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Synthesis and X-ray crystal structure of the first dinuclear 1,1,2-tris(pyrazol-1-yl)ethene–zinc chloride complex

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ABSTRACT

Complexes of 1,1,2-tris(pyrazol-1-yl)ethene (Pz_3) with zinc(II), cadmium and mercury(II) ions were prepared and characterized by IR spectroscopy. Cadmium and mercury(II) complexes are insoluble solids of polymeric structure, while zinc complex is a discrete dinuclear complex $(Pz_3)_2Zn_2Cl_4$, the structure of which was determined by X-ray crystallography. Zinc complex contains five- and four-coordinated PzN_4Cl and $PzNCl_3$ zinc centers. Two Pz_3 ligands in the complex are unequivalent, one of them is coordinated by two zinc centers in a bridging mode, while the other is a terminal ligand linked to only one of zinc ions.

1. Introduction

Poly(pyrazol-1-yl)alkanes are widely used as ligands in the complexes of transition metals and some main-group elements [1,2]. Zinc complexes of some bis(pyrazole) ligands have been proposed as models for zinc-containing enzymes [3], cadmium and mercury complexes also have been reported [4,5]. Recently, we have prepared several new pyrazole derivatives, including bis- and tris(pyrazol-yl)ethylenes (Pz_2, Pz_3, Scheme 1) [6]. These compounds constitute a new class of pyrazole-containing polydentate ligands and thus it is of great interest to study their coordination chemistry. In this contribution we report the synthesis of the first 1,1,2-tris(pyrazol-1-yl)ethene (Pz_3) complexes with group 12 metals, as well as an X-ray crystal structure of $ZnCl_2$–Pz_3 complex.

2. Experimental

2.1. Materials and instruments

Elemental analyses were carried out on a Carlo Erba analyzer. Infrared (IR)-spectra of solid samples as KBr pellets were recorded on a Nicolet 5700 (4000–400 cm^{-1}) spectrophotometer. NMR spectra were recorded on Bruker AV300 instrument operating at 300 MHz for ^1H and 75 MHz for ^{13}C.

Commercially available $CdCl_2{\cdot}2.5H_2O$, $Hg(NO_3)_2{\cdot}H_2O$ and anhydrous $ZnCl_2$ were used as received. 1,1,2-Tris(pyrazol-1-yl)ethene (Pz_3) was prepared following a previously reported procedure [6].

2.2. X-ray crystallography

Single crystal of complex **1** for crystal structure determination were mounted in inert oil and transferred to the cold gas stream of the diffractometer. The structure was determined at 153 K by conventional single crystal X-ray diffraction techniques using an automated four-circle Bruker-Nonius X8 Apex diffractometer equipped with a 2-D CCD detector and graphite monochromated molybdenum source ($\lambda = 0.71073$ Å). Intensity data were collected by φ-scanning of narrow frames (0.5°) to $2\theta = 54.96°$. Absorption correction was applied empirically by the program SADABS [7]. The structure was solved by the direct method and refined using the full-matrix least-squares technique in the anisotropic approximation for nonhydrogen atoms with the program package SHELX-97 [8]. Hydrogen atoms were localized geometrically.

Crystallographic data for complex **1**: empirical formula $C_{22}H_{20}Cl_4N_{12}Zn_2$; formula weight 725.04; $Z = 2$; triclinic crystal system, $P\bar{1}$ space group, $a = 8.4969(10)$ Å, $b = 11.4691(13)$ Å, $c = 15.2022(17)$ Å, $\alpha = 98.234(2)°$, $\beta = 101.441(2)°$, $\gamma = 99.679(2)°$; $V = 1407.3(3)$ Å^3; $D_{calc} = 1.711$ mg m^{-3} crystal size 0.18 × 0.14 × 0.14 mm; $\mu = 2.12$ mm^{-1}, Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 100$ K, θ range = 2.5–31.5°; 15 593 measured reflections; 6745 independent

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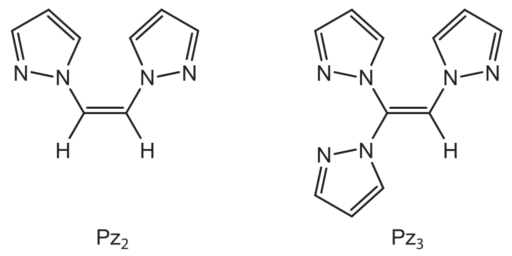

Scheme 1.

reflections; 5899 reflections with $I > 2\sigma(I)$; $R_{int} = 0.024$; 361 parameters; 0 restraints; $R[F^2 > 2\sigma(F^2)] = 0.027$; $wR(F^2) = 0.070$; $\Delta\rho_{max} = 0.74$ e Å^{-3}; $\Delta\rho_{min} = -0.50$ e Å^{-3}.

