Studies on Metal Complexes of Isocytosine Derivatives: The Crystal Structures of Mercury(II) and Nickel(II) Complexes of 2-Hydrazino-4-hydroxy-6-methylpyrimidine[1)]

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The preparation and crystal structure of mercury(II) and nickel(II) complexes of 2-hydrazino-4-hydroxy-6-methylpyrimidine (LH) are described. The crystal of the mercury(II) complex, $[HgCl_4](LHH)_2 \cdot 2H_2O$ is triclinic with $a=7.481(2)$, $b=19.535(6)$, $c=7.482(2)$ Å, $\alpha=94.77(3)°$, $\beta=106.28(5)°$, $\gamma=85.24(3)°$, $V=1043.8(6)$ Å^3, $D_x=2.102$ g·cm^{-3}, $Z=2$, and space group $P\bar{1}$. The atomic parameters were refined to a final R value of 0.044 for 3115 reflections. In the mercury(II) complex, one $[HgCl_4]^{2-}$ group which completes a regular tetrahedral coordination and two LHH^+ molecules which take a keto form ($>C(4)=O$), constitute a double salt type structure, in which both units are bound together through hydrogen bonds. It is notable that two different modes of stackings along the a and c axis are found between pyrimidine rings in the crystal. The crystal of the nickel(II) complex, $[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ is triclinic with $a=8.911(2)$, $b=9.197(2)$, $c=6.791(1)$ Å, $\alpha=93.41(3)°$, $\beta=102.31(3)°$, $\gamma=114.32(4)°$, $V=490.1(3)$ Å^3, $D_x=1.633$ g·cm^{-3}, $Z=1$, and space group $P\bar{1}$. The atomic parameters were refined to a final R value of 0.049 for 1310 reflections. The nickel(II) ion completes an octahedral coordination with two ring nitrogen N(3) and two hydrozino N_{amino} nitrogen atoms of the two neighboring ligand molecules and two water molecules. The chloride ion is not bonded to nickel(II) ion but is hydrogen bonded to N(1)–H of the pyrimidine base. The length of C(4)–O(9), 1.249 Å, in the LH residue suggests the keto form. Therefore, in the same preparation method with excess protons, the mercury(II) complex forms a double salt type structure, $[HgCl_4](LHH)_2 \cdot 2H_2O$, whereas the nickel(II) complex forms a chelate type structure, $[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$.

Keywords X-ray analysis; crystal structure determination; 2-hydrazino-4-hydroxy-6-methylpyrimidine; double salt complex; chelate compound; mercury(II) complex; nickel(II) complex; isocytosine derivative

Previously it was shown that 2-hydrazino-4-hydroxy-6-methylpyrimidine (LH) is an excellent chemotherapeutic agent for *Mycobacterium tuberculosis* (human type H_2-strain).[2)] This compound has a structure with the hydrazino group attached to C(2) of the isocytosine ring. LH is not only an important chemotherapeutic agent, but also it is worthy of study because of its possible multi-faced coordination with metal ions. Shiho and Takabayashi observed that LH acts as a color reagent for metal cations, but the structures of these color reaction products have not yet been fully investigated.[3)]

We have worked on the reaction of an isocytosine derivative (LH) with various metal ions and isolated some LH–metal complexes.[4)] Recent crystallographic studies on the two metal complexes, $[Zn(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$[5)] and $[Cu(LH)_2(H_2O)]Cl_2 \cdot 2H_2O$[6)] crystallized from dilute hydrochloric acid solutions (with excess protons), have shown that the ligation sites of LH are N(3) and hydrazino N_{amino} nitrogen atoms. On the other hand, in $[PtCl_6](LHH)_2$[7)] obtained by the same preparation method, platinum (IV) ion is coordinated to Cl atoms but no direct Pt(IV)–LH coordination bond was found by X-ray analysis.

As a part of our research on metal complexes with nucleotide bases, we have determined the structures of the complexes between metal ions (Hg(II) and Ni(II)) and an isocytosine derivative (LH). In these new metal(II) complexes prepared in the presence of excess protons, the hydroxyl group at C(4) of LH was suggested by us[4)] to be keto form based on the infrared (IR) spectra. But it is difficult to determine to which N of the pyrimidine ring the proton is transferred, or where the coordination site to the metal ion is. We found that the nickel(II) complex ($[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$) takes a chelate type structure with direct Ni(II)–LH coordinations, like the zinc(II) complex,[5)] whereas the mercury(II) complex ($[HgCl_4](LHH)_2 \cdot 2H_2O$) having a double salt type structure does not have direct Hg(II)–LH coordination, like the platinum(IV) complex.[7)]

Experimental

Preparations of $[HgCl_4](LHH)_2 \cdot 2H_2O$ (1) and $[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (2) Two moles of each reactant were used. Each metal chloride was dissolved in water. An aqueous solution of LH was added to the metal chloride solution. A few drops of 6 N HCl were then added, and the solution was kept at 40 °C for 15 min, and allowed to evaporate at room temperature under a reduced pressure. The crystals obtained after several hours were washed with a small amount of ice-cold water and air-dried.

Anal. Calcd for $C_{10}H_{22}Cl_4HgN_8O_4$ (colorless prisms of **1**): C, 18.17; H, 3.35; N, 16.96. Found: C, 18.05; H, 3.23; N, 16.90. *Anal.* Calcd for $C_{10}H_{24}Cl_2N_8NiO_6$ (violet prisms of **2**): C, 24.91; H, 5.01; N, 23.25; Ni, 12.18. Found: C, 24.82; H, 4.99; N, 22.85; Ni, 12.45.

