

Bis(L-histidinato)nickel(II) Monohydrate

BY TOSIO SAKURAI AND HITOSHI IWASAKI

The Institute of Physical and Chemical Research, Rikagaku Kenkyusho, Wakoshi, Saitama 351, Japan

AND TOORU KATANO AND YUJI NAKAHASHI

Department of Engineering Chemistry, College of Science and Engineering, Nihon University, Kanda, Tokyo 101, Japan

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Abstract. $\text{Ni}(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, monoclinic, $C2$, $a = 29.406$ (4), $b = 8.2675$ (9), $c = 6.3135$ (6) Å, $\beta = 90.01$ (1)°, $U = 1534.9$ (3) Å³, $D_m = 1.66$, $D_x = 1.666$ g cm⁻³, $Z = 4$. The structure is isomorphous with the cobalt(II) complex [Harding & Long, *J. Chem. Soc. A* (1968), pp. 2554–2559]. The conformations of the histidine molecule in various complexes are shown in a conformational energy map.

Introduction. The crystal structures of histidine and its metal complexes have been extensively studied because of the importance of the imidazole moiety in various enzymatic activities. Among the metal complexes, the Ni complex with DL-histidine is known to form an orthorhombic monohydrate (Fraser & Harding, 1967). Recently, we found that the Ni complex of L-histidine crystallizes in another form with monoclinic symmetry.

Nickel carbonate was added to an aqueous solution of L-histidine and kept at 0°C for several days. Needle-shaped violet crystals were obtained. The X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer, with graphite-monochro-

matized Cu $K\alpha$ radiation. Within the range $2\theta \leq 140^\circ$, 1410 independent reflections were observed. The size of the crystal was $0.7 \times 0.3 \times 0.1$ mm, and no absorption correction was applied.

From the lattice parameters and the observed structure factor values, the structure was found to be isomorphous with the Co monohydrate complex (Harding & Long, 1968). Therefore, the structure was directly refined starting from the coordinates of the latter compound.* All H atoms were deduced from a difference Fourier synthesis. Block-diagonal least squares, with anisotropic temperature factors for all non-hydrogen atoms, reduced the R index to 2.9%. Atomic parameters are given in Table 1.†

* Because of the slight deviation of the β angle from 90°, the signs of the y and z coordinates are reversed from those of the Co complex.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33079 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

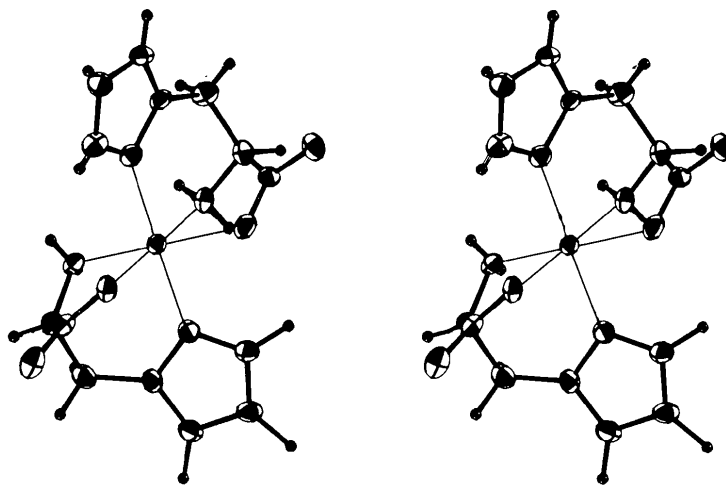


Fig. 1. A stereodrawing of bis(L-histidinato)nickel(II).

