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Metal complexes with pyrazole-derived ligands
Part I. Synthesis and crystal structures of 3-amino-4-acetyl-5-methylpyrazole (L) and of the tetrahedral complexes $ZnL_2(NO_3)_2$ and ML_2Cl_2 (M = Cu(II), Hg(II))

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Abstract

A new pyrazole-derived ligand 3-amino-4-acetyl-5-methylpyrazole (L) has been synthesized and structurally characterized. In order to examine its coordination properties the metal complexes $ZnL_2(NO_3)_2$, CuL_2Cl_2 and HgL_2Cl_2 have been prepared and their crystal and molecular structures determined by X-ray structure analysis. The crystals of the ligand are triclinic, space group $P\bar{1}$ with unit cell dimensions $a = 14.433(4)$, $b = 7.406(1)$, $c = 6.794(4)$ Å, $\alpha = 99.81(4)$, $\beta = 92.10(9)$, $\gamma = 105.55(6)°$, $V = 686.8(5)$ Å^3; $ZnL_2(NO_3)_2$ is orthorhombic, space group *Pbca*, $a = 18.420(2)$, $b = 14.892(2)$, $c = 14.114(2)$ Å, $V = 3872(1)$ Å^3; CuL_2Cl_2 is monoclinic, space group $I2/a$, $a = 13.804(3)$, $b = 8.835(1)$, $c = 14.264(4)$ Å, $\beta = 100.50(3)°$, $V = 1710.5(7)$ Å^3; HgL_2Cl_2 is monoclinic, space group $I2/a$, $a = 14.075(2)$, $b = 9.002(2)$, $c = 14.303(3)$ Å, $\beta = 97.39(2)°$, $V = 1797.2(6)$ Å^3. The two latter complexes are isostructural. The ligand L acts as a monodentate ligand through the tertiary ring nitrogen atom. The complexes contain metal atoms in the distorted tetrahedral coordination realized by two nitrogen atoms from the two ligands L and two nitrate-oxygen atoms in the zinc complex and two chlorine atoms in the copper and mercury complexes. All four structures are built up from individual molecules linked together by hydrogen bonding interactions N–H...O achieved between 'pyrrole' ring nitrogens of one molecule and the acetyl-oxygen atoms from the adjacent molecules. In the free ligand the additional hydrogen bondings N–H...N occur also between amino and 'pyridine' nitrogen atoms of the neighbouring molecules. The general physicochemical characteristics as well as the IR and ^{1}H NMR spectra are in accordance with the observed molecular structures.

Introduction

Synthetic and structural studies of the metal complexes with pyrazole-based ligands are receiving significant attention due to different complexing behaviour of such ligands and consequently different coordination possibilities with the metal atoms [1–4]. Of particular interest is the relationship between the coordination of the metal centres and the reactivity of various biologically active molecules with pyrazole-derived ligands. Some pyrazole derivatives may be used as extracting agents for various metal ions [1]. Also, pyrazoles appear as components of many drugs, herbicides and fungicides [5].

A common feature of these ligands is that they are coordinated via the 'pyridine' nitrogen atom. However, in the case of the pyrazolato anion, which is formed by deprotonation of the 'pyrrole' nitrogen, the latter nitrogen atom takes also part in coordination, which results in the formation of polynuclear complexes in which the ligand plays a bridging role [1, 6–8]. When the pyrazole derivatives have substituents with different donor atoms in the position 1, 3 or 5, they can be coordinated either as bridging

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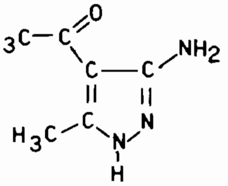
or non-bridging polydentate ligands [9]. Let us mention here, for example, 1-acetyl-pyrazole which is coordinated as a bidentate ligand through the 'pyridine' nitrogen and carbonyl-oxygen atoms [10].

To our knowledge, there are no reports in the literature on metal complexes with 3-amino-4-acetyl-5-methylpyrazole (L).



In view of the presence and the positions of potential electron-donor atoms, it can be supposed that this ligand can be coordinated in several ways. In order to obtain information on the coordination properties of the new ligand we have prepared the complexes $ZnL_2(NO_3)_2$ and ML_2Cl_2 (M = Cu(II), Hg(II)) and have determined the crystal structure of the ligand itself as well as the structures of these metal complexes.