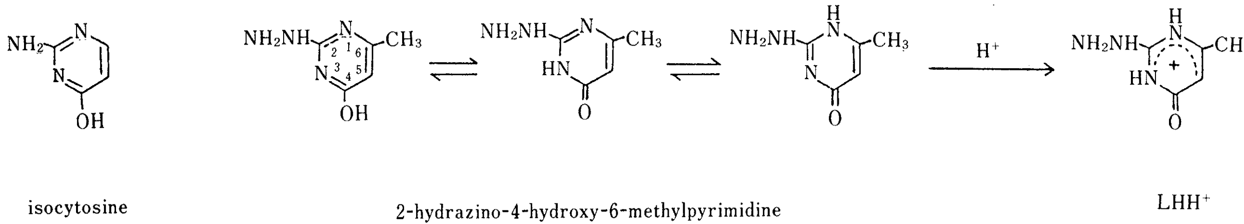

Chart 1

Crystals of $[HgCl_4](LHH)_2 \cdot 2H_2O$ (1) Crystal Data: The specimen used for the data collection, with dimensions of 0.1 × 0.2 × 0.1 mm, was mounted on a glass rod. The crystal data are given in Table I. The intensities were measured on a Rigaku four-circle automatic diffractometer with MoK_α radiation monochromated by using a graphite plate. The intensities of reflection with 2θ values up to 60° were collected by the $\theta-2\theta$ scan method with a 2θ scan rate of 2° min^{-1}. The background level was measured at each end of the scan range for 10 s. The intensities were corrected for Lorentz and polarization factors but not for absorption factors. The total number of independent, observed reflections above the $3\sigma(F)$ level was 3115 out of 6127 theoretically possible reflections.

Determination and Refinement of the Structure: The crystal structure was solved using the heavy-atom method. The single high peak at $u=0.07$, $v=0.53$, $w=0.06$ on the three-dimensional Patterson map indicated the position of the mercury(II) ion at *ca.* (0.035, 0.265, 0.03). Refinement of the structure was carried out by the full-matrix least-squares method.[8] A refinement with one mercury(II) and four chlorine atoms gave $R=0.29$. A subsequent structure factor Fourier calculation led to the positioning of the remaining 22 non-hydrogen atoms [twenty atoms in isocytosine derivatives (2LH) and two oxygen atoms of water molecules]. Another four cycles of isotropic least-squares calculations .for all 27 non-hydrogen atoms reduced the R value to 0.070. Finally, four cycles of anisotropic least-squares refinement gave the R index of 0.044. In this calculation, anisotropic thermal motions were applied for all 27 atoms and the following weighting system was applied: $\sqrt{w}=30/F_O$, when $F_O \geqq 30$ and $\sqrt{w}=1$ otherwise. The atomic scattering factors used for the calculations were taken from International Tables for X-Ray Crystallography[9] and from Cromer and Mann.[10] The final atomic coordinates are listed in Table II.[11] No further refinement including hydrogen atoms was attempted, since mercury(II) is a very heavy atom and the hydrogen atoms were not clearly visualized on the difference electron-density map.

TABLE I. Crystal Data for Mercury(II) and Nickel(II) Complexes of LH

	$[HgCl_4](LHH)_2 \cdot 2H_2O$ (1)	$[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (2)
Formula	$C_{10}H_{22}Cl_4HgN_8O_4$	$C_{10}H_{24}Cl_2N_8NiO_6$
Formula weight	660.74	481.95
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Cell constants	a = 7.481 (2) Å	a = 8.911 (2) Å
	b = 19.535 (6) Å	b = 9.197 (2) Å
	c = 7.482 (2) Å	c = 6.791 (1) Å
	α = 94.77 (3)°	α = 93.41 (3)°
	β = 106.28 (5)°	β = 102.31 (3)°
	γ = 85.24 (3)°	γ = 114.32 (4)°
	V = 1043.8 (6) Å^3	V = 490.1 (3) Å^3
Z	2	1
Density (D_x)	2.102 g·cm^{-3}	1.633 g·cm^{-3}

$LH = C_5H_8N_4O$, $LHH^+ = C_5H_9N_4O^+$.

Crystals of $[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (2) Crystal Data: The specimen used for the data collection had dimensions of 0.4 × 0.4 × 0.2 mm, and was mounted on a glass rod. THe crystal data are given in Table I. The intensities were measured with CuK_α radiation monochromated by a graphite plate. The intensities of reflection with 2θ values up to 140° were collected by the $\theta-2\theta$ scan method with a 2θ scan rate of 2° min^{-1}. The background was measured at each end of the scan range for 10 s. The intensities were corrected for Lorentz and polarization factors but not for absorption factors. The total number of independent observed reflections above the $3\sigma(F)$ level was 1310 out of 1780 theoretically possible reflections.

Determination and Refinement of the Structure: The crystal structure was solved by the heavy-atom technique. Since the space group is $P\bar{1}$ and $Z=1$, the nickel(II) ion was placed at (0, 0, 0). The resulting Fourier map revealed all atoms except for hydrogen atoms. Refinement of the structure was carried out by the block-diagonal least-squares method.[12] Finally, five cycles of anisotropic least-squares refinement for all 14 non-hydrogen atoms gave the R index of 0.049. In this calculation, anisotropic thermal motions were applied for all 14 atoms and the following weighting scheme was used: $\sqrt{w}=30/F_O$, when $F_O \geqq 30$ and $\sqrt{w}=1$ otherwise. The atomic scattering factors used for the calculations were taken from International Tables for X-Ray Crystallography.[9] The final atomic coordinates are listed in Table III.[11] The difference electron density map was calculated at this stage to find the hydrogen atoms. The four hydrogen atoms bonded to N(1), N(7), N(8) were clearly seen on the map and it was confirmed that the LH residue existed in a keto form. No further refinement including hydrogen atoms was attempted.

