

and magnetic data. The two O atoms are crystallographically equidistant from the Ni atom. The observed O–O distance of 1.45 (1) Å is close to the value of 1.45 (4) Å found in [Pt(O₂)(PPh₃)₂].1.5C₆H₆ (Kasai, Kashiwagi, Yasuoka, Kakudo, Takahashi & Hagihara, 1969); these values correspond to those in O₂²⁻ (1.49 Å) (Herzberg, 1950) and in excited O₂(³Σ_u⁺)* (1.42 Å) (Herzberg, 1950) rather than that in free oxygen (1.21 Å). Thus the lengthening of the O–O bond on coordination and the geometry of the Ni–O₂ group may be accommodated within the usual description of π-bonding of an olefin to a transition metal. Table 2 summarizes the stereochemistry of the metal–O₂ segments and the properties of oxygen uptake in dioxygen complexes obtained so far.

The observed Ni–O distance is somewhat shorter than the single-bond distance predicted by summing the covalent radii: 1.35 Å for Ni (Andrianov, Biryukov & Struchkov, 1969) and 0.66 Å for O. The Ni–C and C≡N distances compare with the corresponding bond lengths of 1.866 (5) and 1.143 (5) Å in Ni [(CN)₂C=C(CN)₂] [t-BuNC]₂ (Stalick & Ibers, 1970), and 1.841 (5) and 1.156 (5) Å in Ni(PhN=NPh) [t-BuNC]₂ (Dickson & Ibers, 1972).

The crystal structure viewed along *c* is shown in Fig. 2. In the crystal the complex molecules lie on the mirror planes at *z/c* = ¼ and ¾ to form a layer structure, the interlayer spacing being *c*/2 = 3.53 Å. No unusual intermolecular contacts were found in contrast to previous inferences from the spectroscopic study (Otsuka *et al.*, 1969, 1971).

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* An MO calculation on the Ni(O₂)(HNC)₂ model with the INDO approximation shows that the coordinated oxygen molecule assumes an excited O₂(³Σ_u⁺) character (Tatsumi, Fueno, Nakamura & Otsuka, 1975).

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Tetraimidazolezinc(II) Perchlorate

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Abstract. C₁₂H₁₆ZnCl₂O₈N₈, monoclinic, *C*2/*c*, *a* = 18.113 (9), *b* = 7.107 (2), *c* = 20.163 (9) Å, β = 117.58 (9)°, *U* = 2300.4 Å³, *Z* = 4, *D*_x = 1.55, *D*_m = 1.60 (3) g cm⁻³, *F*(000) = 1120. The Zn atom lies on a twofold axis and is approximately tetrahedrally

coordinated by four imidazole molecules. The independent Zn–N distances are 1.997 (7) and 2.001 (7) Å.

Introduction. Crystals of the compound are colourless, ill-formed plates, generally elongated parallel to the *b*

Table 1. *Positional and thermal parameters*

Numbers in parentheses denote e.s.d.'s right-adjusted to the least significant digit of the preceding values. The temperature factors have the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	10^4x	10^4y	10^4z	$10^4\beta_{11}$	$10^3\beta_{22}$	$10^4\beta_{33}$	$10^3\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Zn	0	632 (2)	2500	42 (1)	19.9 (3)	39 (1)	0	9.7 (4)	0
Cl	1372 (2)	2499 (4)	765 (1)	58 (2)	33.2 (7)	42 (1)	2.9 (3)	13 (1)	-17 (2)
O(1)	588 (6)	3308 (16)	411 (4)	93 (6)	97 (4)	73 (3)	20 (1)	-8 (4)	-95 (9)
O(2)	1398 (6)	1017 (14)	319 (4)	122 (7)	82 (4)	73 (3)	20 (1)	-15 (4)	-125 (9)
O(3)	1962 (8)	3854 (19)	830 (6)	146 (8)	99 (5)	107 (5)	-15 (2)	58 (5)	10 (10)
O(4)	1635 (6)	1925 (13)	1500 (4)	128 (7)	71 (3)	55 (2)	-1 (1)	22 (4)	15 (8)
N(1)	903 (5)	2221 (9)	3269 (3)	52 (5)	25 (2)	45 (3)	-1.7 (7)	14 (3)	-23 (5)
N(2)	2085 (6)	3737 (13)	3873 (6)	67 (6)	34 (2)	76 (4)	-5 (1)	13 (4)	-6 (8)
N(3)	512 (4)	-1073 (8)	2039 (3)	52 (4)	23 (2)	37 (2)	0.7 (6)	8 (2)	-11 (5)
N(4)	681 (6)	-2950 (13)	1244 (5)	84 (6)	39 (2)	61 (4)	-0 (1)	34 (4)	-35 (7)
C(1)	1640 (8)	2593 (13)	3275 (6)	59 (6)	31 (2)	69 (5)	-6 (1)	28 (4)	-37 (8)
C(2)	1640 (10)	4073 (15)	4242 (6)	94 (9)	35 (3)	64 (5)	-4 (1)	35 (5)	-56 (9)
C(3)	887 (8)	3141 (16)	3872 (6)	82 (7)	38 (3)	69 (5)	-3 (1)	31 (5)	-58 (9)
C(4)	197 (6)	-1575 (14)	1313 (5)	59 (6)	32 (2)	51 (4)	-2 (1)	17 (4)	-33 (7)
C(5)	1340 (7)	-3310 (15)	1946 (6)	82 (7)	37 (3)	62 (4)	2 (1)	25 (5)	-22 (9)
C(6)	1231 (6)	-2143 (13)	2436 (5)	65 (6)	34 (2)	52 (4)	4 (1)	12 (4)	-2 (8)