Table 1. Atomic parameters

Positional parameters are multiplied by 10^4 for non-hydrogen atoms, and by 10^3 for hydrogen atoms. Anisotropic temperature factors have been deposited,* and the equivalent temperature factors are given.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Ni	1323 (0)	0 (2)	2319 (1)	1.4
O(1A)	1374 (1)	-2485 (4)	3179 (5)	2.0
O(2A)	1795 (1)	-4589 (4)	2193 (6)	2.2
N(1A)	1386 (1)	-1101 (5)	-627 (6)	1.8
N(2A)	2034 (1)	16 (7)	2626 (5)	1.8
N(3A)	2695 (1)	75 (7)	4251 (6)	2.3
C(1A)	1615 (1)	-3238 (6)	1837 (7)	1.6
C(2A)	1705 (2)	-2468 (6)	-316 (7)	1.7
C(3A)	2200 (2)	-1859 (7)	-408 (8)	2.2
C(4A)	2336 (2)	-946 (6)	1508 (8)	1.7
C(5A)	2265 (2)	598 (7)	4257 (7)	2.1
C(6A)	2745 (2)	-908 (7)	2526 (8)	2.2
O(1B)	1267 (1)	1097 (5)	5314 (5)	1.9
O(2B)	937 (1)	3216 (5)	6822 (5)	2.5
N(1B)	1245 (1)	2408 (5)	1419 (6)	1.7
N(2B)	620 (1)	-237 (6)	2331 (6)	1.9
N(3B)	-64 (1)	-1289 (7)	2528 (6)	2.4
C(1B)	1056 (2)	2435 (7)	5238 (7)	1.7
C(2B)	934 (2)	3113 (6)	3037 (7)	1.8
C(3B)	439 (2)	2755 (7)	2404 (8)	2.3
C(4B)	306 (2)	1020 (7)	2437 (7)	1.8
C(5B)	386 (2)	-1609 (7)	2404 (8)	2.2
C(6B)	-118 (1)	349 (7)	2566 (7)	2.3
O(W)	801 (1)	-3471 (5)	6665 (6)	2.7

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(C2A)	160 (2)	-334 (9)	-131 (10)	4.5 (1.6)
H(1C3A)	238 (2)	-269 (9)	-50 (9)	3.9 (1.5)
H(2C3A)	223 (2)	-112 (9)	-171 (10)	5.4 (1.7)
H(C5A)	217 (2)	100 (7)	523 (8)	2.0 (1.1)
H(C6A)	301 (2)	-127 (8)	220 (9)	3.2 (1.3)
H(1N1A)	148 (2)	-42 (7)	-162 (8)	2.6 (1.2)
H(2N1A)	111 (2)	-151 (8)	-110 (8)	2.8 (1.2)
H(N3A)	286 (2)	12 (10)	524 (8)	3.7 (1.3)
H(C2B)	95 (3)	404 (11)	385 (13)	8.8 (2.4)
H(1C3B)	39 (2)	325 (9)	57 (10)	4.6 (1.6)
H(2C3B)	28 (3)	343 (11)	369 (11)	7.3 (2.1)
H(C5B)	50 (2)	-281 (9)	218 (10)	4.9 (1.6)
H(C6B)	-46 (2)	85 (10)	271 (11)	6.2 (1.9)
H(1N1B)	109 (2)	261 (8)	-16 (9)	3.9 (1.4)
H(2N1B)	143 (2)	290 (10)	92 (11)	6.3 (1.9)
H(N3B)	-37 (3)	-215 (11)	267 (12)	9.1 (2.5)
H(10W)	99 (2)	-320 (10)	576 (11)	5.6 (1.9)
H(20W)	78 (2)	-414 (10)	670 (11)	6.1 (2.0)

* See footnote on p. 660.