TABLE II. Atomic Parameters of $[HgCl_4](LHH)_2 \cdot 2H_2O$ (1)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	365 (0.6)	2500 (0.2)	365 (0.6)	44 (0.6)	37 (0.6)	36 (0.6)	−2 (0.2)	10 (0.2)	−1 (0.2)
Cl(1)	2728 (4)	1530 (2)	996 (4)	53 (2)	54 (2)	60 (2)	14 (1)	19 (1)	15 (1)
Cl(2)	−2698 (4)	2022 (1)	−3 (4)	42 (2)	39 (2)	63 (2)	−7 (1)	12 (1)	−9 (1)
Cl(3)	−10 (4)	2976 (1)	−2701 (3)	72 (2)	41 (2)	29 (1)	3 (1)	10 (1)	2 (1)
Cl(4)	997 (5)	3471 (2)	2726 (4)	72 (2)	51 (2)	44 (2)	−22 (1)	21 (1)	−18 (1)
N(1)	−542 (10)	943 (4)	3601 (11)	30 (4)	29 (4)	37 (4)	−2 (3)	6 (3)	0 (3)
C(2)	1189 (13)	1034 (5)	4630 (13)	41 (5)	23 (5)	33 (5)	0 (4)	13 (4)	2 (4)
N(3)	2568 (10)	554 (4)	4563 (10)	31 (4)	29 (4)	26 (4)	1 (3)	8 (3)	−2 (3)
C(4)	2267 (13)	−62 (5)	3442 (12)	33 (5)	31 (5)	30 (5)	−1 (4)	7 (4)	−7 (4)
C(5)	374 (13)	−146 (5)	2378 (13)	33 (5)	34 (5)	34 (5)	−1 (4)	7 (4)	1 (4)
C(6)	−980 (13)	345 (5)	2461 (12)	38 (5)	35 (5)	23 (4)	−3 (4)	3 (4)	10 (4)
N(7)	1586 (12)	1618 (4)	5688 (12)	46 (5)	34 (5)	43 (5)	2 (4)	12 (4)	−15 (4)
N(8)	3473 (12)	1713 (5)	6689 (13)	40 (5)	44 (5)	57 (6)	−10 (4)	10 (4)	−19 (4)
O(9)	3578 (10)	−479 (4)	3478 (11)	39 (4)	41 (4)	59 (5)	4 (3)	1 (4)	−18 (4)
C(9)	−2979 (14)	301 (6)	1402 (15)	27 (5)	52 (7)	47 (6)	−3 (5)	−5 (4)	5 (5)
N(11)	3597 (11)	4061 (4)	−553 (10)	36 (4)	37 (5)	23 (4)	−1 (4)	2 (3)	−2 (3)
C(12)	4613 (14)	3950 (5)	1220 (13)	40 (5)	31 (5)	27 (5)	−3 (4)	7 (4)	−7 (4)
N(13)	4533 (10)	4445 (4)	2566 (10)	31 (4)	32 (4)	21 (4)	3 (3)	3 (3)	−3 (3)
C(14)	3460 (14)	5058 (5)	2277 (12)	42 (5)	33 (5)	22 (5)	2 (4)	5 (4)	−1 (4)
C(15)	2365 (14)	5153 (5)	374 (12)	43 (6)	36 (5)	25 (5)	−4 (4)	2 (4)	−6 (4)
C(16)	2499 (14)	4651 (5)	−967 (12)	41 (5)	38 (5)	16 (4)	−7 (4)	−2 (4)	5 (4)
N(17)	5668 (13)	3387 (4)	1568 (11)	52 (5)	34 (5)	34 (4)	9 (4)	4 (4)	−3 (4)
N(18)	6695 (14)	3298 (5)	3477 (12)	66 (6)	45 (6)	35 (5)	17 (5)	8 (4)	−1 (4)
O(19)	3499 (12)	5478 (4)	3580 (9)	77 (6)	35 (4)	30 (4)	14 (4)	4 (4)	−8 (3)
C(19)	1401 (15)	4699 (6)	−2983 (13)	48 (6)	58 (7)	19 (5)	−10 (5)	−7 (4)	−1 (5)
O(1)	6549 (14)	1780 (5)	4428 (16)	83 (7)	53 (6)	121 (8)	16 (5)	64 (6)	14 (5)
O(2)	4430 (16)	3225 (5)	6548 (13)	127 (8)	53 (5)	65 (6)	−13 (5)	63 (6)	−14 (4)

Non-hydrogen atoms. Values are × 10^4. Anisotropic temperature factors are of the form: $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

