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Transition metal complexes with pyrazole-derived ligands. X. $[Zn(CH_3COO)_2L_2]\cdot 2MeOH$ (L = 3-amino-5-phenylpyrazole)

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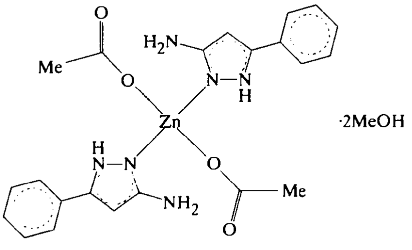
Abstract

Monocrystals of the title complex, bis(acetato-O)bis(3-amino-5-phenylpyrazole-N^2)zinc(II) dimethanol solvate, $[Zn(C_2H_3O_2)_2(C_9H_9N_3)_2]\cdot 2CH_4O$, were obtained by crystallization from a methanolic solution of $Zn(OAc)_2\cdot 2H_2O$ and 3-amino-5-phenylpyrazole (L) (1:2 molar ratio). The two pyridine-N atoms from the pyrazole derivative and two O atoms from the acetate groups are coordinated to the Zn atom in a distorted tetrahedral arrangement. The phenyl and aminopyrazole rings in both ligand molecules are planar within experimental accuracy. As a consequence of the arrangement of the molecules in the unit cell, the dihedral angles between the phenyl and aminopyrazole ring planes in the two ligand molecules are 5.6 (2) and 27.4 (2)°.

Comment

Pyrazole derivatives and their metal complexes have recently attracted the attention of numerous researchers, which is evident from the publication of a large number of research papers and several reviews (Trofimenko, 1972, 1986, 1993; Cosgriff & Deacon, 1998). This class of ligand is characterized by a diversity of coordination modes whereby, in addition to the usual monodentate N-coordination, there are examples of *exo*- and less often *endo*-bidentate N,N-coordination of the pyrazole ring (Cosgriff & Deacon, 1998; Trofimenko, 1993). As a continuation of our research on the structures of metal complexes with this class of ligand (Herold-Brundić *et al.*, 1991; Kukushkin *et al.*, 1992; Jaćimović, Prelesnik *et al.*, 1998), the present work is concerned with the crystal and molecular structure of the newly synthesized complex of $Zn(OAc)_2$ with 3-amino-5-phenylpyrazole (L) of formula $[Zn(OAc)_2L_2]\cdot 2MeOH$, (I).



(I)

The zinc ion is coordinated with two O atoms from the carboxylate groups and two pyridine-N atoms from 3-amino-5-phenylpyrazole ligands in a distorted tetrahedral arrangement. Deviations from tetrahedral symmetry include widening of the N1A—Zn—N1B and O1A—Zn—N1B angles to 115.9 (1) and 114.5 (1)°, respectively, and narrowing of the O1B—Zn—N1B and O1A—Zn—O1B angles to 101.8 (1) and 102.9 (1)°, respectively. The bond distances between Zn and the pyrazole N atoms of 2.010 (3) and 1.995 (3) Å for Zn—N1A and Zn—N1B, respectively, are comparable with the values reported for $[Zn(NO_3)_2(L')_2]$ (L' = 3-amino-4-acetyl-5-methylpyrazole; Herold-Brundić *et al.*, 1991), $[ZnCl_2(L'')_2]$ (L'' = 3,5-dimethylpyrazole; Bouwman *et al.*, 1984) and $[Zn_2(L''')_4(HL''')_2]$ (L''' = 3,5-dimethylpyrazolate; Ehlert *et al.*, 1990), ranging from 1.991 (3) to 2.025 (3) Å. The Zn—O bond lengths are 1.960 (2) and 1.975 (2) Å for the A and B O atoms, respectively. These distances are within the range reported previously. In $Zn(CH_3COO)_2$ (Clegg *et al.*, 1986), where the acetate ligand acts as a bridge between Zn atoms, the average Zn—O distance is 1.957 (2) Å. In $[Zn_2(CH_3COO)_3(OCH_3)]$ (Chandler *et al.*, 1993), where the acetate group also acts as a bridge, this distance ranges from 1.948 (3) to 1.974 (7) Å. There are no significant differences between the bond lengths and angles involving the ring atoms of ligands A and B. All the values are comparable to those reported previously for pyrazole and phenyl rings (Herold-Brundić *et al.*, 1991; Kukushkin *et al.*, 1992; Jaćimović, Tomić *et al.*, 1998; Francisko *et al.*, 1980; Zukerman-Schpector *et al.*, 1990). The pyrazole and phenyl rings in the A and B ligands are planar within experimental accuracy. Maximum deviations from the least-squares planes are 0.003 (3) and 0.002 (4) Å for atoms C3A and C6A,

