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The preparation, spectral and X-ray crystallographic characterization of 2,6-diacetylpyridinedihydrazone complex with lead(II) nitrate

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Abstract—The reaction of 2,6-diacetylpyridinedihydrazone with lead(II) nitrate gives the complex with metal-ligand stoichiometry equal to 1:1, irrespective of the molar ratio of starting materials. The complex has been characterized by spectral data (IR, ^1H and ^{13}C NMR), elemental and X-ray crystal structure analysis. © 1997 Elsevier Science Ltd

Keywords: lead(II)complex; hydrazone complex; X-ray structure.

The chemistry of hydrazones have been intensively investigated in recent years, owing to their coordinating capability, pharmacological activity, antibacterial and antifungal properties and the use in analytical chemistry as highly selective extractants [1–9]. In view of the steady and enormous growth of the amount of lead released to the environment by human activities the design and synthesis of potential therapeutic chelating agents for purpose of removing this toxic metal from the human body is a field of growing importance [10–15].

In seeking the new strong chelators that might coordinate the toxic heavy metals we describe here the synthesis, spectral characterization and X-ray crystal structure of the complex of 2,6-diacetylpyridinedihydrazone with lead(II) nitrate.

EXPERIMENTAL

The 2,6-diacetylpyridine, hydrazine hydrate (Aldrich Chemical Company) and lead nitrate (Merck product) were used without further purification. The 2,6-diacetylpyridinedihydrazone was prepared as described earlier [7].

Preparation of 2,6-diacetylpyridinedihydrazone complex of lead(II) nitrate

To a solution of lead(II) nitrate (0.2 mmol) in methanol (15 cm^3), 2,6-diacetylpyridinedihydrazone (0.2 or 0.4 mmol) in methanol (15 cm^3) was added dropwise with stirring. The reactions were continued for 2–8 h at temperatures ranging from 20 to 50°C. The reaction volumes were then reduced to 10 cm^3 by rotoevaporation and resulting yellow precipitates were filtered, washed with diethyl ether and dried in open air; yield, 92.8%. Found: C, 20.4; H, 2.6; N, 18.4. Calc. for $Pb(C_9H_{13}N_5)NO_3)_2 \cdot H_2O$: C, 20.0; H, 2.8; N, 18.2%. IR (CsI pellets, cm^{-1}): 3540m, br, $\nu(OH)$; 3360m, 3200m, 1640w, $\nu(NH_2)$; 1545s, $\nu(C{=}N)$; 1590m, 1040w, 675w, (py): 1175m, $\nu(N{-}N)$; 1765w, 1740w, 1380br, 820m, (NO_3). ^1H NMR (DMSO-d_6, ppm): 2.53 (s, 6H, CH_3), 7.98–8.30 (m, 3H, py), 7.23 (s, 4H, NH_2). ^{13}C NMR (DMSO-d_6, ppm): 11.69 (q, CH_3), 139.32 (s, C=N), 153.11 (s, C—α, py), 119.79 (d, C—β, py) 142.93 (d, C—γ, py).

Measurements

IR spectra were recorded using CsI pellets in the range 4000–200 cm^{-1} on a Perkin–Elmer 580 spectrophotometer. ^1H NMR and proton noise decoupled and off-resonance decoupled ^{13}C NMR spectra were

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run in DMSO-d_6 on a Varian Gemini 300 spectrometer using TMS as an internal reference.

X-ray crystal structure analysis

Crystals of the complex were pale yellow, very thin plates. Observation of crystals under polarized light showed that they were twinned. For further studies a crystal fragment with dimensions 0.15 × 0.10 × 0.01 mm was cut from the twinned specimen. The data were collected on a Kuma Diffraction KM4 diffractometer, using graphite monochromatized Mo–Kα radiation. Lattice parameters were obtained from least-squares refinement of 44 reflections with $11 \leqslant 2\theta \leqslant 24°$. Intensities were measured using $\omega/2\theta$ scan technique up to $2\theta_{max}$, 48° at variable speed 0.9–9.0° min^{-1}. Intensities of three reflections were checked every 100 measurements to monitor instrument and crystal stability. Their intensity variation was within 2.3%. The data were corrected for Lorentz and polarization factors. Out of 2426 reflections measured 1874 with $I \geqslant 2\sigma(I)$ were classified observed. The structure was solved by heavy atom Patterson method with the program SHELXS-86 [16] and refined by full-matrix least-squares on F^2 with SHELXL-93 [17]. After the refinement with isotropic displacement parameters for non-H atoms, an empirical absorption correction with maximum and minimum coefficients of 0.795 and 1.273, respectively, was applied using the program DIFABS [18]. Subsequently the refinement was continued with anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms of water molecule were not localized. The positions of H-atoms bonded to C and N atoms were calculated assuming C–H and N–H distances 0.96 and 0.90 Å, respectively. $R1$ and $wR2$ values, goodness-of-fit, largest difference peak and hole are given, together with some other crystal data, in Table 1. Selected bond lengths and angles are listed in Table 2. Atom labeling is shown in Fig. 1.