TABLE III. Atomic Parameters of $[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (**2**)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0	0	89 (2)	82 (2)	82 (3)	42 (2)	46 (2)	24 (2)
Cl	1717 (2)	7103 (2)	4315 (2)	143 (2)	123 (2)	118 (3)	82 (2)	66 (2)	28 (3)
O(0)	2200 (4)	−116 (4)	1695 (5)	110 (6)	115 (6)	138 (9)	63 (5)	42 (6)	35 (7)
N(1)	2115 (5)	5059 (5)	943 (6)	112 (7)	88 (7)	138 (10)	40 (6)	70 (8)	39 (8)
C(2)	1371 (6)	3439 (6)	944 (7)	85 (8)	79 (8)	74 (10)	41 (7)	38 (8)	6 (9)
N(3)	1403 (5)	2354 (5)	−360 (5)	88 (6)	78 (7)	72 (9)	40 (6)	43 (7)	9 (7)
C(4)	2223 (6)	2855 (6)	−1903 (7)	84 (8)	98 (9)	81 (11)	39 (7)	34 (8)	33 (9)
C(5)	3080 (6)	4569 (6)	−1884 (7)	106 (9)	97 (9)	102 (11)	45 (8)	45 (9)	26 (10)
C(6)	3025 (6)	5640 (6)	−493 (7)	88 (8)	88 (8)	98 (11)	42 (7)	44 (8)	27 (9)
N(7)	521 (5)	2982 (5)	2414 (6)	150 (8)	80 (7)	136 (11)	44 (7)	99 (8)	32 (8)
N(8)	−160 (5)	1293 (5)	2538 (6)	128 (7)	58 (7)	97 (9)	42 (6)	60 (7)	4 (7)
O(9)	2195 (4)	1810 (4)	−3190 (5)	140 (7)	91 (6)	98 (8)	47 (5)	78 (6)	5 (6)
C(9)	3870 (7)	7442 (6)	−285 (8)	136 (10)	74 (9)	187 (15)	29 (8)	73 (10)	33 (11)
O(1)	4407 (5)	2588 (5)	4375 (6)	133 (7)	161 (8)	153 (10)	35 (6)	75 (7)	10 (8)

Non-hydrogen atoms. Values are $\times 10^4$. Anisotropic temperature factors are of the form: $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

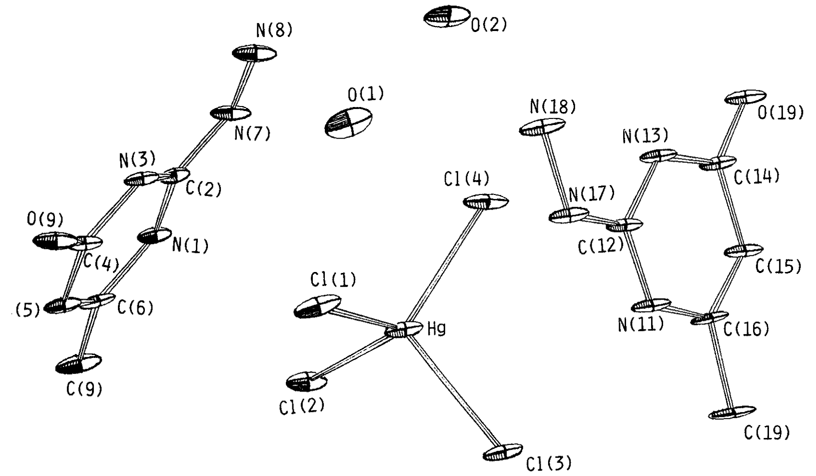

Fig. 1. Nomenclature and Perspective View of $[HgCl_4](LHH)_2 \cdot 2H_2O$ (**1**)

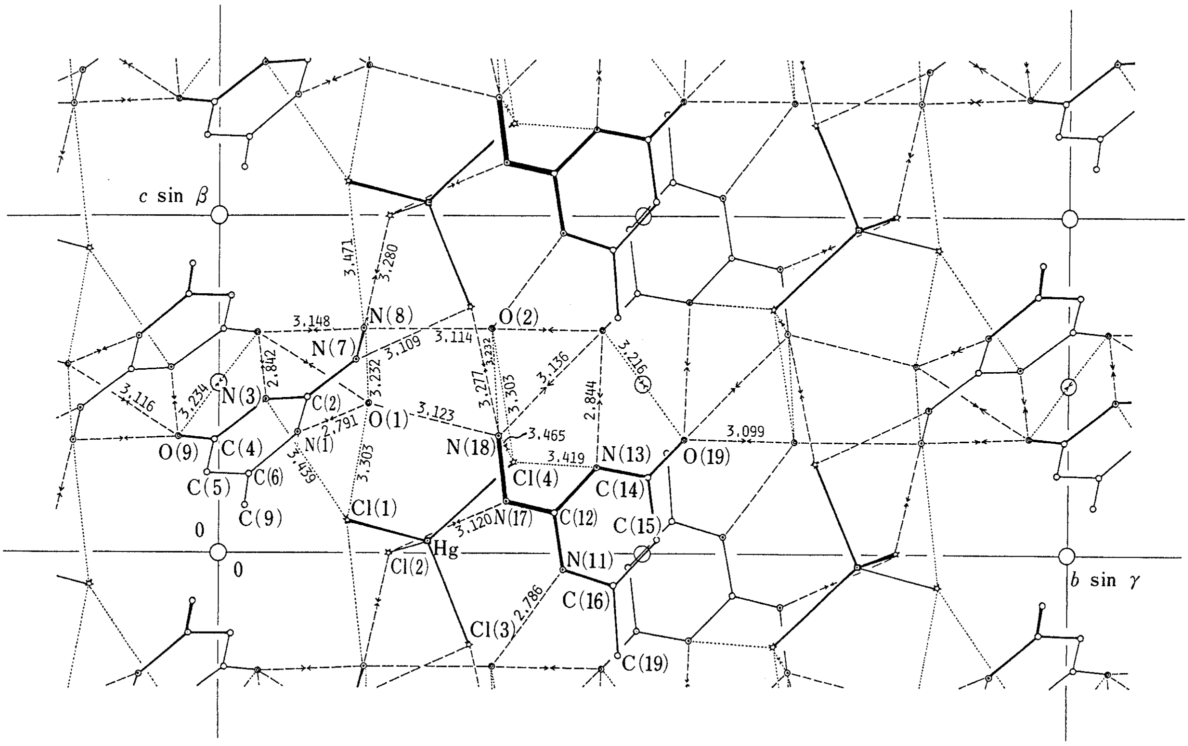

Fig. 2. Projection of the Crystal Structure along the *a* Axis in $[HgCl_4](LHH)_2 \cdot 2H_2O$ (**1**)

Centers of symmetry are denoted by ○. Hydrogen bonds are shown by broken lines, other intermolecular interactions at less than 3.5 Å are shown by dotted lines.