2.3. Computational chemistry details

Shielding constants were calculated using GIAO methodology [9] at DFT B3LYP [10–12] level of theory and 6-31++G(d,p) basis set [13,14]. Conformational search was performed for Pz$_3$ ligand taking into account rotations around all of C(alkene)–N(pyrazole) bonds. Semi-empirical PM3 method was employed for preliminary scans of the conformational space and DFT B3LYP 6-31G(d) [15] geometry optimizations were performed for all found minima. Frequency calculations were run for all found conformers in order to establish the nature of the stationary points. Lack of imaginary vibration modes for all of the optimized structures indicate that the stationary points found corresponded to minima on the potential energy surface. Minimal energy conformation was used as a starting point for further more accurate geometry optimization at RI DFT BP86 [16] level of theory and TZVPP [17] basis set (TZV/J auxiliary basis set [18,19]). Structure thus obtained was used for shielding constant calculations.

Geometry optimizations at PM3 and B3LYP levels of theory as well as shielding constant calculations were carried out using GAUSSIAN 09W package [20], while RI BP86 calculations were performed using the ORCA 2.8.0.2 package [21].

2.4. Synthesis of the complexes

*Trichloro-μ-(1,1,2-tris(pyrazol-1-yl)ethene)zinc-chloro-1,1,2-tris-(pyrazol-1-yl)ethene-zinc (**1**).* To a solution of 60 mg (0.265 mmol) of Pz$_3$ ligand in 2 ml of diethyl ether 54 mg (0.397 mmol) of $ZnCl_2$ in 3 ml of the same solvent were added. White gummy precipitate was filtered and immediately recrystallized from ethanol. Yield 36 mg (37%), colorless prisms, m.p. 150 °C (dec.). *Anal.* Calc. for $C_{11}H_{10}Cl_2N_6Zn$: C, 36.44; H, 2.78; N, 23.18. Found: C, 36.52; H, 2.78; N, 23.51%. IR bands, $\tilde{\nu}$, cm^{-1}: 1699 ($\nu_{C=C}$), 1521, 1457, 1441, 1426, 1407 (ν_{Pz}), 1392 (β_{CH}), 953 (Pz ring breathing), 604 (β_{Pz}). NMR ^{1}H (CD_3OD), δ, ppm: 6.36 t (H^4, Pz^{II}, J 2 Hz), 6.53 br (H^4, Pz^{III}), 6.66 br (H^4, Pz^{II}), 6.73 d (H^5, Pz^I, J 2 Hz), 7.52 br (H^3, Pz^I), 7.66 (H^5, Pz^I; H^5, Pz^{II}), 7.77 (H^3, Pz^{III}), 7.89 (C=CH), 7.93 (H^3, Pz^{II}). NMR ^{13}C (CD_3OD), δ, ppm: 109.2 (C^4, Pz^{II}), 109.6 (C^4, Pz^{III}), 110.1 (C^4, Pz^I), 118.8 (Pz$\underline{C}$H=CPz$_2$), 126.4 (PzCH=$\underline{C}$Pz$_2$), 130.8 (C^5, Pz^{III}), 131.1 (C^5, Pz^I), 134.6 (C^5, Pz^{II}), 143.0 (C^3, Pz^{III}), 143.7 (C^3, Pz^I), 144.5 (C^3, Pz^{II}).

1,1,2-Tris(pyrazol-1-yl)ethene–CdCl$_2$ complex (**2**). To a solution of 30 mg (0.133 mmol) of Pz$_3$ ligand in 1 ml of ethanol 30 mg (0.133 mmol) of $CdCl_2 \cdot 2.5H_2O$ in 1 ml of the same solvent were added. White precipitate formed immediately, which was filtered and washed with ethanol. Yield 83 mg (70%), colorless powder. *Anal.* Calc. for $C_{11}H_{10}Cl_2CdN_6$: C, 32.26; H, 2.46; N, 20.52. Found: C, 31.92; H, 2.22; N, 20.18%. IR bands, $\tilde{\nu}$, cm^{-1}: 1693 ($\nu_{C=C}$), 1525, 1455, 1402 (ν_{Pz}), 1341 (β_{CH}), 980 (Pz ring breathing), 604 (β_{Pz}).

