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Structure of Dichlorobis(3,5-dimethylpyrazole-*N*²)zinc(II), [ZnCl₂(C₅H₈N₂)₂]

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Abstract. $M_r = 328.55$, monoclinic, $C2/c$, $a = 15.013$ (3), $b = 8.300$ (2), $c = 23.988$ (7) Å, $\beta = 95.85$ (2)°, $V = 2973.6$ Å³, $Z = 8$, $D_x = 1.468$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 20.27$ cm⁻¹, $F(000) = 1347.83$, $T = 295$ K, final $R = 0.033$ for 2430 significant reflexions. The Zn^{II} ion is coordinated to the Cl⁻ ions and the organic ligands in an irregular tetrahedral arrangement. The dimethylpyrazole molecules are planar. The least-squares planes of these molecules intersect at an angle of 84.9 (1)°. Hydrogen bonding between the N–H group of the pyrazole ring and the Cl⁻ ions is relatively weak.

Introduction. 3,5-Dimethylpyrazole (abbreviated dmpz) forms a variety of complexes with transitional-metal ions. Metal-to-ligand bond formation occurs through the pyridine-type N atom. The chemical aspects of Zn(dmpz)₂Cl₂ and related compounds have been discussed earlier (Guichelaar, van Hest & Reedijk, 1976). Although several X-ray structure analyses of pyrazole and pyrazole derivatives have been described, as for instance [Ni(pyrazole)₆](BF₄)₂ (ten Hoedt, Driessen & Verschoor, 1983) and [Co₂F₂(3,5-dimethylpyrazole)₆](BF₄)₂ (Jansen & van Koningsveld, 1976), structures of compounds with formula $M(3,5\text{-dimethylpyrazole})_2X_2$ have not yet been reported. We have undertaken the X-ray structural analysis of Zn(dmpz)₂Cl₂, because of the stereochemical implications of the substituents at ring positions 3 and 5 and the influence of hydrogen-bond formation (N–H to anion) on the stoichiometry and structural details of this type of compound.

Experimental. Colourless prisms grown from ethanol at room temperature. Crystal approximately 0.6 × 0.3 × 0.25 mm. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$. Cell constants from setting angles of 24 reflexions. Corrections for Lorentz and polarization effects and absorption (transmission coefficients 0.87 to 1.11). $\theta_{\text{max}} = 27.5^\circ$; $h - 18$ to 18, $k 0$ to 10, $l 0$ to 30. Standard reflexions 242, 531 and $\bar{1}39$, intensity variation 4.1%. 7264 measured reflexions, 3634 independent, $R_{\text{int}} = 0.017$, 1186 unobserved with $I < 2\sigma(I)$. F used in LS refinement. Two out of three of the methyl H atoms placed 0.95 Å from the parent atoms, the others found in difference Fourier maps. Least-squares refinement of positional (H and non-H) and anisotropic (non-H) thermal parameters; positional parameters of hydrogen atoms coupled to parent atoms; fixed isotropic thermal factor of 4.0 Å² for the H atoms. Direct methods. $S = 4.789$, $w = 1/\sigma^2(F)$, $R_w = 0.039$. $A_{\text{max}}/\sigma < 0.15$. Max., min. $\Delta\rho$ excursions in final difference synthesis 0.34, -0.35 e Å⁻³. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Leiden University computer (Amdahl V7B); programs written or modified by Mrs E. W. Rutten-Keulemans and R. A. G. de Graaff.

Discussion. Positional parameters and isotropic thermal parameters for the non-hydrogen atoms are listed in Table 1.† Relevant bond distances and angles

† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39516 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional coordinates (Zn, Cl $\times 10^5$, others $\times 10^4$) and equivalent isotropic thermal parameters (Zn $\times 10^3$, others $\times 10^2$ Å²) of the nonhydrogen atoms in Zn(dmpz)₂Cl₂

E.s.d.'s in the least significant digits are given in parentheses.
 $B_{eq} = \frac{3}{2}\pi^2 \text{trace } \bar{U}$.

	x	y	z	B _{eq}
Zn	11576 (2)	27963 (5)	87884 (1)	3682 (9)
Cl(1)	-120 (5)	38594 (12)	82708 (3)	581 (3)
Cl(2)	17456 (7)	40985 (11)	95459 (4)	590 (3)
N(11)	1782 (2)	2463 (3)	7649 (1)	416 (8)
N(12)	2016 (2)	2369 (3)	8211 (1)	381 (7)
C(13)	2848 (2)	1807 (4)	8267 (1)	396 (9)
C(14)	3138 (2)	1564 (4)	7740 (1)	466 (10)
C(15)	2441 (2)	1998 (4)	7358 (1)	458 (9)
C(16)	3318 (2)	1519 (5)	8828 (1)	621 (12)
C(17)	2337 (3)	1969 (5)	6734 (1)	672 (13)
N(21)	1191 (2)	226 (3)	9640 (1)	455 (8)
N(22)	935 (2)	588 (3)	9096 (1)	407 (7)
C(23)	600 (2)	-771 (4)	8873 (1)	445 (9)
C(24)	652 (2)	-1976 (4)	9269 (1)	520 (11)
C(25)	1029 (2)	-1316 (5)	9756 (1)	473 (10)
C(26)	249 (3)	-841 (5)	8265 (1)	677 (13)
C(27)	1254 (3)	-1974 (5)	10329 (1)	664 (13)