Description of the Structures and Discussion

Structure of $[HgCl_4](LHH)_2 \cdot 2H_2O$ (1) The mercury(II) complex (**1**) has no direct LH–metal coordinations such as were observed in $[Zn(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$[5] and $[Cu(LH)_2(H_2O)]Cl_2 \cdot 2H_2O$.[6] In the present mercury(II) complex, as in $[PtCl_6](LHH)_2$,[7] one $[HgCl_4]^{2-}$ group, two LHH^+ molecules, and two crystal water molecules are linked through hydrogen bonds to constitute a double salt complex (see Figs. 1 and 2).

The bond lengths and angles of (**1**) are listed in Table IV. The coordination distances of Hg–Cl(1), Hg–Cl(2), Hg–Cl(3), and Hg–Cl(4) are 2.463 (3), 2.482 (3), 2.481 (3), and 2.462 (3) Å, respectively. It is clear that the $[HgCl_4]^{2-}$ ion forms a regular tetrahedron as judged from the bond angles formed by the ligated Cl^- ions around mercury(II). On the other hand, the lengths of C(4)–O(9) and C(14)–O(19) in the LHH^+ ions suggest the keto form ($>C=O$ double bond), because these bond lengths are 1.218 (12) and 1.217 (11) Å, respectively. Therefore, in the complex (**1**) prepared with excess protons, the structure of LH takes the form of the LHH^+ cation in which H^+ is added to N(3) or N(1) of oxo-amino LH (Chart 1). This is further supported by the observation that the angles of C(2)–N(1)–C(6), C(2)–N(3)–C(4), C(12)–N(11)–C(16), and C(12)–N(13)–C(14) are wider than 120°, being closer to those found for the six-membered heterocyclic compounds with extra-annular hydrogen attached to the ring nitrogen.[13] From the hydrogen bonding types in the crystal structure of the complex (**1**), it is suggested that hydrogen atoms are attached to N(1), N(3), N(11), and N(13) of the pyrimidine rings (Fig. 2 and Table V).

The planarities of the two different pyrimidine rings are shown in Table VI in terms of the deviations of atoms from the least-squares planes for each of the planar groups. These pyrimidine rings N(1)–C(6) and N(11)–C(16), as well as that in platinum(IV) complex,[7] show good planarity with no strain and are different from those found in nickel(II), zinc(II),[5] and copper(II)[6] complexes involving direct metal–LH chelate bonds (Table VI).

The *a* axis projection of the crystal structure of mercury(II) complex (**1**) is shown in Fig. 2. In the unit cell, there are two complex molecules involving two $[HgCl_4]^{2-}$ anions and four LHH^+ cations. The hydrogen bonds connecting these ions are N(3)–H···O(9), N(7)–H···Cl(3), N(8)–H···Cl(2), N(8)–H···O(9), N(13)–H···O(19), N(17)–H···Cl(2), N(18)–H···Cl(3), and N(18)–H···O(19), and their lengths are shown in Table V. The other hydrogen bonds are formed through the oxygen

TABLE IV. Bond Lengths (Å) and Angles (°) with Their Estimated Standard Deviations in Parentheses