Table 2. *Dimensions of Zn(ImH)₄(ClO₄)₂*

Symmetry code

(') $\bar{x}, y, \frac{1}{2} - z$; (") $\frac{1}{2} - x, y, \frac{1}{2} - z$; (""') $\frac{1}{2} + x, \bar{y}, \frac{1}{2} + z$ with respect to the coordinates listed in Table 1.

(a) Bonds and hydrogen bonds

Zn—N(1)	2.001 (7) Å	Zn—N(3)	1.997 (7) Å	Cl—O(1)	1.368 (8) Å
N(1)—C(1)	1.36 (1)	N(3)—C(4)	1.35 (1)	Cl—O(2)	1.400 (7)
C(1)—N(2)	1.37 (1)	C(4)—N(4)	1.36 (1)	Cl—O(3)	1.40 (1)
N(2)—C(2)	1.35 (1)	N(4)—C(5)	1.39 (1)	Cl—O(4)	1.392 (8)
C(2)—C(3)	1.38 (1) _s	C(5)—C(6)	1.37 (1)	N(2)···O(2'')	2.95 (2)
N(1)—C(3)	1.39 (1)	N(3)—C(6)	1.40 (1)	N(4)···O(4'')	3.06 (2)

(b) Angles

N(1)—Zn—N(1')	113.3 (3)°	N(3)—Zn—N(3')	105.3 (3)°
N(1)—Zn—N(3)	108.3 (3)	N(1)—Zn—N(3')	111.8 (3)
Zn—N(1)—C(1)	124.4 (7)	Zn—N(3)—C(4)	127.6 (6)
Zn—N(1)—C(3)	127.0 (8)	Zn—N(3)—C(6)	125.1 (6)
C(1)—N(1)—C(3)	109 (1)	C(4)—N(3)—C(6)	106.9 (8)
N(1)—C(1)—N(2)	107.5 (9)	N(3)—C(4)—N(4)	109.4 (8)
C(1)—N(2)—C(2)	110 (1)	C(4)—N(4)—C(5)	108.5 (8)
N(2)—C(2)—C(3)	108.0 (9)	N(4)—C(5)—C(6)	106.2 (9)
C(2)—C(3)—N(1)	106 (1)	C(5)—C(6)—N(3)	108.9 (8)
O(1)—Cl—O(2)	108.2 (5)	C(1)—N(2)···O(2'')	146.5 (8)
O(1)—Cl—O(3)	108.6 (8)	C(2)—N(2)···O(2'')	103.9 (9)
O(1)—Cl—O(4)	115.7 (7)	N(2)···O(2'')—Cl''	111.0 (7)
O(2)—Cl—O(3)	109.1 (8)	C(4)—N(4)···O(4'')	88.7 (8)
O(2)—Cl—O(4)	111.6 (6)	C(5)—N(4)···O(4'')	162.2 (9)
O(3)—Cl—O(4)	103.4 (6)	N(4)···O(4'')—Cl''	126.9 (7)

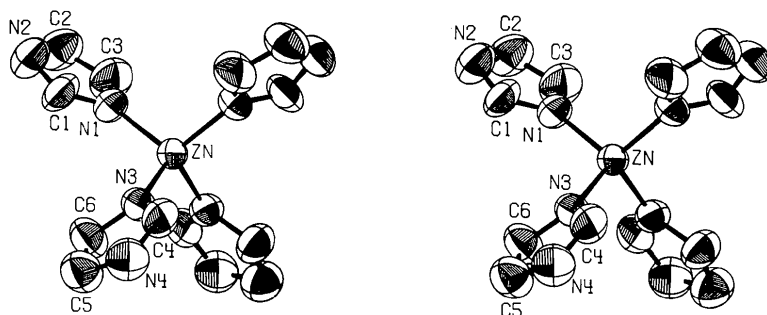


Fig. 1. Stereoscopic view of one Zn(ImH)_4^{2+} ion, showing vibrational ellipsoids (50% probability level). The twofold axis is vertical.