RESULTS AND DISCUSSION

The lead(II) nitrate complex of 2,6-diacetylpyridinedihydrazone was prepared by direct reaction of the metal salt with ligand in methanol and identified (see Experimental) by spectral data (IR, ^{1}H NMR and ^{13}C NMR), elemental and X-ray crystal structure analysis. Various reaction condition were employed (reaction time, range of temperatures, excess of ligand) and in all cases the complex with metal-hydrazone stoichiometry equal to 1:1 was isolated.

The complex is yellow, air stable solid, appreciably soluble in DMSO.

The IR spectrum taken in the region 4000–200 cm^{-1} provides some information regarding the mode of

Table 1. Crystal data and summary of intensity data collection and structure refinement

Empirical formula	$C_9H_{15}N_7O_7Pb$
Formula weight	540.47
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.540(3)
b (Å)	8.927(4)
c (Å)	11.317(4)
α (°)	76.96(3)
β (°)	93.72(3)
γ (°)	80.25(3)
Volume (Å^3)	768.9(5)
Z	2
Density (calculated) (Mg/m^3)	2.334
Absorption coefficient (mm^{-1})	11.022
F(000)	512
θ range for data collection (°)	1.99 to 24.15
Index ranges	$-8 < h \leqslant 9$, $-9 \leqslant k \leqslant 10$, $0 \leqslant l \leqslant 13$
Reflections collected	2426
Reflections with $I > 2\sigma(I)$	1874
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1874/0/217
Goodness-of-fit on F^2	1.139
Final R indices [$I > 2\sigma(I)$]	$R1^a = 0.0747$, $wR2^b = 0.1963$
Largest diff. peak and hole	4.54 and −1.807 e Å^{-3}

$^aR1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$.

$^bwR2 = [\Sigma[w(F_0^2-F_c^2)/\Sigma[w(F_0^2)^2]]^{0.5}$.

Table 2. Selected bond lengths (Å) and angles (°)

Bond	d(Å)	Bond	d(Å)
Pb(1)—N(1)	2.49(3)	Pb(1)—O(1a)	2.93(3)
Pb(1)—N(4)	2.50(2)	Pb(1)—O(1b)	2.86(3)
Pb(1)—O(3b)	2.52(2)	Pb(1)—O(2b^{i})	3.19(2)
Pb(1)—O(3a)	2.58(3)	Pb(1)—O(2a^{ii})	3.08(3)
Pb(1)—N(2)	2.59(2)		
N(4)—Pb(1)—N(2)	128.9(8)	O(1a)—Pb(1)—N(2)	115.12(9)
N(1)—Pb(1)—N(2)	65.6(8)	O(1a)—Pb(1)—N(4)	63.4(10)
N(1)—Pb(1)—N(4)	64.3(9)	O(1a)—Pb(1)—N(1)	78.9(12)
O(2a^{ii})—Pb(1)—N4	78.2(8)	O(1a)—Pb(1)—O(2a^{ii})	71.0(11)
N(2)—Pb(1)—O(2a^{ii})	152.7(8)	N(2)—Pb(1)—O(2b^{i})	73.9(7)
O(1a)—Pb(1)—O(2b^{i})	142.5(11)	N(1)—Pb(1)—O(2b)	132.7(7)
O(3a)—Pb(1)—O(2b^{i})	117.6(6)	N(4)—Pb(1)—O(2b^{i})	141.1(7)
O(1b)—Pb(1)—N(2)	120.5(8)	O(2a^{ii})—Pb(1)—O(2b^{i})	85.9(7)
O(1b)—Pb(1)—N(4)	71.9(8)	O(3a)—Pb(1)—N(2)	76.2(7)
O(1b)—Pb(1)—N(1)	112.2(8)	O(3a)—Pb(1)—N(1)	75.4(7)
O(1b)—Pb(1)—O(2a^{ii})	66.2(7)	O(3a)—Pb(1)—N(4)	99.8(7)
O(3b)—Pb(1)—N(4)	81.5(7)	O(3a)—Pb(1)—O(2a^{ii})	98.1(6)
O(3b)—Pb(1)—N(1)	78.5(7)	O(3b)—Pb(1)—N(2)	79.9(7)
O(3b)—Pb(1)—O(2a^{ii})	110.2(6)		

Symmetry operators: (i) $-x, 2-y, 1-z$; (ii) $1-x, 1-y, 1-z$.