Experimental

Synthesis of the ligand

S-Methylisothiosemicarbazidehydrogen-iodide [11] (12.0 g) was dissolved by heating in a mixture of 2,4-pentanedione (10 cm^3) and EtOH (20 cm^3). The obtained solution was heated gently for 5 min. After cooling the solution to room temperature the crystallization was initiated by rubbing the vessel wall with a glass stick. After 12 h the crystals were separated by filtration and washed several times with Et_2O and finally with Me_2CO. Yield ~10 g (62%). The results of elemental analysis of the product recrystallized from EtOH suggested that 2,4-pentanedione-mono(*S*-methylisothiosemicarbazonehydrogen-iodide) was formed. *Anal.* Found: C, 27.30; H, 4.59; N, 13.22; S, 10.51. Calc. for $C_7H_{14}N_3OSI$ (M_r = 315.17): C, 26.68; H, 4.48; N, 13.33; S, 10.17%.

The ligand, 3-amino-4-acetyl-5-methylpyrazole, was obtained by cyclization of 2,4-pentanedione-mono(*S*-methylisothiosemicarbazonehydrogen-iodide) in an aqueous-alkaline solution, accompanied by elimination of the CH_3S^- fragment. On dissolving of the above isothiosemicarbazone (10 g) and NaOH (4 g) in H_2O (40 cm^3) at room temperature, white needle-like crystals of 3-amino-4-acetyl-5-methylpyrazole, formed in the yellowish solution. They were separated after 15 h and washed thoroughly with water. Yield of air-dried product: 1.9 g (43%). *Anal.* Found: C, 51.43; H, 6.77; N, 29.85. Calc. for $C_6H_9N_3O$ (M_r = 139.16):C, 51.78; H, 6.52; N, 30.19%.

Synthesis of complexes

$ZnL_2(NO_3)_2$

A mixture of the ligand (0.30 g; 2.2 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.40 g; 1.3 mmol) was dissolved by heating in EtOH (10 cm^3) and left at room temperature. The white crystals which separated after 50 h were washed with EtOH and Et_2O. Yield 0.30 g (30%). *Anal.* Found: C, 31.29; H, 4.10; N, 24.48. Calc. for $ZnL_2(NO_3)_2$ (M_r = 467.69): C, 30.81; H, 3.88; N, 23.96%.

CuL_2Cl_2

A warm solution of the ligand (0.30 g; 2.2 mmol) in EtOH (10 cm^3) was mixed with a warm solution of $CuCl_2 \cdot 2H_2O$ (0.25 g; 1.5 mmol) in EtOH (5 cm^3). When the dark solution was left at room temperature crystals of two colours, yellowish and black, started to crystallize. After 20 h, the yellowish crystals were completely transformed into black needle-like ones which were separated and washed with EtOH and Et_2O. Yield 0.40 g (45%). *Anal.* Found: C, 35.46; H, 4.81; N, 20.82. Calc. for CuL_2Cl_2 (M_r = 412.50): C, 34.94; H, 4.40; N, 20.36%.

HgL_2Cl_2

A warm solution of $HgCl_2$ (0.27 g; 1.0 mmol) in H_2O (5 cm^3) was mixed with a warm solution of the ligand (0.28 g; 2.0 mmol) in EtOH (10 cm^3). After 50 h the white crystals were filtered off and washed with EtOH and Et_2O. Yield 0.40 g (37%). *Anal.* Found: C, 26.52; H, 3.18; N, 15.53. Calc. for HgL_2Cl_2 (M_r = 549.81): C, 26.21; H, 3.30; N, 15.28%.

Crystal structure determination

Data for all four structures were collected on a Philips PW 1100 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Unit-cell parameters were determined by least-squares refinement by using from 16 to 24 reflections in the range $3 \leq \theta \leq 15°$. Crystal stabilities were monitored by recording three check reflections every two hours. The data were corrected for Lorentz and polarization effects. Absorption correction was applied only for the mercury compound [12]. The structure of the ligand was solved by direct methods by using SHELXS86 [13]; those of the metal complexes by Patterson syntheses. All structures were revealed by Fourier and difference Fourier calculations. In each case non-hydrogen atoms were refined with anisotropic temperature factors while the hydrogen atoms were positioned in the difference Fourier maps and included in the structure factor calculations with the isotropic temperature factors. The function minimized in the least-squares procedures was $\Sigma\omega(|F_o|-|F_c|)^2$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [14]. All calculations were performed using an IBM PC/AT compatible microcomputer (processor 80386/20MHz and mathematical coprocessor 80387) with CRYSRULER package [15]. Atom coordinates for each structure are listed in Table 1. The crystals of Cu(II) and Hg(II) complexes are isostructural having metal atoms in a special positions (4e) of the space group $I2/a$.