Table 2. Bond distances (Å) and bond angles (°) for Zn(dmpz)₂Cl₂

Zn-Cl(1)	2.224 (1)	Zn-Cl(2)	2.216 (1)
Zn-N(12)	2.019 (2)	Zn-N(22)	2.017 (3)
N(11)-N(12)	1.361 (3)	N(21)-N(22)	1.354 (3)
N(12)-C(13)	1.326 (3)	N(22)-C(23)	1.325 (4)
C(13)-C(14)	1.393 (4)	C(23)-C(24)	1.376 (5)
C(14)-C(15)	1.366 (4)	C(24)-C(25)	1.360 (4)
C(15)-N(11)	1.325 (4)	C(25)-N(21)	1.338 (4)
C(13)-C(16)	1.473 (4)	C(23)-C(26)	1.499 (4)
C(15)-C(17)	1.491 (4)	C(25)-C(27)	1.485 (4)
Cl(1)-Zn-Cl(2)	119.2 (1)	N(12)-Zn-N(22)	103.5 (1)
Cl(1)-Zn-N(12)	102.2 (1)	Cl(2)-Zn-N(22)	102.1 (1)
Cl(1)-Zn-N(22)	114.4 (1)	Cl(2)-Zn-N(12)	114.8 (1)
N(12)-N(11)-C(15)	112.0 (2)	N(22)-N(21)-C(25)	112.0 (3)
Zn-N(12)-N(11)	123.5 (2)	Zn-N(22)-N(21)	120.9 (2)
Zn-N(12)-C(13)	131.0 (2)	Zn-N(22)-C(23)	134.2 (2)
N(11)-N(12)-C(13)	105.2 (2)	N(21)-N(22)-C(23)	104.9 (3)
N(12)-C(13)-C(14)	110.0 (3)	N(22)-C(23)-C(24)	110.4 (3)
N(12)-C(13)-C(16)	120.3 (3)	N(22)-C(23)-C(26)	120.4 (3)
C(14)-C(13)-C(16)	129.8 (3)	C(24)-C(23)-C(26)	129.2 (3)
C(13)-C(14)-C(15)	106.2 (3)	C(23)-C(24)-C(25)	106.8 (3)
N(11)-C(15)-C(14)	106.6 (3)	N(21)-C(25)-C(24)	105.9 (3)
C(14)-C(15)-C(17)	131.5 (3)	C(24)-C(25)-C(27)	132.9 (4)
N(11)-C(15)-C(17)	121.9 (3)	N(21)-C(25)-C(27)	121.1 (3)

are given in Table 2. An ORTEP projection (Johnson, 1965) of the molecular entity Zn(dmpz)₂Cl₂ and the atomic labelling are given in Fig. 1. The Zn^{II} ion is surrounded by two Cl⁻ ions and two N atoms in a distorted tetrahedral geometry. The largest angular deviation from tetrahedral is 119.2 (1)° for Cl-Zn-Cl. This deviation is apparently caused by intermolecular hydrogen bonding between Cl(1') (at the equivalent position -x, y, 1.5-z) and H(111) and intramolecular hydrogen bonding between Cl(2) and H(211) (N-H ca 0.85 Å, Cl...H ca 2.74 Å). The Cl(1')...N(11) and Cl(2)...N(21) distances are 3.470 (3) and 3.333 (3) Å

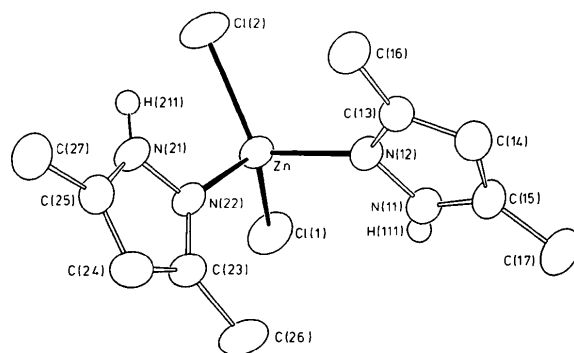


Fig. 1. ORTEP projection (Johnson, 1965) and atomic labelling of Zn(dmpz)₂Cl₂.

respectively. The shifts of the N-H stretching vibration to lower frequencies and the N-H bending vibration to higher frequencies of dimethylpyrazole in its transitional-metal chlorides, compared with a 3,5-dimethylpyrazole solution in CCl₄ ($\nu_{N-H} = 3484$ cm⁻¹; Zecchina, Cerruti, Coluccia & Borello, 1967) are due to relatively weak hydrogen bonding to the anions. In solid Zn(dmpz)₂Cl₂ the N-H stretching vibrations are observed at 3340 and 3315 cm⁻¹. The lowering of the N-H stretching frequency and the actual N-H...Cl distances fit fairly well the relationship developed by Bellamy & Owen (1969). The slight variation of bond lengths in the pyrazole ring systems shows the same sequence in both cases (see Table 2). The dimethylpyrazole ligands are planar to within ± 0.03 Å. The corresponding hydrogen-bonded Cl⁻ ion lies within 0.1 Å of the least-squares plane of each dimethylpyrazole ring. X-ray powder diagrams have shown (Guichelaar *et al.*, 1976) that Co(dmpz)₂Cl₂ is isomorphous with the title compound.

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