Dioxygen-bis-(t-butylisocyanide)nickel

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Abstract. $C_{10}H_{18}N_2O_2Ni$, orthorhombic, *Cmcm*, $a = 11\cdot53$ (1), $b = 16\cdot55$ (2), $c = 7\cdot05$ (5) Å (at $-25°C$), $Z = 4$, $D_x = 1\cdot27$ g cm^{-3}. The molecular symmetry is *mm* (C_{2v}). The dioxygen ligand coordinates to the Ni atom 'side-on', the O–O bond length being $1\cdot45$ (1) Å.

Introduction. Single crystals grown from a toluene solution were pale-green prisms elongated along [001]. The very air-sensitive and thermally unstable crystal was sealed in a nitrogen-filled glass capillary tube and exposed to X-rays at $-25°C$. Owing to the deterioration observed even at the low temperature, the specimen was replaced after every exposure of a Weissenberg layer. Intensities were estimated visually from multiple-film equi-inclination Weissenberg photographs ($hk0 \sim$

*hk*6) taken with Co-filtered Ni *Kα* radiation. Observed systematic extinctions yielded three possible space groups, *Cmcm*, *C2cm* and *Cmc2*$_1$; the latter two were eliminated in the interpretation of a Patterson map and by significance tests on the crystallographic *R* index (Hamilton, 1965).

The structure was solved by the heavy-atom method, and the atomic parameters together with the inter-layer scale factors were refined by the block-diagonal least-squares method. Anisotropic thermal vibrations were assumed for the non-hydrogen atoms. Not all of the H atoms were fully revealed from difference maps. The final refinements were carried out to give an *R* value $\sum||F_o| - |F_c||/\sum|F_o|$, and an R_w value, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0·097 and 0·123 respectively for the 469 non-zero reflexions. The weighting scheme $1/w = a + |F_o| + c|F_o|^2$ was assumed (Cruickshank, 1961), where $a = 2|F_o|_{min} = 2\cdot35$ and $c = 2/|F_o|_{max} = 0\cdot048$. The atomic scattering factors of Cromer & Waber (1965) were used and the values for the anomalous dispersion terms were taken from the calculations of Cromer & Liberman (1970). All the numerical calculations were carried out on a FACOM 270-20 computer of this University using the programs written in our laboratory. The resulting positional and thermal parameters are given in Table 1.*

Discussion. The complex, Ni(O$_2$) (t-BuNC)$_2$, prepared by irreversible oxygenation of Ni(t-BuNC)$_4$ exhibits interesting chemical properties (Otsuka, Nakamura & Tatsuno, 1969; Otsuka, Nakamura, Tatsuno & Yamamoto, 1971) and the present study has been undertaken
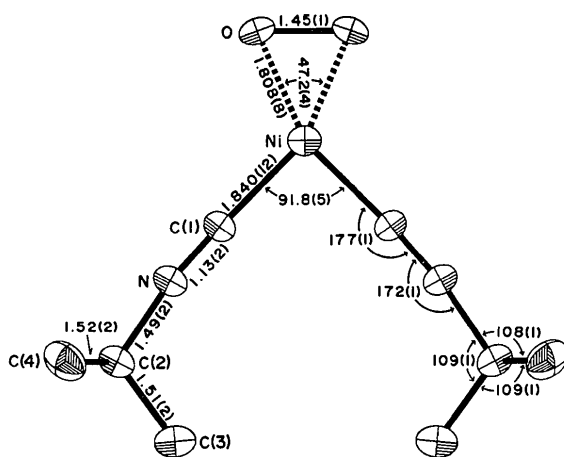

Fig. 1. The molecular structure of Ni(O$_2$) (t-BuNC)$_2$ viewed perpendicular to the molecular plane. Thermal ellipsoids are scaled to include 50% probability. In both t-Bu groups the third methyl C atoms are not depicted because of overlap with the C(4) atoms caused by the horizontal mirror plane.