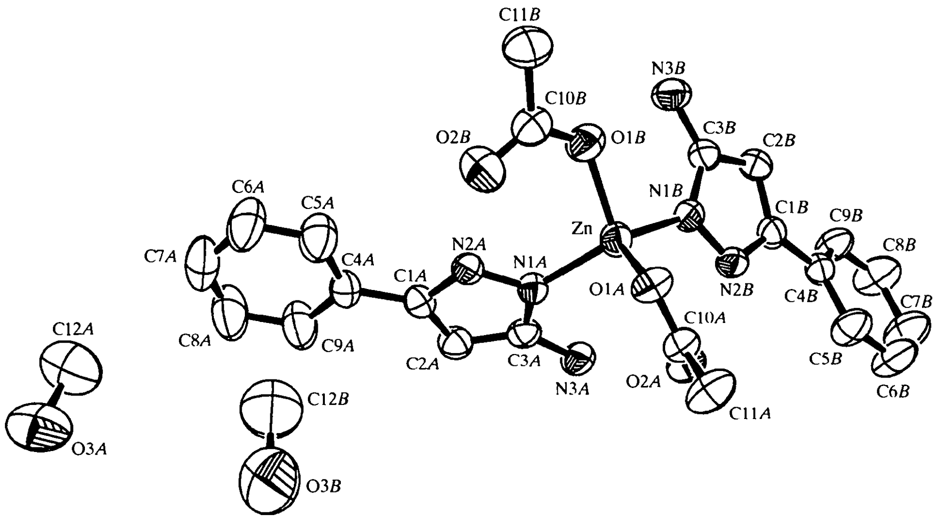


Fig. 1. The molecular geometry and atom-labelling scheme for (I). Displacement ellipsoids are plotted at the 50% probability level.

respectively, and 0.011 (6) and 0.009 (5) Å for atoms C2*B* and C8*B*, respectively. The amino nitrogen N3 deviates from the mean plane of the pyrazole ring by 0.092 (3) and 0.011 (3) Å in ligands *A* and *B*, respectively. The bond length C3—N3 is 1.372 (4) Å in ligand *A* and 1.361 (4) Å in ligand *B*. Slight variations in the geometry of the amino nitrogen to pyrazole-ring bond lengths are in agreement with the different interactions between the O atoms and the amino group. In ligand *A*, the amino group forms a hydrogen bond with the O atom from a solvent methanol molecule, whereas in ligand *B*, such a bond is formed with the coordinated acetate O atom. The geometry of these interactions is given in Table 2.

The dihedral angles between the pyrazole and phenyl planes are 5.6 (2) and 27.4 (2)° in ligands *A* and *B*, respectively. This difference can be ascribed to steric forces between the *A* and *B* phenyl rings of neighbouring molecules (due to translation along the *c* axis, where $x' = x$, $y' = y$ and $z' = z - 1$) causing rotation of the phenyl planes. Thus, the dihedral angle between the mean planes of the two phenyl rings in neighbouring molecules along the *c* axis is 88.2 (2)°. The distances shorter than 4 Å between non-H atoms in neighbouring rings range from 3.814 (7) to 3.992 (8) Å for C8*A*···C9*B* and C8*A*···C5*B*, respectively.

The bond lengths between the C10 and O1 atoms (coordinated to Zn) of 1.285 (4) and 1.264 (4) Å in the *A* and *B* acetate groups, respectively, are longer than those found for the monodentate acetate ligand, *i.e.* 1.249 (3) Å (Jaćimović, Tomić *et al.*, 1998) and 1.25 (1) Å (Yampolskaya *et al.*, 1987). For bidentate acetate ligands, these distances are 1.256 (7) and 1.260 (7) Å (Ishioka *et al.*, 1997), and 1.290 (7), 1.24 (1) and 1.244 (8) Å (Chandler *et al.*, 1993). The distances between C10 and O2 of 1.243 (4) Å in ligand *A* and 1.235 (5) Å in ligand *B* are within the range reported for the acetate ligand (Porai-Koshits, 1980). The O1*A*—C10*A*—O2*A* angle of 122.1 (3)° is comparable to the previously reported values (Porai-Koshits, 1980). This angle is smaller than the angle O1*B*—C10*B*—O2*B* of 124.1 (3)°, which is close to the value of 125.0 (1)° found for the bridging acetate ligand in $[Zn_2(CH_3COO)_3(OCH_3)]$ (Chandler *et al.*, 1993). It is interesting to note this difference in view of the presence of the hydrogen bond (Table 2) between the O2*B* and amino H atom, so that the coordination mode of acetate group *B* can be described as 'pseudo-bridging' (Deacon & Phillips, 1980).