Crystal data for the ligand L

$C_6H_9N_3O$, prismatic crystals, dimensions $0.30\times0.14\times0.13$ mm, triclinic, $a=14.433(4)$, $b=7.406(1)$, $c=6.794(4)$ Å, $\alpha=99.81(4)$, $\beta=92.10(9)$, $\gamma=105.55(6)$°, $V=686.8(5)$ Å^3, space group $P\bar{1}$, $Z=4$, $D_x=1.346$ g cm^{-3}, $F(000)=296$, $\mu=0.90$ cm^{-1}. Using 1.6° ω-scan technique 2137 unique reflections were collected within $2<\theta<30$° and index range $h-19/20$, $k-10/10$, l 0/9. Of these 1958 with $I\geq3\sigma(I)$ were used in the structure refinement. To H atoms bonded to the N atom of the pyrazole ring an isotropic thermal parameter $U_{iso}=0.063$ Å^2 was assigned; to those attached to the amino and methyl groups $U_{iso}=0.060$ and 0.085 Å^2, respectively. The refinement converged at $R=0.051$ ($R_w=0.074$, $w=1/[\sigma^2(F_o)+0.003304\ (F_o)^2]$). Maximum and minimum heights in the final difference Fourier map were 0.26 and -0.23 e Å^{-3}, respectively.

Crystal data for $ZnL_2(NO_3)_2$

$C_{12}H_{18}ZnN_8O_8$, crystal dimensions $0.27\times0.14\times0.29$ mm, orthorhombic, $a=18.420(2)$, $b=14.892(2)$, $c=14.114(2)$ Å, $V=3872(1)$ Å^3, space group $Pbca$ $Z=8$, $D_x=1.605$ g cm^{-3}, $F(000)=1920$, $\mu=13.53$ cm^{-1}. Using 1.6° ω-scans 2959 reflections were collected within $2<\theta<30$°, index range h 0/25, k 0/20, l 0/19 at room temperature. Of these, 2794 having $I\geq3\sigma(I)$ were used in the structure refinement. To H atoms attached to N12 and N22 the isotropic thermal parameters $U_{iso}=0.043$ Å^2 were assigned; to those attached to N13 and N23 $U_{iso}=0.049$ Å^2 and to all other H atoms $U_{iso}=0.097$ Å^2. The refinement converged with $R=0.037$ ($R_w=0.052$, $w=0.08594/[\sigma^2(F_o)+0.000723(F_o)^2]$). Maximum and minimum heights in the final difference Fourier map were 0.36 and -0.33 e Å^{-3}, respectively.

Crystal data for CuL_2Cl_2

$C_{12}H_{18}Cl_2CuN_6O_2$, brown prisms, dimensions $0.29\times0.07\times0.10$ mm, monoclinic, $a=13.804(3)$, $b=8.835(1)$, $c=14.264(4)$ Å, $\beta=100.50(3)$°, $V=1710.5(7)$ Å^3 space group $I2/a$, $Z=4$, $D_x=1.603$ g cm^{-3}, $F(000)=844$, $\mu=16.11$ cm^{-1}. Using 1.2° $\Theta-2\Theta$ scan technique 1161 unique reflections were collected

TABLE 1. Atomic coordinates $(\times 10^4)$ and equivalent isotropic thermal parameters $(\times 10^4)$ with e.s.d.s in parentheses

Atom	x	y	z	U_{eq} (Å^2)^a
$C_6H_9N_3O$				
O11	2353(1)	5329(3)	−4691(3)	550(7)
N11	1203(1)	6793(3)	730(3)	411(8)
N21	2084(1)	7939(3)	1629(3)	380(6)
N31	0701(2)	4953(4)	−2493(3)	533(9)
C11	2801(2)	8042(3)	438(3)	312(7)
C21	2399(2)	6878(3)	−1408(3)	316(8)
C31	1402(2)	6147(3)	−1105(4)	358(8)
C41	3799(2)	9244(4)	1216(4)	436(9)
C51	2842(2)	6444(4)	−3224(4)	369(9)
C61	3897(2)	7357(5)	−3365(5)	523(12)
O22	7381(1)	9496(3)	4659(3)	508(7)
N12	6237(1)	5855(3)	−796(3)	385(8)
N22	7116(1)	6239(3)	−1621(3)	380(7)
N32	5734(1)	6969(3)	2320(3)	474(8)
C12	7833(2)	7451(3)	−395(4)	327(8)
C22	7435(2)	7955(3)	1400(3)	298(8)
C32	6435(2)	6907(3)	1030(4)	330(8)
C42	8825(2)	8012(4)	−1099(4)	437(9)
C52	7877(2)	9206(3)	3246(4)	346(8)
C62	8942(2)	10147(4)	3485(5)	501(10)
$ZnL_2(NO_3)_2$				
Zn	772.7(2)	1286.6(3)	2201.1(2)	342(1)
O1	1441(1)	1180(2)	1117(2)	520(10)
O2	2145(2)	2116(3)	1825(3)	1055(18)
O3	2242(2)	1895(4)	320(3)	1329(25)
N1	1963(2)	1757(3)	1088(3)	691(16)
O4	612(2)	2370(2)	2999(2)	536(10)
O5	556(2)	2908(2)	1581(2)	599(11)
O6	387(3)	3776(2)	2780(2)	838(15)
N2	522(2)	3053(2)	2442(2)	481(11)
O11	−1141(1)	967(2)	−1097(2)	473(9)
N11	−143(1)	920(2)	1542(2)	304(7)
N12	−763(2)	647(2)	2011(2)	359(9)
N13	117(2)	1276(2)	−43(2)	404(10)
C11	−1323(2)	547(2)	1446(2)	366(11)
C12	−1093(2)	777(2)	526(2)	295(9)
C13	−345(2)	997(2)	629(2)	275(9)
C14	−2035(2)	223(4)	1823(3)	659(18)
C15	−1481(2)	809(2)	−368(2)	368(11)
C16	−2288(2)	667(3)	−398(3)	599(15)
O22	868(2)	−228(2)	6084(2)	470(9)
N21	1016(2)	394(2)	3206(2)	315(8)
N22	1180(2)	−478(2)	2946(2)	345(9)
N23	806(2)	1103(2)	4664(2)	419(10)
C21	1207(2)	−1032(2)	3671(2)	331(9)
C22	1060(2)	−530(2)	4484(2)	307(9)
C23	949(2)	371(2)	4155(2)	304(10)
C24	1386(3)	−2003(3)	3499(3)	503(14)
C25	973(2)	−805(2)	5468(2)	355(10)
C26	1007(2)	−1774(3)	5731(3)	518(15)
CuL_2Cl_2				
Cu	2500(0)	703(1)	0(0)	356(2)
Cl	3227(1)	2338(2)	−839(1)	776(6)
O	3681(2)	−1909(3)	3852(2)	382(10)