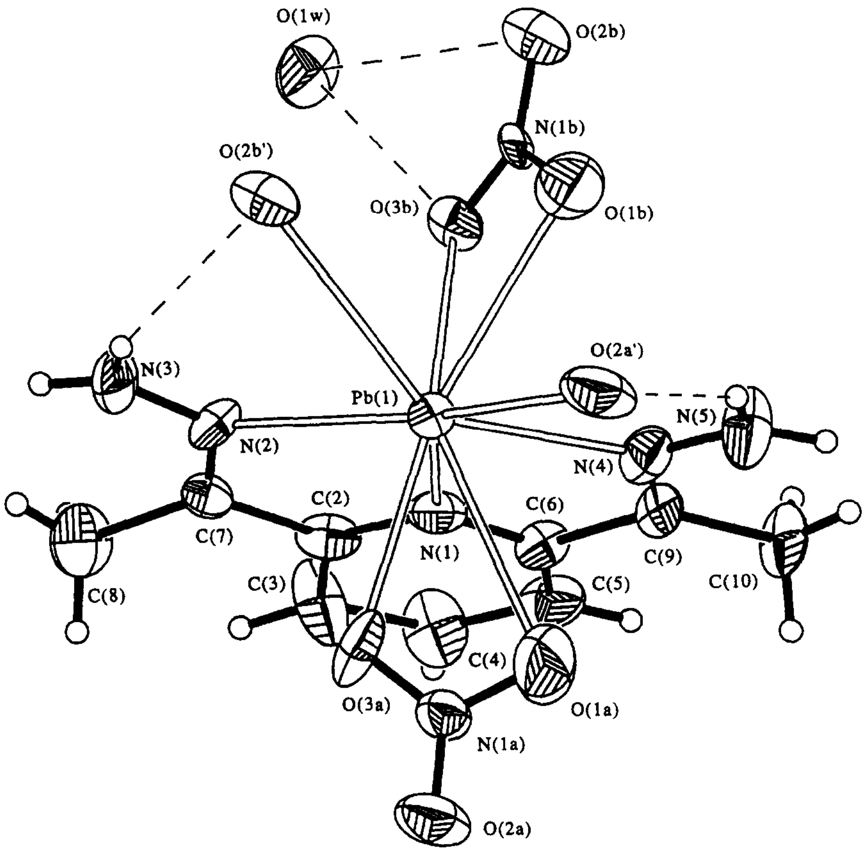

Fig. 1. Atom labeling of the complex.

coordination in the complex and was analysed in comparison with that of the free ligand. The most significant variations between free ligand and complex concern the ν(C=N), ν(N—N) and pyridine ring vibrations. The band at 1605 cm^{-1} in the free ligand attributable to ν(C=N) stretching vibration is shifted to lower frequency upon complexation as expected from reducing the electron density on the nitrogen atom due to coordination with metal cation. The N–N frequency found at 1155 cm^{-1} in the ligand increases in the complex suggesting the involvement of one of the nitrogen atoms of each N–N bond in the coordination. This causes a reduction in electron repulsion by the lone pairs on adjacent nitrogen atoms [8]. The non-bonding of the NH_2 nitrogen atoms is confirmed by the persistence of the NH_2 vibrations in the free ligand and complex. Evidence for the coordination of the pyridine nitrogen atom in the complex comes from the increase in frequency of high and low energy pyridine ring vibrations found at 1565, 990 and 642 cm^{-1} in the spectrum of the ligand. The complex shows the broad diffuse band centered at *ca* 3540 cm^{-1} due to the stretching and bending modes of water. The presence of coordinated nitrates may be inferred from ν(N—O) stretching frequency observed as a very strong broad band centered at 1380 cm^{-1}, medium sharp band at 820 cm^{-1} and in addition two weak bands at 1765 and 1740 cm^{-1}. Especially the latter bands are indicative of monodentate and/or bidentate nitrate groups [19–21].