Discussion. The Ni atom is octahedrally coordinated (Fig. 1). The octahedron is slightly deformed. The bond lengths and angles shown in Fig. 2 are similar to those of the orthorhombic Ni complex. The metal–N distance (*ca* 2.09 Å in the present case) is slightly shorter than the 2.17 Å found in the Co complex. As a ligand, the histidine molecule is known to have four different forms (Table 2). The first (which occurs in Ni and Co complexes) is tridentate with O(1), N(1) and

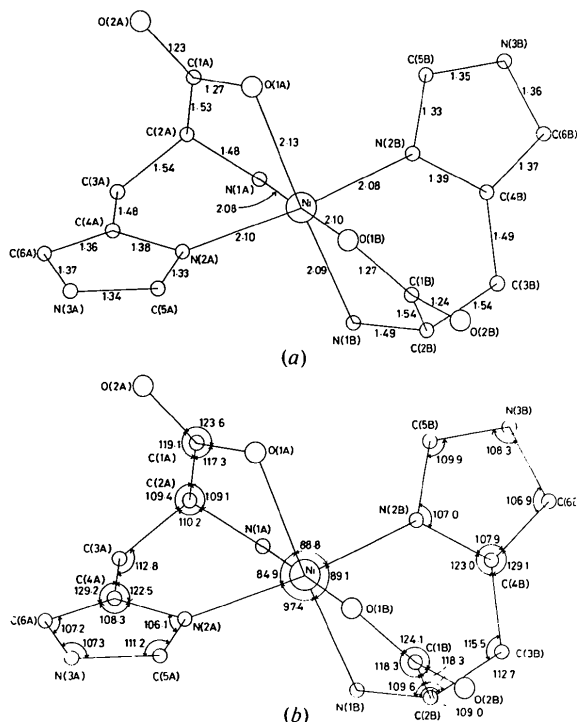


Fig. 2. (a) Bond distances (Å). Standard deviations are: 0.006 Å for metal–other-atom distances; 0.008 Å for distances between non-metal atoms. (b) Bond angles (°). Standard deviations are: 0.2° for the metal atom at the apex; 0.5° for others.

N(2) coordinating to the metal atom at almost equal distances. The second (which appears in Zn and Cd complexes) is also tridentate, but the metal–O(1) distance is considerably longer than metal–N distances. The third (in the Cu complex) is bidentate with O(1) and N(1) coordinating to the metal atom. The fourth (in the HgCl₂ complex) is monodentate with O(2) coordinating to the metal atom.*

Depending on these different environments, the histidine molecule is known to have various 'closed' or 'open' conformations. The main flexibility is due to the rotations about two single bonds: C(2)–C(3) and C(3)–C(4). In order to see the relation between the various conformations, the intramolecular van der Waals energy was calculated for the rotation about the C(2)–C(3) and C(3)–C(4) bonds (Sakurai & Kobayashi, 1972). For this calculation, planarity of the N–C–CO₂ moiety was assumed, and the possibility of a hydrogen bond was neglected. The result is shown in Fig. 3. There are many low-energy regions in this map. The tridentate forms are 'folded', a conformation which is limited to a very narrow region of (–)-*gauche*–(–)-*gauche*. This is because the orientation of the

* Since the structure has pseudo mirror planes, and the possibility of random distribution could not be completely ruled out, this structure is omitted from further discussion.

Table 2. Comparison of important torsion angles in the various conformations of L-histidine

Complex	Coordination number	Coordination atoms	C(1)–C(2)–C(3)–C(4)	C(2)–C(3)–C(4)–N(2)	O(1)–C(1)–C(2)–N(1)	References
Ni(L-hi) ₂	3	O(1), N(1), N(2)	-47°	-33°	-14°	Present work
Ni(hi) ₂			-56	-21	-23	
Co(L-hi) ₂			-57	-21	-14	Fraser & Harding (1967) Harding & Long (1968)
Co(DL-hi)			-48	-27	-10	
Zn(L-hi) ₂			-53	-22	-21	
Cd(L-hi) ₂	-58	-19	-15	Candlin & Harding (1970) Harding & Cole (1963)		
Cu(L-hi) ₂	3	N(1), N(2), O(1)	-49		-42	-4
	2	O(1), N(1)	-43	-55	-24	Fuess & Bartunik (1976) Evertsson (1969)
			-178	126	17	
HgCl ₃ (L-hi)	1	O(2)	-179	-62	19	Adams, Hodgkin & Raeburn (1970) Oda & Koyama (1972); Fuess, Hohlwein & Mason (1977)
L-hi.HCl			-174	87	87	
L-hi (orthorhombic)			-53	-120	-2	Madden, McGandy & Seeman (1972) Madden, McGandy, Seeman, Harding & Hoy (1972)
L-hi (monoclinic)			181	57	-27	
			181	53	-28	