(*continued*)

TABLE 1. (*continued*)

Atom	x	y	z	U_{eq} (Å^2)^a
N1	3061(2)	−823(4)	961(2)	267(10)
N2	3512(2)	−2103(4)	690(2)	280(10)
N3	2853(3)	136(4)	2451(2)	394(12)
C1	3922(3)	−2954(5)	1421(2)	278(12)
C2	3745(3)	−2216(4)	2252(2)	239(12)
C3	3197(3)	−902(4)	1921(2)	254(10)
C4	4412(4)	−4403(5)	1247(3)	466(16)
C5	4020(3)	−2639(5)	3244(3)	318(13)
C6	4720(4)	−3900(7)	3546(3)	574(19)
HgL_2Cl_2				
Hg	2500(0)	839(1)	0(0)	506(1)
Cl	3497(2)	2348(2)	−884(2)	907(8)
O	3668(3)	−1899(4)	3871(2)	452(11)
N1	3180(3)	−937(4)	1003(2)	372(11)
N2	3579(3)	−2235(4)	738(2)	379(11)
N3	2945(4)	147(5)	2456(3)	664(15)
C1	3936(3)	−3059(5)	1473(3)	353(12)
C2	3767(3)	−2285(5)	2283(3)	327(12)
C3	3272(3)	−983(4)	1944(3)	323(10)
C4	4366(5)	−4552(6)	1309(4)	546(18)
C5	4005(3)	−2639(5)	3271(3)	376(13)
C6	4701(6)	−3853(8)	3582(5)	684(23)

$^a U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*a_ia_j$.

within $2 < \theta < 27°$ and index range h −16/16, k 0/11, l 0/17. Of these, 1118 with $I \geqslant 3\sigma(I)$ were used in the structure refinement. In the final round of calculation to all H atoms belonging to the methyl groups and attached to N2 and N3 the overall isotropic thermal factors U_{iso} of 0.118, 0.061 and 0.047 Å^2, respectively, were assigned. The refinement converged with $R = 0.036$ ($R_w = 0.045$, $w = 1.0698/[\sigma^2(F_o) + 0.00005(F_o)^2]$). Maximum and minimum heights in the final difference Fourier map were 0.34 and −0.33 e Å^{-3}, respectively.

Crystal data for HgL_2Cl_2

$C_{12}H_{18}Cl_2HgN_6O_2$, white prismatic crystals, dimensions 0.48×0.21×0.18 mm, monoclinic, $a = 14.075(2)$, $b = 9.002(2)$, $c = 14.303(3)$ Å, $\beta = 97.39(2)°$, $V = 1797.2(6)$ Å^3, space group $I2/a$, $Z = 4$, $D_x = 2.032$ g cm^{-3}, $F(000) = 1048$, $\mu = 85.35$ cm^{-1}. Using 1.2° ω-scan technique 1909 reflections were collected within $2 < \theta < 30°$, index range: h −20/19, k 0/12, l 0/19 at room temperature. Of these 1826 with $I \geqslant 3\sigma(I)$ were used in the calculations and refinement. Maximum and minimum transmission factors were 0.215 and 0.369, respectively. To H atoms bonded to N2, N3 and to the methyl groups the isotropic thermal factors U_{iso} of 0.059, 0.151 and 0.098 Å^2, respectively, were assigned. The refinement procedure converged with $R = 0.029$ ($R_w = 0.043$, $w = 0.7063/[\sigma^2(F_o) + 0.00165\ (F_o)^2]$). Maximum and minimum heights in the final difference Fourier map were 0.67 and −0.88 e Å^{-3}, respectively.