	$[HgCl_4](LHH)_2 \cdot 2H_2O$ (1)			$[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (2)	
Bond lengths					
	Hg–Cl(1)	2.463 (3)		Ni–O(0)	2.099 (4)
	Hg–Cl(2)	2.482 (3)		Ni–N(3)	2.067 (4)
	Hg–Cl(3)	2.481 (3)		Ni–N(8)	2.099 (4)
	Hg–Cl(4)	2.462 (3)			
N(1)–C(2)	1.326 (11)	N(11)–C(12)	1.356 (11)	N(1)–C(2)	1.358 (6)
N(1)–C(6)	1.392 (12)	N(11)–C(16)	1.363 (12)	N(1)–C(6)	1.392 (7)
C(2)–N(3)	1.343 (12)	C(12)–N(13)	1.346 (12)	C(2)–N(3)	1.308 (7)
C(2)–N(7)	1.339 (12)	C(12)–N(17)	1.300 (13)	C(2)–N(7)	1.363 (7)
N(3)–C(4)	1.405 (12)	N(13)–C(14)	1.381 (12)	N(3)–C(4)	1.397 (6)
C(4)–C(5)	1.432 (12)	C(14)–C(15)	1.449 (12)	C(4)–C(5)	1.439 (7)
C(4)–O(9)	1.218 (12)	C(14)–O(19)	1.217 (11)	C(4)–O(9)	1.249 (7)
C(5)–C(6)	1.347 (14)	C(15)–C(16)	1.361 (13)	C(5)–C(6)	1.346 (8)
C(6)–C(9)	1.490 (13)	C(16)–C(19)	1.508 (12)	C(6)–C(9)	1.495 (7)
N(7)–N(8)	1.419 (12)	N(17)–N(18)	1.436 (11)	N(7)–N(8)	1.432 (6)
Bond angles					
	Cl(1)–Hg–Cl(2)	106.7 (1)		O(0)–Ni–N(3)	91.5 (2)
	Cl(1)–Hg–Cl(3)	113.0 (1)		O(0)–Ni–N(3)[a]	88.5 (1)
	Cl(1)–Hg–Cl(4)	113.9 (1)		O(0)–Ni–N(8)	91.9 (2)
	Cl(2)–Hg–Cl(3)	103.2 (1)		O(0)–Ni–N(8)[a]	88.1 (2)
	Cl(2)–Hg–Cl(4)	113.0 (1)		N(3)–Ni–N(8)	79.1 (2)
	Cl(3)–Hg–Cl(4)	106.7 (1)		N(3)–Ni–N(8)[a]	100.9 (2)
				Ni–N(3)–C(2)	113.6 (3)
				Ni–N(3)–C(4)	127.0 (3)
				Ni–N(8)–N(7)	110.1 (3)
C(2)–N(1)–C(6)	121.0 (8)	C(12)–N(11)–C(16)	121.2 (8)	C(2)–N(1)–C(6)	118.9 (4)
N(1)–C(2)–N(3)	120.4 (8)	N(11)–C(12)–N(13)	118.2 (8)	N(1)–C(2)–N(3)	124.6 (5)
N(1)–C(2)–N(7)	120.0 (9)	N(11)–C(12)–N(17)	119.8 (8)	N(1)–C(2)–N(7)	114.9 (4)
N(3)–C(2)–N(7)	119.5 (8)	N(13)–C(12)–N(17)	122.0 (8)	N(3)–C(2)–N(7)	120.5 (5)
C(2)–N(3)–C(4)	122.7 (7)	C(12)–N(13)–C(14)	124.6 (7)	C(2)–N(3)–C(4)	119.1 (4)
N(3)–C(4)–C(5)	115.1 (8)	N(13)–C(14)–C(15)	115.7 (8)	N(3)–C(4)–C(5)	117.2 (4)
N(3)–C(4)–O(9)	119.1 (8)	N(13)–C(14)–O(19)	119.8 (8)	N(3)–C(4)–O(9)	118.9 (4)
C(5)–C(4)–O(9)	125.7 (9)	C(15)–C(14)–O(19)	124.5 (9)	C(5)–C(4)–O(9)	123.9 (5)
C(4)–C(5)–C(6)	120.9 (8)	C(14)–C(15)–C(16)	118.5 (9)	C(4)–C(5)–C(6)	121.3 (5)
N(1)–C(6)–C(5)	119.8 (8)	N(11)–C(16)–C(15)	121.7 (8)	N(1)–C(6)–C(5)	118.7 (7)
N(1)–C(6)–C(9)	115.7 (8)	N(11)–C(16)–C(19)	115.8 (8)	N(1)–C(6)–C(9)	114.5 (4)
C(5)–C(6)–C(9)	124.5 (9)	C(15)–C(16)–C(19)	122.5 (9)	C(5)–C(6)–C(9)	126.8 (5)
C(2)–N(7)–N(8)	118.3 (8)	C(12)–N(17)–N(18)	117.1 (8)	C(2)–N(7)–N(8)	115.6 (4)

a) Inverted by a center of symmetry at (0, 0, 0).

Table V. Important Intra- and Intermolecular Interactions less than 3.5 Å in Mercury(II) and Nickel(II) Complexes

No.	$[HgCl](LHH)_2 \cdot 2H_2O$ (**1**)	Distance (Å)	No.		Distance (Å)	No.	$[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (**2**)	Distance (Å)
1	N(3) Cl(1)$^{a)}$	3.439 (9)	13	N(13) Cl(4)$^{a)}$	3.419 (9)	1	Cl······H–N(1)$^{a)}$	3.048 (5)$^{o)}$
2	O(1) Cl(1)$^{a)}$	3.303 (10)	14	O(2) Cl(4)$^{a)}$	3.303 (9)	2	O(0)–H····O(1)$^{a)}$	2.696 (4)$^{o)}$
3	N(8) O(1)$^{a)}$	3.232 (17)	15	N(18) O(2)$^{a)}$	3.232 (16)	3	Cl······H–O(0)$^{m)}$	3.143 (4)$^{o)}$
4	N(8)····H–O(2)$^{a)}$	3.114 (14)$^{o)}$	16	N(18)···H–O(1)$^{a)}$	3.123 (14)$^{o)}$	4	N(7) O(9)$^{d)}$	3.480 (6)
5	N(3)–H····O(9)$^{g)}$	2.842 (10)$^{o)}$	17	N(13)–H···O(19)$^{b)}$	2.844 (9)$^{o)}$	5	N(8)–H····O(9)$^{d)}$	3.076 (5)$^{o)}$
6	N(8)–H····O(9)$^{g)}$	3.148 (12)$^{o)}$	18	N(18)–H···O(19)$^{b)}$	3.136 (12)$^{o)}$	6	O(1)–H····O(9)$^{d)}$	2.738 (6)$^{o)}$
7	O(9) O(9)$^{g)}$	3.234 (10)	19	O(19) O(19)$^{b)}$	3.216 (10)	7	Cl······H–N(7)$^{n)}$	3.271 (5)$^{o)}$
8	O(9)····H–O(1)$^{g)}$	3.116 (14)$^{o)}$	20	O(19)···H–O(2)$^{b)}$	3.099 (14)$^{o)}$	8	Cl N(8)$^{n)}$	3.354 (5)
9	N(7)–H····Cl(3)$^{d)}$	3.109 (9)$^{o)}$	21	N(17)–H···Cl(2)$^{c)}$	3.120 (9)$^{o)}$	9	Cl······H–O(1)$^{b)}$	3.264 (5)$^{o)}$
10	N(8) Cl(1)$^{d)}$	3.471 (11)	22	N(18) Cl(4)$^{c)}$	3.465 (12)	10	N(8)–H····O(9)$^{j)}$	2.804 (5)$^{o)}$
11	N(1)–H····O(1)$^{f)}$	2.791 (13)$^{o)}$	23	N(11)–H···O(2)$^{h)}$	2.786 (13)$^{o)}$			
12	N(8)–H····Cl(2)$^{e)}$	3.280 (9)$^{o)}$	24	N(18)–H···Cl(3)$^{e)}$	3.277 (9)$^{o)}$			

