) was also observed here in the monodentate pyrazole ligand, where this distance is 1.342 (4) Å. Previously reported values for this distance in the same ligand are 1.340 (5) and 1.332 (4) Å for [Zn(HL)₂]-

(NO₃)₂], 1.330 (5) Å for [Cu(HL)₂Cl₂] and 1.364 (6) Å for [Hg(HL)₂Cl₂], while in the free ligand, this distance is 1.364 (5) and 1.368 (4) Å. In the report on these results, the explanation for this was given in terms of π -delocalization and intramolecular interactions of the NH₂ group with the acetyl O atom. The C9–N6 distance is significantly longer [1.370 (5) Å], which suggests less π -delocalization, *i.e.* a lower capability of the pyrazole system for accepting additional electrons from the C–NH₂ bond. In both pyrazole ligands, the central ring and substituent non-H atoms are coplanar within experimental accuracy. The twisting of the acetyl groups is rather small, the torsion angles being 5.9 (7) and 3.0 (7)° for C5–C4–C7–O3 and C9–C10–C12–O4, respectively.

The bond distance between Zn and the carboxylate O atom is 1.933 (3) Å, which is significantly shorter than the values reported for the analogous distance (Ishioaka *et al.*, 1997; Chandler *et al.*, 1993; Yampolskaya *et al.*, 1987; Jaćimović *et al.*, 1999) which range from 1.954 (6) to 2.189 (5) Å. The geometry of the carboxylate ligand is in agreement with reported values (Porai-Koshits, 1980). The structure is stabilized by hydrogen bonds between the amino H atoms and O atoms of the carboxylate and acetyl groups whose geometries are given in Table 2.

In the IR spectrum of the uncomplexed HL ligand, three strong bands appeared in the region of the NH vibrations at 3442, 3274 and 3182 cm⁻¹. In the corresponding region of the spectrum of the complex, the first band is split at 3451 and 3420 cm⁻¹, while the other two are slightly shifted to 3299 and 3166 cm⁻¹. The characteristic strong band of C–O(acetyl) stretching modes, observed at 1608 cm⁻¹ in the uncomplexed ligands, is shifted to 1646 cm⁻¹ in the complex. This is consistent with the somewhat shorter C–O(acetyl) bonds in the complex [1.230 (5) and 1.225 (5) Å] compared with the same distances in the uncomplexed ligand [1.237 (3) and 1.242 (4) Å]. Two strong bands in the spectrum of the complex at 1608 and 1449 cm⁻¹ can be assigned to the asymmetric and symmetric vibrations of the COO⁻ group. The difference ($\Delta = 159$ cm⁻¹) is consistent with the presence of hydrogen bonds

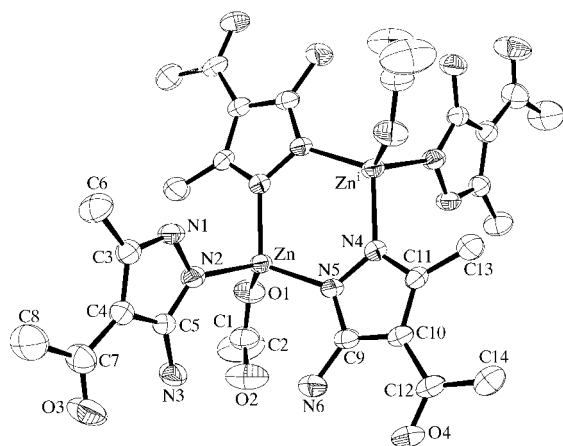


Figure 1
The molecular geometry and atom-labeling scheme (50% probability level) for [Zn(μ -L)(HL)(OAc)]₂.

between the non-coordinated carboxylate O and amino H atoms, and is of the same order of magnitude as those reported for the 'pseudo-bridging' arrangement (Deacon & Phillips, 1980), where the acetate O atom that is not coordinated to the metal forms a hydrogen bond with the other ligand, as is the case in (I). According to the literature (Nakamoto, 1997), the monodentate acetate group exhibits three bands in the range 720–950 cm⁻¹ due to the COO deformation modes that correspond to three bands at 749, 804 and 830 cm⁻¹ in the spectrum of (I). In the region of the C–N stretching vibrations, the IR spectrum of the uncomplexed ligand HL contains a band at 1338 cm⁻¹ whose frequency in the spectrum of (I) is shifted to 1299 cm⁻¹. This change is consistent with the weaker C–N(amino) bond in the bridging pyrazolate ligand. The absorption band in the spectrum of the uncomplexed HL ligand at 1478 cm⁻¹, assignable to ring stretching modes, is split into the 1476 and 1488 cm⁻¹ bands in the spectrum of (I). The 951 cm⁻¹ band in the spectrum of HL, due to ring bending in-plane vibrations, is split into the 960 and 934 cm⁻¹ bands. The observation that bands produced by the ring vibrations are split is consistent with two modes of pyrazole coordination.