1,1,2-Tris(pyrazol-1-yl)ethene–Hg(NO$_3$)$_2$ complex (**3**). To a solution of 30 mg (0.133 mmol) of Pz$_3$ ligand in 1 ml of ethanol 68 mg (0.133 mmol) of $Hg(NO_3)_2 \cdot H_2O$ in 1 ml of the same solvent were added. White precipitate formed immediately, which was filtered and washed with ethanol. Yield 74 mg (98%), colorless powder. *Anal.* Calc. for $C_{11}H_{10}HgN_8O_6$: C, 23.98; H, 1.83; N, 20.19. Found: C, 23.59; H, 1.67; N, 20.19%. IR bands, $\tilde{\nu}$, cm^{-1}: 1522, 1394 (ν_{Pz}), 1359 (β_{CH}), 1385 ($\nu_{a\,NO_3}$) and 1303 ($\nu_{s\,NO_3}$), 604 (β_{Pz}).

3. Results and discussion

3.1. Synthesis of the complexes

Complexes of 1,1,2-tris(pyrazol-1-yl)ethene were prepared by the reaction of the ligand with zinc chloride, cadmium chloride or mercury(II) nitrate in diethyl ether or ethanol. All three compounds, which are colorless solids, gave correct elemental analysis consistent with 1:1 metal-to-ligand ratio. Zinc chloride complex (**1**) has a sharp melting point and is soluble in ethanol, indicative of its discrete structure. On the contrary, cadmium and mercury(II) complexes **2** and **3** are insoluble in ethanol and other common solvents, which is probably due to their polymeric nature. Complexes **2** and **3** dissolve only in strong donor solvents such as dimethylsulfoxide. The NMR ^{1}H and ^{13}C spectra of solutions in DMSO-d_6 prepared from compounds **2** and **3** were identical to the spectra of the free ligand, indicating the complete dissociation of these complexes in strong donor DMSO solvent.

Complexes **1**–**3** were characterized by IR spectroscopy and, in case of zinc complex **1**, by NMR ^{1}H and ^{13}C spectroscopy. Very low solubility of cadmium and mercury(II) complexes prevented the registration of NMR spectra.

3.2. Crystal structure of 1,1,2-tris(pyrazol-1-yl)ethene–zinc chloride complex (1)

Recrystallization of complex **1** from ethanol gave single crystals suitable for X-ray crystal structure determination. Molecular structure of complex **1** is shown in Fig. 1, selected bond lengths and angles are given in Table 1.

Complex **1** crystallizes in a triclinic system, and the elementary cell contains two formula units of the complex. The asymmetric unit consists of one binuclear complex molecule (Scheme 2, pyrazole ring numbering is also shown). One of zinc coordination center adopts a tetrahedral geometry. For this center, the τ_4 parameter, defined by Houser and co-workers [22] as

$$\tau_4 = \frac{360 - (\alpha + \beta)}{141},$$

where α and β are the two largest angles of a four coordinated polyhedron, equals to 0.939. For ideal tetrahedral coordination center τ_4 is 1, while for trigonal pyramidal it is 0.85 [22]. Therefore, τ_4 parameter for four-coordinated zinc center in complex **1** indicates some distortion towards trigonal pyramidal geometry. One apex of a tetrahedron is occupied by nitrogen atom of pyrazole ring (Pz^I), while three chloride ions are located in the remaining apices.

The coordination polyhedron of the second five-coordinated zinc center is best described as a trigonal bipyramid, based on the Addison's τ_5 criterion [23] of 0.711. For ideal trigonal bipyramidal geometry τ_5 equals 1, while for square pyramidal it is zero [23]. Four coordination places of zinc are occupied by pyrazole nitrogen atoms (Pz^{II} and Pz^{III}) of two 1,1,2-tris(pyrazol-1-yl)ethene ligands. One of these ligands is bridging two zinc centers (μ-Pz$_3$), while in another ligand the third pyrazolyl moiety remains uncoordinated (terminal ligand trm.-Pz$_3$). The chloride ion occupies the fifth coordination place of trigonal bipyramid in equatorial position.