Key to the symmetry operations: *a*) x, y, z; *b*) $1-x, 1-y, 1-z$; *c*) $1+x, y, z$; *d*) $x, y, 1+z$; *e*) $1+x, y, 1+z$; *f*) $x-1, y, z$; *g*) $1-x, -y, 1-z$; *h*) $x, y, z-1$; *i*) $-x, -y, 1-z$; *j*) $-x, -y, -z$; *k*) $-1-x, -y, 1-z$; *l*) $-1-x, -y, -z$; *m*) $x, 1+y, z$; *n*) $-x, 1-y, 1-z$.
o) Hydrogen bond suggested.

Table VI. Deviations of Atoms (Å) from the Least-Squares Planes in Pyrimidine Rings

$[HgCl_4](LHH)_2 \cdot 2H_2O$ (**1**)			
N(1)	0.007	N(11)	0.003
C(2)	−0.006	C(12)	−0.008
N(3)	0.000	N(13)	0.004
C(4)	0.005	C(14)	0.005
C(5)	−0.005	C(15)	−0.010
C(6)	−0.001	C(16)	0.006
N(7)$^{a)}$	0.029	N(17)$^{a)}$	0.010
N(8)$^{a)}$	0.088	N(18)$^{a)}$	−0.016
O(9)$^{a)}$	−0.015	O(19)$^{a)}$	0.034
C(9)$^{a)}$	−0.009	C(19)$^{a)}$	−0.022
$[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (**2**)			
N(1)	−0.019	N(7)$^{a)}$	−0.014
C(2)	0.005	N(8)$^{a)}$	0.112
N(3)	0.016	O(9)$^{a)}$	−0.061
C(4)	−0.022	C(9)$^{a)}$	0.059
C(5)	0.009	Ni$^{a)}$	−0.074
C(6)	0.011		

a) These atoms were not included in the least-squares calculation.

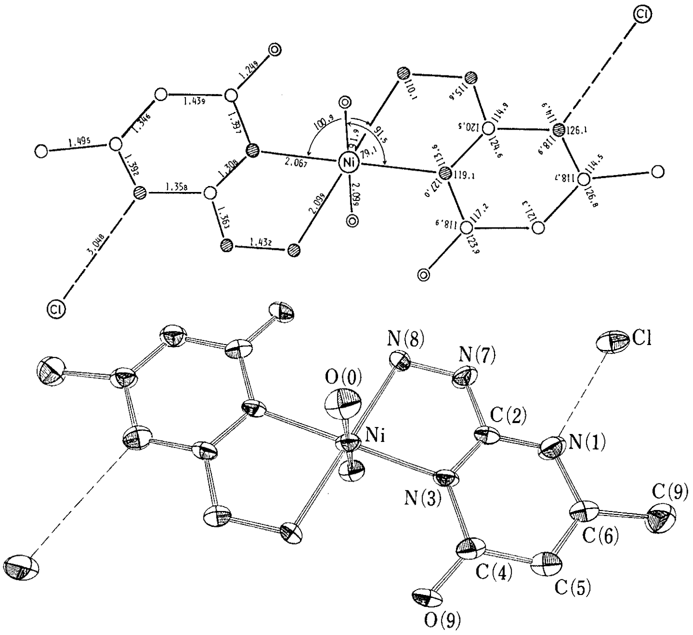

Fig. 3. Bond Lengths and Angles, and Perspective View of $[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (**2**)

The nickel(II) ion is on the crystallographic center of symmetry.

atoms of water molecules. It is notable that two different stacking modes are found between pyrimidine rings in the crystal (see Fig. 2): one is formed between pyrimidine rings arranged in parallel to each other across the center of symmetry at (0, 0, 0) and (0, 0, 1/2), and stacked along the *c* axis. These rings are separated by 3.156 and 3.390 Å, respectively. The other is formed between the pyrimidine rings arranged in parallel across the center of symmetry at (0, 1/2, 0) and (1/2, 1/2, 0), and stacked along the *a* axis. These rings are separarted by 3.205 and 3.390 Å, respectively.

Structure of $[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (2) There is one complex molecule having two five-membered chelate rings in the unit cell. The nickel(II) ion is situated at the crystallographic center of symmetry and assumes an octahedral coordination (see Fig. 3). The ligand molecule, LH is coordinated to the nickel(II) ion through N(3) of the pyrimidine ring and also through its nitrogen atom N(8) of the hydrazino group. The two LH residues are coordinated *trans* to each other, forming a square-planar coordination. The fifth and sixth coordination sites are occupied by the two water oxygen atoms.

In Table IV and Fig. 3, all the bond lengths and angles in the LH residue are listed. The bond length of C(4)–O(9) is 1.249(7) Å, indicating the keto form. As described before, the difference electron density map also showed that the hydrogen of the hydroxyl group is transferred to N(1) and forms a hydrogen bond to the chloride ion (the N(1)–H···Cl distance is 3.048(5) Å). The coordination bond lengths, Ni–O(0), Ni–N(3), and Ni–N(8) are 2.099(4), 2.067(4), and 2.099(4) Å, respectively. The planarities of the pyrimidine ring and the chelate ring are shown in Table VI in terms of the deviations of atoms from the least-squares planes for each planar group.