Results and discussion

Description of the structures

The essential characteristic of all four structures is the linkage of individual molecules realized through N–H...O hydrogen bonds between the 'pyrrole' nitrogen of one molecule and the acetyl-oxygen atom from the neighbouring molecule. These interactions are considerably strong amounting to 2.800(3) Å in the free ligand, 2.767(4) and 2.710(4) Å in the structure of the zinc complex and 2.813(4) and 2.760(4) Å in the copper and mercury complexes, respectively. In the free ligand there are also additional hydrogen bondings of the type N–H..N between amino and 'pyridine' nitrogen atoms of the adjacent molecules. These hydrogen bonds are weaker and have the lengths 3.086(4) and 3.065(3) Å. In all structures the ligand is best described in terms of two planes: the pyrazole ring plane and the acetyl group plane. The angles between these two planes are 1.9(2) and 2.8(1)° in the ligand itself, 6.5(2) and 6.8(2)° in zinc, 9.2(2)° in copper and 12.6(2)° in the mercury complex. A significantly short C–N bond between the carbon atom (in the vicinity of the tertiary ring nitrogen atom and in the complexes coordinated to the metal atoms) and the NH_2-nitrogen atom attached to it is another common characteristic of all four structures. These bond lengths are 1.364(5) and 1.368(4) Å in the structure of the free ligand, 1.340(5) and 1.332(4) Å in the structure of the zinc complex and 1.330(5) and 1.364(6) Å in the copper and mercury complexes, respectively. This shortening as well as uniformity of the bond lengths within the pyrazole rings in all four structures suggest resonance between several structures. A similar explanation was given in describing the structure of pyrazole itself [16] as well as that of bis[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]copper(II) [17]. The intramolecular interactions between these NH_2 groups and the acetyl-oxygen atoms most probably contribute also to the shortening of the C3–N3 bond lengths. These N...O distances are 2.835(4) and 2.829(3) Å in the structure of the ligand, 2.792(4) and 2.821(4) Å in the zinc complex, and 2.781(4) and 2.810(5) Å in the copper and mercury complexes, respectively.

The structures of the metal complexes contain metal atoms in the tetrahedral coordinations realized by two tertiary ring nitrogen atoms from two ligands and by two nitrate oxygens in the structure of the zinc complex and two chlorine atoms in the structures of the copper and mercury complexes. In all three complex structures the coordination tetrahedra are significantly distorted with the angles at the metal atoms varying from 98.4(1)–126.8(1)° in the zinc complex, from 94.0(1)–131.0(1)° and from 90.3(1)–118.7(1)° in the copper and mercury complexes, respectively.

The structure of the 3-amino-4-acetyl-5-methylpyrazole ligand (L) is shown in Fig. 1; bond lengths and angles in Table 2. The structure of zinc(II) complex is represented in Fig. 2; its distances and angles in Table 3. The ligand L as well as the nitrate ions act as the monodentate ligands. The mean values of the bond distances Zn–O (1.980(3) Å) as well as of Zn–N (1.999(3) Å) agree well with the values already found for such bonds in analogous tetrahedral Zn(II) complexes (see, for example, refs. 18 and 19). Similarly, as can be seen from Table 4, the Cu–Cl and Cu–N bond lengths of 2.228(2) and 1.977(3) Å, respectively, correspond to the values already established in different structures of Cu(II) complexes (e.g. refs. 20–22). The same applies to the Hg–Cl and Hg–N bond lengths of 2.426(3) and 2.268(3) Å, respectively, also already found in the structures of Hg(II) complexes [23–25]. The structure of the mercury complex is shown in Fig. 3; that of the copper complex is not shown due to its complete analogy to the structure of the mercury complex. The bond lengths and bond angles in the structure of Hg complex are given in Table 5.

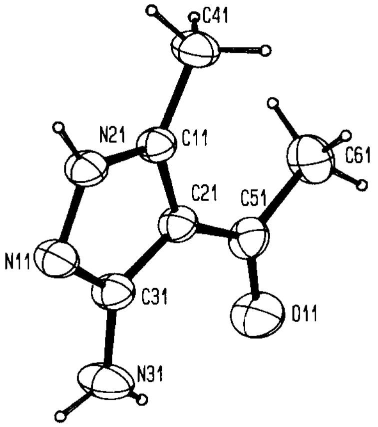


Fig. 1. The molecular structure of 3-amino-4-acetyl-5-methylpyrazole (L) showing the atom numbering scheme. Only one molecule is shown since the other crystallographically independent molecule has the same structure and analogous atom labelling.