Coordination of the nitrogen atoms of $CH_3C{=}N$ groups and pyridine to metal ion in this complex is confirmed by the deshielding of the methyl and ring protons observed at δ 2.25 and 7.82, respectively, in the ^1H NMR spectrum of the ligand. The signal at δ 7.28 assigned to the NH_2 protons in the ligand shifts slightly upfield in the complex, which is considered diagnostic of non-coordination of the terminal amino nitrogen atoms. The integrated intensities of the signals are in good agreement with the required ratio consistent with the proposed formulation of the complex.

The ^{13}C NMR spectrum is also used in an attempt to confirm the possible coordination mode of the ligand molecule in the complex. The correctness of the assignments is certified by the off-resonance decoupled ^{13}C NMR spectrum recorded in non-decoupled conditions. The 2,6-diacetylpyridinedihydrazone displays five signals arising from the methyl carbon atoms (δ 9.56 ppm, quartet), azomethine carbons (δ 135.60 ppm, singlet), the pyridine ring carbon atoms α to nitrogen (δ 155.05 ppm, singlet), β to nitrogen (δ 116.21 ppm, doublet) and γ to nitrogen (δ 142.73 ppm, doublet). The spectrum of lead(II) nitrate complex with 2,6-diacetylpyridinedihydrazone presents a similar pattern with five resonances. However, the effect of coordination strongly influences the chemical shifts in the complex, particularly those signals which are related to the carbon atoms next to the donor sites [15,22–24]. The signals due to the azomethine and methyl carbons undergo a significant downfield shift in the spectrum of the complex compared to the free ligand as a result of the lowering of electron density from this atom upon coordination of the nitrogen. The upfield shift is found for the pyridine carbons α to nitrogen, while those in β position are deshielded on coordination. Such a tendency is characteristic of coordinated pyridine ring, having been already reported [15,24,25]. The upfield shift for C–α can be rationalized in terms of the lower π character of the N—C–α bond upon coordination of the pyridine nitrogen, the effect analogous to the upfield protonation shift [26]. The chemical shift of the pyridine carbon γ to nitrogen is, as expected, only slightly affected by coordination due to the greater distance from the donor sites. This data support the conclusion drawn on the basis of the IR and ^1H NMR spectra about the tridentate behaviour of the hydrazone molecule in this complex. The stability of the complex in DMSO solution is demonstrated by the absence of any signals due to the free ligand. Hence, it is evident that no metal-ligand dissociation occurs even in the solvent which is known to compete with the ligand for the metal ion. [27,28]

In order to establish the structure of this complex an X-ray analysis was performed. The Pb^{2+} cation is surrounded by nine ligating atoms, three nitrogen atoms from the organic ligand and six oxygen atoms from nitrate anions (Fig. 1). The metal ion lies in the plane of organic ligand closing two five-membered chelate rings. The mean of the Pb–N distances is 2.53 Å. The nitrate anions are placed at the opposite sides of this plane and are approximately perpendicular to the ligand–Pb^{2+} plane. Two of them are chelating the metal ion, however the Pb–O distances within the chelate rings are strongly differentiated [2.58(3), 2.93(3) Å for O3a, O1a and 2.52(2), 2.86(3) Å for O3b, O1b]. A notable feature is an open face on metal ion opposite the organic ligand. From this direction the Pb^{2+} cation is partially blocked by two O atoms, $O(2a^{1-x,1-y,1-z})$ and $O(2b^{-x,2-y,1-z})$, from the nitrate groups. These O atoms are at the distances of 3.08(3) and 3.19(2) Å from Pb^{2+} cation and are additionally hydrogen bonded to the hydrazone NH_2 groups. Inhomogeneity of the set of Pb–O(nitrate) distances indicates different nature of Pb–O interactions which for Pb1–O2a and Pb1–O2b appear to be essentially electrostatic.

The lead centers attain a coordination number of 5 (three short Pb–N and two short Pb–O interactions) or 9 (5+4) if the four long Pb–O distances are also taken into consideration. The coordination polyhedron PbN_3O_6 is quite irregular. The metal ion is surrounded by three O atoms which define the plane above Pb^{2+}. The second plane, defined by N(2), N(1), N(4), O(2a′) and the metal ion, is approximately parallel to it. Large value of the N(2)–Pb(1)–O(2a′) angle, 152°, indicates that the fifth position in this plane can be occupied by stereochemically active lone pair of electrons of Pb^{2+}. From the bottom the metal ion is chelated by the nitrate O(1a) and O(3a) atoms.