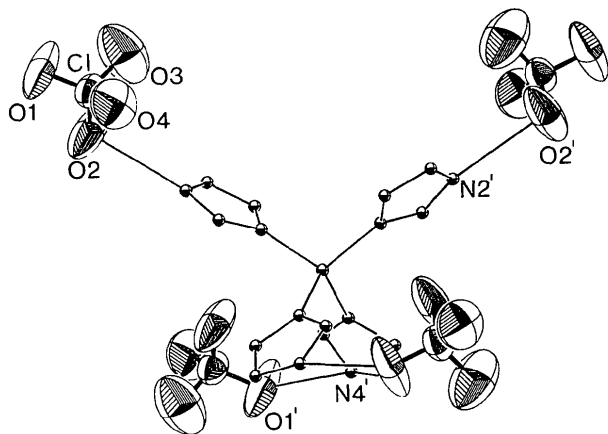


Fig. 2. Hydrogen bonding from one $\text{Zn}(\text{ImH})_2^+$ cation to four perchlorate ions. Only the atoms of the perchlorate ions are represented by their vibrational ellipsoids (50% probability level).

axis. The maximum dimensions of the crystals chosen for data collection were $0.04 \times 0.18 \times 0.12$ mm and $0.23 \times 0.35 \times 0.40$ mm, respectively, with the second dimension in each case parallel to **b**. The intensities of the reflexions were measured on a computer-controlled Supper equi-inclination diffractometer (Freeman, Guss, Nockolds, Page & Webster, 1970). The layers $h0l-h4l$ (1328 reflexions) and $0kl-10kl$ (1694 reflexions) were recorded by the usual ω -scan method using Mo $K\alpha$ radiation. The intensity I of a reflexion with an integrated peak count P and background counts B_1 and B_2 was given by $I = P - (B_1 + B_2)$ with variance $\sigma^2(I) = P + B_1 + B_2$. Reflexions for which $I < 3.5\sigma(I)$ were considered to be unobservably weak. After correction for Lorentz and polarization factors the two data sets were placed on a common scale by the method of Rae & Blake (1966). Absorption corrections were not applied [$\mu(\text{Mo } K\alpha) = 14.1 \text{ cm}^{-1}$]. There were 2092 independent reflexions. The intensities of 1057 reflexions were above the observable threshold. The structure was solved by standard Patterson and Fourier methods and subjected to full-matrix least-squares refinement. The function minimized was $\sum w(\Delta F)^2$. In the final cycles all atoms had anisotropic thermal parameters. The H positions were not determined. The final value of the residual $R = \sum |F_o| - |F_c| / \sum |F_o|$ was 0.071, and the weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ was 0.078. The positional and vibrational parameters are listed in Table 1.*

Discussion. The Zn atom lies on a twofold axis. It is bonded to N atoms of four imidazole molecules (see Fig. 1). The N–Zn–N angles are all within 4.1° of the value 109.4° expected for a tetrahedral coordination

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31254 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

geometry (Table 2). The average of the two crystallographically independent Zn–N(imidazole) bond lengths is 1.999 \AA . Values found in other tetrahedral complexes of zinc are: * $1.99 (1) \text{ \AA}$ in $[\text{Zn}(\text{Im})_2]_\infty$ (Strandberg, Svensson & Brändén, 1966), $2.01 (1) \text{ \AA}$ in $\text{Zn}(\text{ImH})_2\text{Cl}_2$ (Lundberg, 1966), $2.034 (8) \text{ \AA}$ in $\text{Zn}(\text{L-His})_2 \cdot 2\text{H}_2\text{O}$ (Kistenmacher, 1972), and $2.00 (1) \text{ \AA}$ in $\text{Zn}(\text{L-His})(\text{D-His}) \cdot 5\text{H}_2\text{O}$ (Harding & Cole, 1963). The Zn–N(imidazole) bond lengths in $\text{Zn}(\text{ImH})_6\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ are in the range $2.15\text{--}2.26 (3) \text{ \AA}$ (Sandmark & Brändén, 1967), so that there is a significant increase when Zn adopts an octahedral coordination geometry. A similar difference exists between the mean Co–N(imidazole) bond lengths in tetrahedral and octahedral cobalt(II) complexes, 1.99 and 2.17 \AA , respectively (Gadet, 1974; Gadet & Soubeyran, 1974).

The dimensions of the imidazole rings do not differ significantly from those found in more precise determinations [summarized by Freeman, Huq, Rosalky & Taylor (1975)]. The imidazole rings are planar within the limits of precision of the determination. The Zn atom is displaced insignificantly (0.02 \AA) from the plane through N(1)C(1)N(2)C(2)C(3), and 0.21 \AA from the plane through N(3)C(4)N(4)C(5)C(6).

Fig. 2 illustrates the hydrogen bonds from the imidazole 'pyrrole' N atoms to perchlorate ions: N(2)–H...O(2) [$\frac{1}{2} - x, y, \frac{1}{2} - z$] = $2.95 (2) \text{ \AA}$, and N(4)–H...O(1) [$\frac{1}{2} + x, \bar{y}, \frac{1}{2} + z$] = $3.06 (2) \text{ \AA}$. The perchlorate ions are close to tetrahedral with O–Cl–O angles of $103.4\text{--}115.7^\circ$ (Table 2). The temperature factors of the O(perchlorate) atoms are large, but the disorder which often affects perchlorate ions is not observed.

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* Abbreviations: ImH = neutral imidazole, $\text{C}_3\text{N}_2\text{H}_4$; His[−] = histidinate anion, $\text{NH}_2\text{--CH}(\text{--CH}_2\text{--C}_3\text{N}_2\text{H}_3)\text{COO}^-$.

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