TABLE 2. Interatomic distances (Å) and angles (°) for $C_6H_9N_3O$

O11–C51	1.237(3)	O22–C52	1.242(4)
N11–N21	1.378(2)	N12–N22	1.385(2)
N11–C31	1.328(3)	N12–C32	1.324(3)
N21–C11	1.331(3)	N22–C12	1.325(3)
N31–C31	1.364(3)	N32–C32	1.368(4)
C11–C21	1.401(3)	C12–C22	1.403(4)
C11–C41	1.498(4)	C12–C42	1.500(4)
C21–C31	1.431(4)	C22–C32	1.434(4)
C21–C51	1.438(4)	C22–C52	1.438(3)
C51–C61	1.505(4)	C52–C62	1.498(4)
N21–N11–C31	103.3(3)	N22–N12–C32	103.7(3)
N11–N21–C11	114.0(2)	N12–N22–C12	114.0(2)
N21–C11–C41	119.8(2)	N22–C12–C42	119.7(3)
N21–C11–C21	106.4(3)	N22–C12–C22	106.3(3)
C21–C11–C41	133.7(3)	C22–C12–C42	133.9(3)
C11–C21–C51	130.4(3)	C12–C22–C52	130.6(3)
C11–C21–C31	103.8(2)	C12–C22–C32	104.2(2)
C31–C21–C51	125.8(3)	C32–C22–C52	125.1(3)
N31–C31–C21	126.3(3)	N32–C32–C22	126.5(3)
N11–C31–C21	112.3(3)	N12–C32–C22	111.7(3)
N11–C31–N31	121.5(3)	N12–C32–N32	121.7(3)
O11–C51–C21	120.0(3)	O22–C52–C22	120.3(3)
C21–C51–C61	120.5(3)	C22–C52–C62	120.1(3)
O11–C51–C61	119.6(3)	O22–C52–C62	119.6(3)

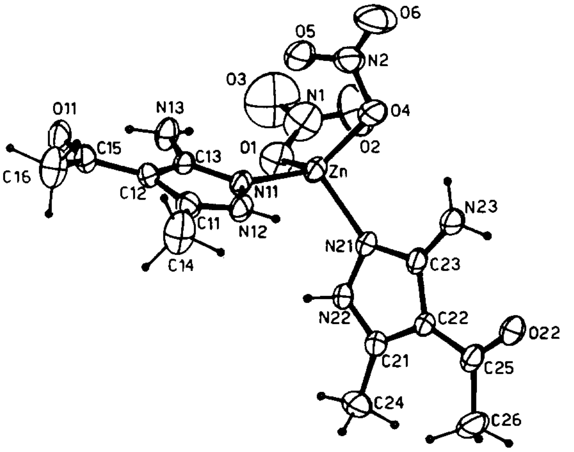


Fig. 2. The molecular structure of the $ZnL_2(NO_3)_2$ complex with the atom numbering scheme.

General physicochemical characteristics of the complexes

The isolated complexes are stable in air, well soluble in DMF, less soluble in MeOH and EtOH and insoluble in Et_2O. In aqueous solutions they decompose with ligand precipitation. The low values for molar conductivities (in DMF) of the chloro-complexes ($\lambda_M = 7.6$ and 23.4 Ω^{-1} cm^2 mol^{-1} for the Hg and Cu complexes, respectively) suggest their partial dissociation. The relatively lower λ_M value for the mercury complex can be explained in terms of the more pronounced covalent nature of the Hg–Cl bond if compared with the Cu–Cl bond. In contrast to these values, the λ_M value for the zinc complex (145.2 Ω^{-1} cm^2 mol^{-1}), corresponding to a 2:1 type of electrolyte [26] suggests that the coordinated nitrate anions have been completely replaced by DMF molecules.