The crystal structure consisting of the complex and solvent molecules connected by hydrogen-bond and van der Waals interactions can be described as two separate rows of complex molecules aligned along the *c* axis, with the solvent methanol molecules between the rows.

Experimental

Monocrystals of the title complex suitable for X-ray analysis were obtained by the reaction of stoichiometric amounts of $Zn(OAc)_2\cdot 2H_2O$ and 3-amino-5-phenylpyrazole (Aldrich). Found: C 52.4, H 4.7, N 16.8%; calculated for $C_{22}H_{24}N_6O_4Zn$ (desolvated complex): C 52.6, H 4.8, N 16.7%. As the solvent evaporated easily at room temperature resulting in the loss of monocrystallinity, the X-ray measurement was carried out on the monocrystal immersed in MeOH in a Lindemann capillary.

Crystal data

$[Zn(C_2H_3O_2)_2(C_9H_9N_3)_2]\cdot 2CH_4O$
$M_r = 565.93$
Triclinic
$P\bar{1}$

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.53$–$16.34°$

$a = 9.377$ (2) Å
$b = 9.940$ (1) Å
$c = 15.344$ (2) Å
$\alpha = 93.06$ (2)°
$\beta = 98.17$ (3)°
$\gamma = 98.23$ (2)°
$V = 1397.2$ (4) Å^3
$Z = 2$
$D_x = 1.345$ Mg m^{-3}
D_m not measured

$\mu = 0.926$ mm^{-1}
$T = 293$ (2) K
Prismatic
0.31 × 0.29 × 0.26 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
7641 measured reflections
6690 independent reflections
4440 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.033$
$\theta_{\rm max} = 29.94°$
$h = -11 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = 0 \rightarrow 21$
2 standard reflections
frequency: 60 min
intensity decay: 30.9%

Refinement

Refinement on F^2
$R(F) = 0.051$
$wR(F^2) = 0.146$
$S = 1.131$
6690 reflections
335 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0935P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$

$\Delta\rho_{\rm max} = 0.529$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.282$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0073 (17)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn—O1*A*	1.960 (2)	N1*A*—N2*A*	1.364 (3)
Zn—O1*B*	1.975 (2)	N1*B*—N2*B*	1.368 (4)
Zn—N1*A*	2.010 (3)	N2*A*—C1*A*	1.341 (4)
Zn—N1*B*	1.995 (3)	N2*B*—C1*B*	1.348 (4)
O1*A*—C10*A*	1.285 (4)	N3*A*—C3*A*	1.372 (4)
O1*B*—C10*B*	1.264 (4)	N3*B*—C3*B*	1.361 (4)
O2*A*—C10*A*	1.243 (4)	C1*A*—C2*A*	1.377 (5)
O2*B*—C10*B*	1.235 (5)	C1*B*—C2*B*	1.368 (4)
N1*A*—C3*A*	1.336 (4)	C2*A*—C3*A*	1.396 (5)
N1*B*—C3*B*	1.347 (4)	C2*B*—C3*B*	1.390 (5)
O1*A*—Zn—O1*B*	102.99 (11)	N2*A*—C1*A*—C2*A*	106.8 (3)
O1*A*—Zn—N1*B*	114.55 (11)	N2*B*—C1*B*—C2*B*	107.0 (3)
O1*B*—Zn—N1*B*	101.84 (11)	C1*A*—C2*A*—C3*A*	106.3 (3)
O1*A*—Zn—N1*A*	112.08 (11)	C1*B*—C2*B*—C3*B*	106.5 (3)
O1*B*—Zn—N1*A*	107.81 (11)	N1*A*—C3*A*—N3*A*	121.6 (3)
N1*A*—Zn—N1*B*	115.90 (12)	N1*B*—C3*B*—N3*B*	121.8 (3)
C1*A*—N2*A*—N1*A*	111.3 (3)	N1*A*—C3*A*—C2*A*	109.6 (3)
C1*B*—N2*B*—N1*B*	111.2 (3)	N1*B*—C3*B*—C2*B*	110.1 (3)
C3*A*—N1*A*—N2*A*	106.0 (3)	N3*A*—C3*A*—C2*A*	128.6 (3)
C3*B*—N1*B*—N2*B*	105.2 (3)	N3*B*—C3*B*—C2*B*	128.1 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2*A*—H3*A*···O2*B*	0.96	1.76	2.698 (4)	167
N3*A*—H2*A*···O3*A*$^{\rm i}$	0.98	1.97	2.915 (5)	161
N3*B*—H1*B*···O1*B*	0.87	2.13	2.917 (4)	151

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

H atoms bonded to C and O atoms from methanol molecules could not be found or added because these molecules were slightly disordered.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *XCAD*4 (Harms, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*93 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1325). Services for accessing these data are described at the back of the journal.

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