Table 1. *Final atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^4$)

The estimated standard deviations are in parentheses. The temperature factors are of the form

$$\exp\left[-2\pi^2(a^{*2}h^2 U_{11} + b^{*2}k^2 U_{22} + c^{*2}l^2 U_{33} + 2a^*b^*hk U_{12} + 2b^*c^*kl U_{23} + 2a^*c^*hl U_{13})\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ni	0	806 (1)	2500	865 (14)	624 (11)	628 (14)	0	0	0
O	628 (8)	1808 (5)	2500	945 (55)	519 (42)	1000 (64)	−173 (41)	0	0
C(1)	1146 (10)	32 (7)	2500	742 (63)	660 (57)	560 (56)	115 (63)	0	0
N	1811 (9)	−472 (6)	2500	844 (67)	652 (54)	737 (65)	149 (56)	0	0
C(2)	2544 (13)	−1211 (8)	2500	946 (86)	707 (71)	771 (79)	158 (71)	0	0
C(3)	1763 (16)	−1941 (9)	2500	1294 (125)	684 (82)	1207 (131)	−60 (92)	0	0
C(4)	3205 (14)	−1207 (7)	689 (18)	1342 (95)	1103 (82)	1067 (84)	345 (77)	101 (68)	401 (81)

to obtain a structural basis for the chemistry of diox-ygen–transition metal complexes.

Fig. 1 shows the molecular structure with crystallo-graphic symmetry *mm* (C_{2v}). With the 'side-on' coor-dinated dioxygen ligand the Ni atom has a square planar coordination. The molecular geometry thus established is essentially in agreement with that de-duced by Otsuka *et al.* (1969) from the spectroscopic

Table 2. *Geometry and chemical properties of the 'side-on' coordinated dioxygen complexes*

Complex	O–O	M–O	O–M–O	Oxygen uptake*	Ref-erence
$Ir(O_2)Cl(CO)(PPh_3)_2$	1·30 (3) Å	2·09 (3) Å 2·04 (3)	36·7 (9)°	*R*	*a*
$Ir(O_2)Cl(CO)(PPh_2Et)_2$	1·461 (14)	2·084 (10) 2·036 (10)	41·5§	*R*	*b*
$[Ir(O_2)I(CO)(PPh_3)_2].CH_2Cl_2$	1·51 (3)	2·04 (2) 2·08 (2)	43·0 (7)	*I*	*c*
$[Ir(O_2)(diphos†)_2][PF_6]$	1·63 (2)	1·96 (2) 1·99 (2)	48·6 (7)	*I*	*d*
$[Rh(O_2)(diphos†)_2][PF_6]$	1·42 (1)	2·03 (1) 2·03 (1)	41·0 (3)	*R*	*e*
$[Pt(O_2)(PPh_3)_2].1·5C_6H_6$	1·45 (4)	2·01 (2) 2·01 (3)	43 (1)	*I*	*f*
$[Pt(O_2)(PPh_3)_2].2CHCl_3$	1·505 (16)	2·006 (7)	44·06 (40)	*I*	*g*
$[Co(O_2)(2=phos‡)_2][BF_4]$	1·420 (10)	1·871 (7) 1·902 (7)	44·2§	*I*	*h*
$Ni(O_2)(t-BuNC)_2$	1·45 (1)	1·808 (8)	47·2 (4)	*I*	*i*

References: (*a*) La Placa & Ibers (1965). (*b*) Weininger, Taylor & Amma (1971). (*c*) McGinnety, Doedens & Ibers (1967). (*d*) McGinnety & Ibers (1968); Ibers, McGinnety & Payne (1969). (*e*) Ibers, McGinnety & Payne (1969). (*f*) Kasai, Kashiwagi, Yasuoka, Kakudo, Takahashi & Hagihara (1969). (*g*) Cheng, Cook, Nyburg & Wan (1971). (*h*) Terry, Amma & Vaska (1972). (*i*) Present work.