TABLE 3. Interatomic distances (Å) and angles (°) for $ZnL_2(NO_3)_2$

Zn–O1	1.970(3)	C11–C12	1.408(4)
Zn–O4	1.990(3)	C11–C14	1.495(5)
Zn–N11	2.003(2)	C12–C13	1.424(5)
Zn–N21	1.995(3)	C12–C15	1.451(4)
O1–N1	1.290(5)	C15–C16	1.502(5)
O2–N1	1.217(6)	O22–C25	1.238(4)
O3–N1	1.217(6)	N21–N22	1.383(4)
O4–N2	1.296(4)	N21–C23	1.346(4)
O5–N2	1.236(4)	N22–C21	1.315(4)
O6–N2	1.204(4)	N23–C23	1.332(4)
O11–C15	1.227(4)	C21–C22	1.396(4)
N11–N12	1.381(4)	C21–C24	1.503(5)
N11–C13	1.346(4)	C22–C23	1.435(4)
N12–C11	1.312(5)	C22–C25	1.457(4)
N13–C13	1.340(5)	C25–C26	1.491(5)
N11–Zn–N21	109.7(1)	C13–C12–C15	123.9(3)
O4–Zn–N21	99.9(1)	N13–C13–C12	127.9(3)
O4–Zn–N11	111.0(1)	N11–C13–C12	110.2(2)
O1–Zn–N21	111.0(1)	N11–C13–N13	121.9(3)
O1–Zn–N11	98.4(1)	O11–C15–C12	119.0(3)
O1–Zn–O4	126.8(1)	C12–C15–C16	120.5(3)
Zn–O1–N1	115.9(3)	O11–C15–C16	120.6(3)
O2–N1–O3	124.8(4)	Zn–N21–C23	134.8(2)
O1–N1–O3	117.1(4)	Zn–N21–N22	119.1(2)
O1–N1–O2	118.1(4)	N22–N21–C23	105.1(3)
Zn–O4–N2	108.2(2)	N21–N22–C21	113.0(3)
O5–N2–O6	123.8(3)	N22–C21–C24	119.1(3)
O4–N2–O6	119.2(3)	N22–C21–C22	107.2(3)
O4–N2–O5	116.9(3)	C22–C21–C24	133.7(3)
Zn–N11–C13	130.9(2)	C21–C22–C25	130.9(3)
Zn–N11–N12	123.7(2)	C21–C22–C23	105.2(3)
N12–N11–C13	104.8(2)	C23–C22–C25	123.8(3)
N11–N12–C11	113.1(3)	N23–C23–C22	128.3(3)
N12–C11–C14	120.7(3)	N21–C23–C22	109.5(3)
N12–C11–C12	107.2(3)	N21–C23–N23	122.3(3)
C12–C11–C14	132.1(3)	O22–C25–C22	119.5(3)
C11–C12–C15	131.4(3)	C22–C25–C26	120.3(3)
C11–C12–C13	104.7(3)	O22–C25–C26	120.2(3)

TABLE 4. Interatomic distances (Å) and angles (°) for CuL_2Cl_2

Cu–Cl	2.228(2)	N3–C3	1.330(5)
Cu–N1	1.977(3)	C1–C2	1.413(5)
O–C5	1.239(5)	C1–C4	1.490(7)
N1–N2	1.380(5)	C2–C3	1.419(5)
N1–C3	1.350(4)	C2–C5	1.446(5)
N2–C1	1.326(5)	C5–C6	1.486(7)
N1–Cu–N1^{i}	94.0(1)	C2–C1–C4	133.6(3)
Cl–Cu–N1^{i}	103.2(1)	C1–C2–C5	130.3(4)
Cl–Cu–N1	131.0(1)	C1–C2–C3	105.2(3)
Cl–Cu–Cl^{i}	99.2(1)	C3–C2–C5	124.5(3)
Cu–N1–C3	134.7(3)	N3–C3–C2	126.8(3)
Cu–N1–N2	120.3(2)	N1–C3–C2	110.3(3)
N2–N1–C3	104.8(3)	N1–C3–N3	122.9(3)
N1–N2–C1	113.2(3)	O–C5–C2	119.0(4)
N2–C1–C4	119.9(3)	C2–C5–C6	121.2(4)
N2–C1–C2	106.5(3)	O–C5–C6	119.7(4)

Symmetry code: (i) $-x+0.5, y, -z$.

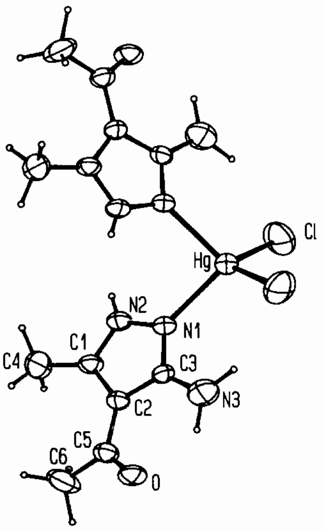


Fig. 3. The molecular structure of the HgL_2Cl_2 complex with the atom numbering scheme. The CuL_2Cl_2 complex is isostructural and has analogous atom labelling.