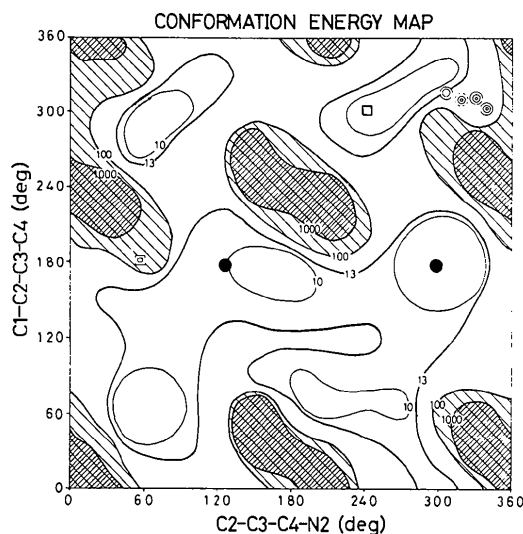


Fig. 3. Intramolecular van der Waals energy. Energies are calculated between the imidazole ring and other parts of the molecule, and the values on the map are kcal mol⁻¹. ⊙ ⊗ ⊛ ⊠ Tridendate complex. ● Bidentate complex. □ Histidine hydrochloride. ⊙ L-Histidine with an intramolecular hydrogen bond.

imidazole ring is restricted by the formation of the complex. The van der Waals energy at this region is slightly higher than the other energy minima. However, this situation may be relieved by the deviation of the N–C–CO₂ moiety from planarity. In the Cu complex, and in the hydrochloride, the orientation of the imidazole ring is not restricted by complex formation, and the conformation is distributed in various minima in the energy map. The choice between these minima depends on the intermolecular interaction in the crystals. In natural L-histidine, because of the formation

of the intramolecular hydrogen bond between N(1) and N(2), which was not accounted for in this calculation, the conformation appears at a higher energy region in this map.

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References

- ADAM, M. J., HODGKIN, D. C. & RAEBURN, U. A. (1970). *J. Chem. Soc. A*, pp. 2632–2635.
- CANDLIN, R. & HARDING, M. M. (1970). *J. Chem. Soc. A*, pp. 384–393.
- EVERTSSON, B. (1969). *Acta Cryst.* B25, 30–41.
- FRASER, K. A. & HARDING, M. M. (1967). *J. Chem. Soc. A*, pp. 415–420.
- FUESS, H. & BARTUNIK, H. (1976). *Acta Cryst.* B32, 2803–2806.
- FUESS, H., HOHLWEIN, D. & MASON, S. A. (1977). *Acta Cryst.* B33, 654–659.
- HARDING, M. M. & COLE, S. J. (1963). *Acta Cryst.* 16, 643–650.
- HARDING, M. M. & LONG, H. A. (1968). *J. Chem. Soc. A*, pp. 2554–2559.
- MADDEN, J. J., MCGANDY, E. L. & SEEMAN, N. C. (1972). *Acta Cryst.* B28, 2377–2382.
- MADDEN, J. J., MCGANDY, E. L., SEEMAN, N. C., HARDING, M. M. & HOY, A. (1972). *Acta Cryst.* B28, 2382–2389.
- ODA, K. & KOYAMA, H. (1972). *Acta Cryst.* B28, 639–642.
- SAKURAI, T., IWASAKI, H., WATANABE, Y., KOBAYASHI, K., BANDO, Y. & NAKAMICHI, Y. (1974). *Rep. Inst. Phys. Chem. Res.* 50, 75–91.
- SAKURAI, T. & KOBAYASHI, K. (1972). *Rep. Inst. Phys. Chem. Res.* 48, 133–142.