The crystallographic data reveals that the coordination number of the Pb^{2+} centers usually exceeds 6 and coordination numbers 8, 9 and 10 with very irregular coordination polyhedra appear to be quite common [29–35]. The failure of the lead(II) ion to form the complex of stoichiometry 1:2 with hydrazone ligand can be understood in terms of the stereochemically active lone pair of valence electrons [11–13,30,31,36,37] which prevents the approach the second molecule of the hydrazone to the coordination sphere on Pb^{2+}.

As shown in Fig. 2 the organic ligand-Pb^{2+} units are bridged by pairs of the nitrate anions, each NO_3^- group being bidentate to one and unidentate to the other cation. Metal ions bridged by anions B are 6.379 Å apart while those bridged by nitrate ions A are at a distance 5.789 Å. Zig-zag chains formed are further connected by hydrogen bonds between hydrazone NH_2 groups, nitrate groups and water molecule into two-dimensional network parallel to (001). The water of crystallization acts as a donor in hydrogen bond with two nitrate groups and as an acceptor of hydrogen bond from the organic ligand.

Supplementary material—Tables of atomic coordinates, thermal parameters, and full listings of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

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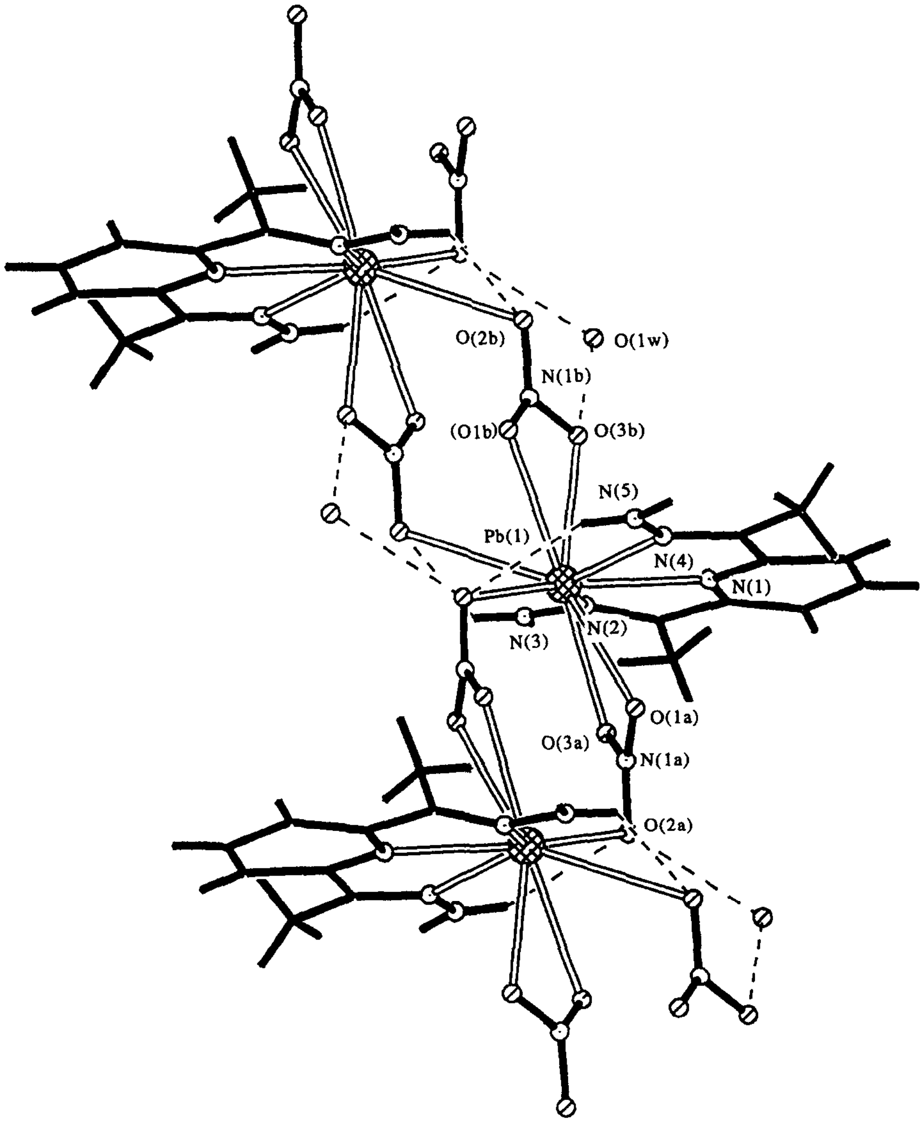

Fig. 2. 2,6-Diacetylpyridinedihydrazone-Pb^{2+} units connected via coordination to NO_3^- anions into zig-zag chains.

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