IR and ^1H NMR spectra

Comparing the IR spectrum of the ligand with the spectra of the complexes (KBr pellet), it can be concluded that they are quite similar in respect of both the number and relative intensities of the ligand bands. However, certain differences can be observed in the positions of some bands. Thus, in the 3500–3100 cm^{-1} range, the three bands observed in the spectrum of the ligand at 3430, 3260 and 3160 cm^{-1}, unambiguously due to ν(NH), are shifted to higher frequencies in the spectra of the complexes (3460, 3340, 3160 (Zn); 3440, 3300, 3170 (Cu) and 3580, 3530, 3450, 3280 (Hg) cm^{-1}. The characteristic and very strong ν(C−O) band, which in the spectrum of the non-coordinated ligand is observed at 1600 cm^{-1}, is also shifted (15–30 cm^{-1}) in the same direction. It should be noticed that this band is located at 1742 cm^{-1} in the spectrum of the non-coordinated 1-acetyl-pyrazole [10]. In the case of our ligand, the position of ν(C=O) is most probably the consequence of the presence of strong hydrogen bonds that exist not only in the crystalline complexes but also in the crystal of the free ligand itself. The shift of the ν(NH) and ν(C=O) bands towards higher frequencies in the complexes is in agreement with the absence of coordination of the nitrogen and oxygen atom of the NH_2 and C=O groups.The in-plane ring deformation band, which in the spectrum of the free ligand is observed at 660 cm^{-1}, is also shifted to higher frequencies (20 (Zn and Cu) and

TABLE 5. Interatomic distances (Å) and angles (°) for HgL_2Cl_2

Hg–Cl	2.426(3)	N3–C3	1.364(6)
Hg–N1	2.268(3)	C1–C2	1.384(6)
O–C5	1.222(6)	C1–C4	1.508(7)
N1–N2	1.373(5)	C2–C3	1.420(6)
N1–C3	1.315(5)	C2–C5	1.425(6)
N2–C1	1.321(5)	C5–C6	1.505(9)
N1–Hg–N1^{i}	90.3(1)	C2–C1–C4	133.9(4)
Cl–Hg–N1^{i}	108.0(1)	C1–C2–C5	130.3(4)
Cl–Hg–N1	118.7(1)	C1–C2–C3	105.7(4)
Cl–Hg–Cl^{i}	111.9(1)	C3–C2–C5	124.0(4)
Hg–N1–C3	129.0(3)	N3–C3–C2	128.9(4)
Hg–N1–N2	126.2(2)	N1–C3–C2	110.2(4)
N2–N1–C3	104.8(3)	N1–C3–N3	120.8(4)
N1–N2–C1	113.4(3)	O–C5–C2	119.1(4)
N2–C1–C4	120.3(4)	C2–C5–C6	120.8(4)
N2–C1–C2	105.8(4)	O–C5–C6	120.0(4)

Symmetry code: (i) $-x+0.5, y, -z$.

TABLE 6. ^{1}H NMR Chemical shifts (ppm) of 3-amino-4-acetyl-5-methylpyrazole (L) free and coordinated to Zn(II) and Hg(II)

Compound^{a}	H_3C-	H_3C-CO-	H_2N-	H-N-
L	2.33	2.38	6.4	11.5
$ZnL_2(NO_3)_2$	2.33	2.38	(6.4)	
HgL_2Cl_2	2.34	2.40		

^{a}Dissolved in DMSO-d^{6}.

15 (Hg) cm^{-1}). While the positive shifting of the stretching vibrations of the NH_2 and C=O groups is, as a rule, explained by the fact that these groups are not involved in the coordination, the positive shift of the in-plane ring deformation band of the coordinated 3-amino-4-acetyl-5-methylpyrazole, similarly to some other pyrazole derivatives [10, 27], indicates the coordination through the tertiary ring nitrogen. This is in concordance with the X-ray structure analysis.

It is known [28] that IR spectra may be efficiently used to distinguish between the non-coordinated and coordinated nitrate. However, the IR spectrum of $ZnL_2(NO_3)_2$, in which both nitrate groups are coordinated as monodentate ligands, exhibits the bands characteristic not only of the monodentate coordination (1420 and 1300 cm^{-1}), but also of the non-coordinated (1390 cm^{-1}) nitrate [28]. As the spectrum was recorded in KBr, the appearance of the latter band is the consequence of a partial replacement of the nitrate by the bromide ion.

The signals of all protons of the free ligand were observable in the ^{1}H NMR spectrum (Table 6), but those bonded to the nitrogen atoms were appreciably broadened. In the complexes, i.e. when coordination of the ligand occurred, the signals characteristic for the protons of the ring nitrogens disappeared. The proton signals of the NH_2 group being very weak in the Zn complex disappear in the Hg complex. In addition, the signal of the water protons (traces from DMSO-d^{6}) broadens simultaneously as that of the NH_2 group disappears. Consequently, it may be concluded that the proton exchange between the ring nitrogen, NH_2 group and water is much faster in the complexed than the free ligand [29]. Obviously, the coordination of one ring nitrogen atom causes the weakening of the N–H bond at the neighbouring ring nitrogen atom.

Supplementary material

Tables of anisotropic thermal parameters, hydrogen atom positions and listings of the observed and calculated structure factors are available from the authors.

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