  * *R*: reversible, *I*: irreversible.
  † diphos: $Ph_2PCH_2CH_2PPh_2$.
  ‡ 2=phos: *cis*-$[(C_6H_5)_2PCH=CHP(C_6H_5)_2]$.
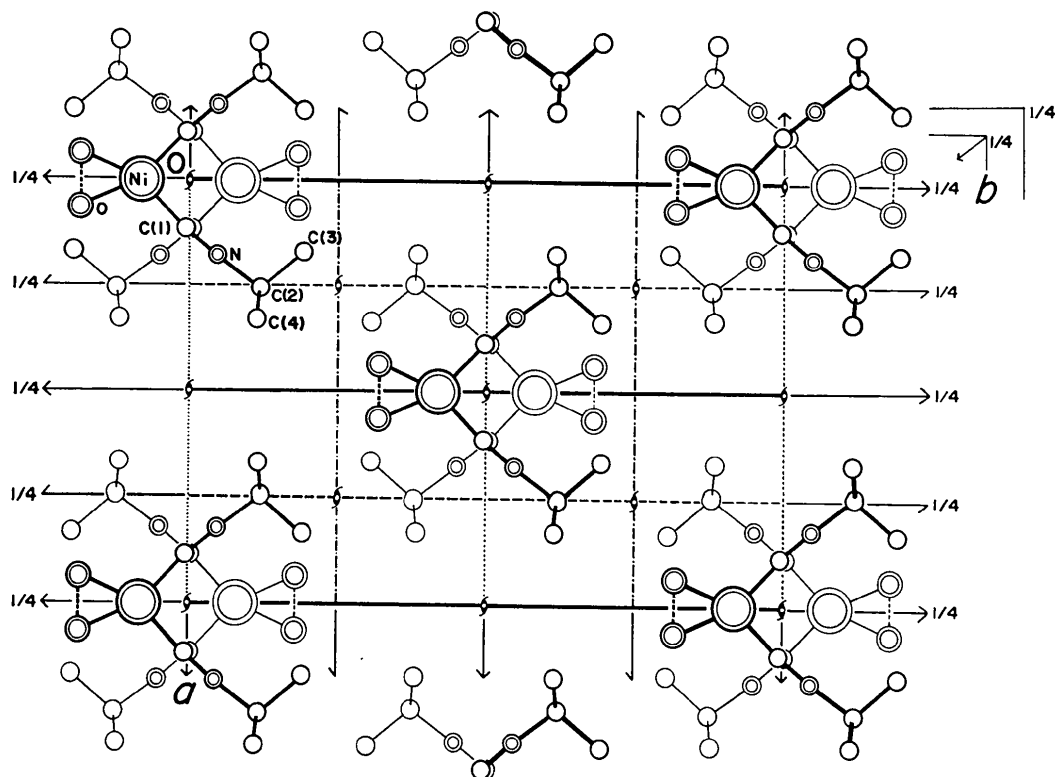 § Calculated by the present authors.

Fig. 2. The crystal structure projected along *c*.

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(O$_2$) (PPh$_3$)$_2$].1·5C$_6$H$_6$ (Kasai, Kashiwagi, Yasuoka, Kakudo, Takahashi & Hagihara, 1969); these values correspond to those in O$_2^-$ (1·49 Å) (Herzberg, 1950) and in excited O$_2$($^3\Sigma_u^+$)* (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–O$_2$ 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–O$_2$ 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)$_2$C=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 $z/c = \frac{1}{4}$ and $\frac{3}{4}$ to form a layer structure, the interlayer spacing being $c/2 = 3\cdot53$ Å. No unusual intermolecular contacts were found in contrast to previous inferences from the spectroscopic study (Otsuka et al., 1969, 1971).

* An MO calculation on the Ni(O$_2$) (HNC)$_2$ model with the INDO approximation shows that the coordinated oxygen molecule assumes an excited O$_2$($^3\Sigma_u^\pm$) character (Tatsumi, Fueno, Nakamura & Otsuka, 1975).

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Tetraimidazolezinc(II) Perchlorate

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Abstract. C$_{12}$H$_{16}$ZnCl$_2$O$_8$N$_8$, monoclinic, $C2/c$, $a = 18\cdot113$ (9), $b = 7\cdot107$ (2), $c = 20\cdot163$ (9) Å, $\beta = 117\cdot58$ (9)°, $U = 2300\cdot4$ Å^3, $Z = 4$, $D_x = 1\cdot55$, $D_m = 1\cdot60$ (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