The *c* axis projection of the crystal structure is shown in Fig. 4. The complex ions are situated at the corners of the unit cells and are linked to the neighboring complex ions in *c* direction mainly through the hydrogen bonds. Table V lists the intra- and intermolecular interatomic distances less than 3.5 Å. In Table V, hydrogen bonds are marked by *o*). The only hydrogen bond directly connecting the

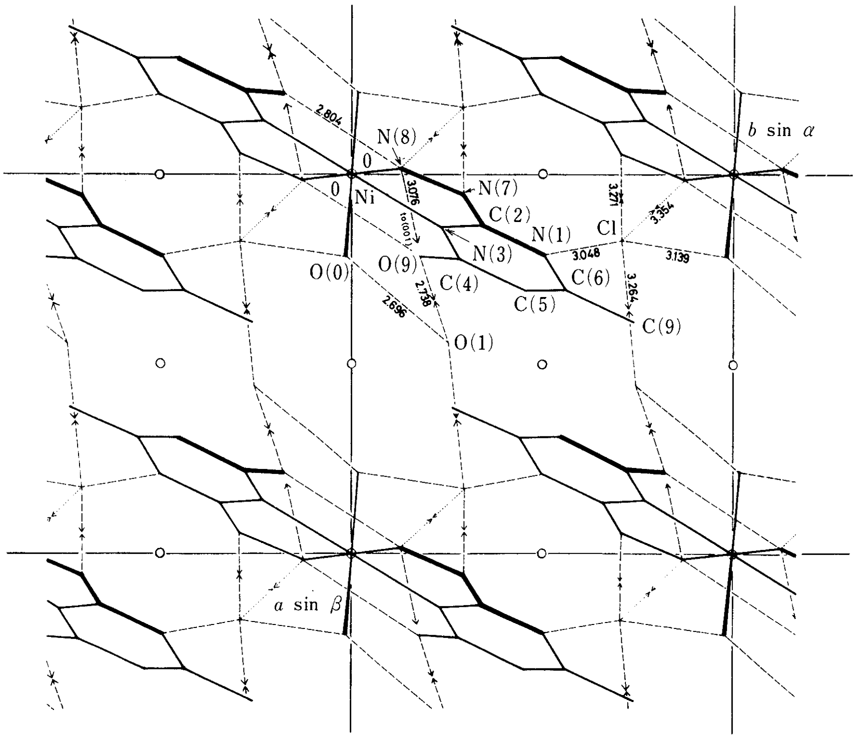

Fig. 4. Projection of the Crystal Structure along the c Axis in $[Ni(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$ (**2**)

Centers of symmetry are denoted by ○. Hydrogen bonds are shown by broken lines, other intermolecular interactions at less than 3.5 Å are shown by dotted lines.

neighboring complex ions is $N(8)–H \cdots O(9)^{d)}$ and its distance is 3.076(5) Å. The other hydrogen bonds are formed through water molecules or chloride ions. Besides the intermolecular hydrogen bonds listed in Table V, there is an intramolecular hydrogen bond $N(8)–H \cdots O(9)^{i)}$ of length 2.804(5) Å which links the two ligand LH molecules coordinated at the same nickel(II) ion. The pyrimidine rings are arranged parallel to each other across the center of symmetry at (0, 1/2, 0) and (1/2, 1/2, 0), and are stacked along the a axis with the separation of 3.525 Å.

Oxo-amino type LH in the mercury(II) complex (**1**) exists as LHH^+ cation (see Chart 1) with addition of a proton, and forms hydrogen bonds involving both N(1) and N(3), as in $[PtCl_6](LHH)_2$.7) LHH^+ cations and $[HgCl_4]^{2-}$ anions are connected by hydrogen bonds. Therefore, the present mercury(II) complex (**1**) can be described as $[HgCl_4]^{2-}(LHH^+)_2 \cdot 2H_2O$, without chelate type coordination.

Both metal–LH bonds of the chelate type (LH coordination sites are N(3) and N_{amino} of the hydrazino group) and metal–OH coordination bonds are observed in the nickel(II) complex (**2**) but there is no direct metal–Cl coordination bonding, as in $[Zn(LH)_2(H_2O)_2]Cl_2 \cdot 2H_2O$5) of octahedral six coordination or $[Cu(LH)_2(H_2O)]Cl_2 \cdot 2H_2O$6) of tetragonal-pyramidal five coordination, even if these complexes are formed under sufficient H^+Cl^- ion concentration. Accordingly, the coordination strengths of the nickel(II), zinc(II), or copper(II) ion with LH are higher than those with Cl^-, but those of mercury(II) or platinum(IV) ion with LH are reversed.

In multi-component systems consisting of base, metal ion, H_2O and Cl^-, $[Cu(Cyt)_2Cl_2]$14) complex has a direct metal–Cl coordination bond besides metal–cytosine(Cyt) coordination. By protonation of the base, $[CuCl_4](CytH)_2$15) and $[ZnCl_4]_{1/2}(Cyt) \cdot (CytH)_2$16) complexes are formed as the double salt type without metal–cytosine coordination and the structures are the double salt type, similar to those found in $[HgCl_4](LHH)_2 \cdot 2H_2O$ (**1**) and $[PtCl_6](LHH)_2$7) complexes. We suggest that the coordinations of LH to nickel(II), zinc(II), and copper(II) ions are stronger than those of cytosine prepared in the presence of excess protons.

References and Notes

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