Experimental

The reaction of a warm MeO–DMF solution of Zn(OAc)₂·2H₂O and HL in a stoichiometric ratio of 1:2 resulted in the formation of the title complex. All chemicals used were of analytical reagent grade (commercially available), except for the ligand HL, which was prepared according to the previously described procedure of Hergold-Brundić *et al.* (1991). A mixture of HL (0.14 g, 1.0 mmol) and Zn(OAc)₂·2H₂O (0.11 g, 0.5 mmol) was dissolved in a mixture of MeOH (2 ml) and DMF (1 ml). The resulting solution was allowed to evaporate slowly and white crystals had appeared after two days. These crystals were filtered off, washed with methanol and dried. Analysis found (calculated) for C₂₈H₄₀N₁₂O₈Zn₂: C 42.23 (41.85), H 4.91 (5.03), N 20.46% (20.92%).

Crystal data

[Zn ₂ (C ₆ H ₈ N ₃ O) ₂ (C ₂ H ₃ O ₂) ₂ · (C ₆ H ₉ N ₃ O) ₂]	Z = 1
<i>M_r</i> = 803.46	<i>D_x</i> = 1.523 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 9.192 (2) Å	Cell parameters from 25 reflections
<i>b</i> = 10.726 (4) Å	θ = 11.7–15.4°
<i>c</i> = 10.904 (2) Å	μ = 1.434 mm ⁻¹
α = 61.30 (3)°	<i>T</i> = 293 (2) K
β = 70.01 (2)°	Prismatic, colourless
γ = 87.69 (3)°	0.36 × 0.29 × 0.22 mm
<i>V</i> = 876.1 (4) Å ³	

Table 1
Selected geometric parameters (Å).

Zn–N5	1.985 (3)	N5–C9	1.333 (4)
Zn–N4 ⁱ	2.002 (3)	C5–C4	1.423 (5)
Zn–N2	2.036 (3)	C4–C3	1.402 (5)
N2–C5	1.330 (4)	C9–C10	1.399 (5)
N1–C3	1.315 (5)	C11–C10	1.400 (5)
N4–C11	1.331 (5)		

Symmetry code: (i) $-x, 1 - y, 1 - z$.

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
 3345 measured reflections
 2991 independent reflections
 2316 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$

$\theta_{\text{max}} = 24.97^\circ$
 $h = -10 \rightarrow 10$
 $k = -2 \rightarrow 12$
 $l = -11 \rightarrow 12$
 3 standard reflections
 frequency: 60 min
 intensity decay: 4.1%

Refinement

Refinement on F^2
 $R(F) = 0.042$
 $wR(F^2) = 0.098$
 $S = 1.017$
 2991 reflections
 226 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0628P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.61 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.61 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1–H1N1 \cdots O4 ⁱ	0.95	1.89	2.757 (4)	151
N3–H1N3 \cdots O2	0.94	1.96	2.895 (6)	173
N3–H2N3 \cdots O3	0.92	2.18	2.773 (6)	122
N6–H1N6 \cdots O2	0.86	2.26	2.992 (5)	143
N6–H2N6 \cdots O4	0.86	2.21	2.774 (6)	124

Symmetry code: (i) $x - 1, y, z$.

H atoms bonded to pyrazole and amino N atoms of the neutral pyrazole ligand were found in a ΔF map, while those bonded to the amino N atom of the anionic pyrazolyl ligand, as well as methyl H atoms, were placed at calculated positions. All H atoms were refined riding on their parent atoms with isotropic displacement parameters fixed at 1.2 or 1.5 (for methyl H atoms) times the U_{eq} of the parent atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1988); data reduction: *XCAD4* (Harms, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* and *PLATON99* (Spek, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1444). Services for accessing these data are described at the back of the journal.

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