The Crystal and Molecular Structure of Bis-(1-methyl-3-*o*-chlorophenyltriazene 1-oxide)nickel(II)

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Crystals of bis-(1-methyl-3-*o*-chlorophenyltriazene 1-oxide)nickel(II) are monoclinic, space group $P2_1/c$, $a = 12\cdot189$, $b = 6\cdot434$, $c = 13\cdot316$ Å, $\beta = 123\cdot1°$. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares technique. The final R index is 0·093. Two ligands in the molecule are related by a centre of symmetry, and act as bidentate with oxygen and nitrogen as coordinating atoms. The coordination around nickel is slightly distorted square planar. The N–Ni–O angle is 84·4° and the Ni–O and Ni–N bond lengths are 1·84 and 1·85 Å respectively. All bond lengths and angles in the molecule are normal.

Introduction

Zacharias & Chakravorty (1971) prepared a series of complexes, shown in Fig. 1, and found that all cobalt complexes, with the exception of one with iodine, were paramagnetic with magnetic moments ranging from 4·7–4·9 B.M. This, coupled with the spectroscopic evidence, led them to conclude that there was pseudo-octahedral coordination around cobalt. A similar structure was postulated for paramagnetic nickel complexes ($X = OCH_3$, OC_2H_5, SCH_3).

Nickel(II) complexes in which X = halogen are diamagnetic in the solid state but become partially paramagnetic in solution (0·5 to 1·5 B.M.).On the basis of spectrophotometric work Zacharias & Chakravorty (1971) postulated that there was a solution equilibrium between the diamagnetic square planar and pseudo-octahedral structure. The halogen suitably attached to the aromatic ring of triazene 1-oxide may take a pseudooctahedral coordination position with cobalt as well as with nickel but the extent of coordination is greater in the former than in the latter. This expectation was confirmed by the crystal structure analysis of bis-(1-methyl-3-*o*-chlorophenyltriazene 1-oxide)cobalt-(II) (Dwivedi & Srivastava, 1971) in which the chlorine atom coordinates weakly with cobalt (Cl–Co distance 2·98 Å) to form a highly distorted octahedral coordination around the cobalt atom. The crystal structure analysis of the corresponding nickel complex is reported here.

Experimental

Crystals of the present complex obtained from methanol at room temperature were green plates elongated along the *b* axis. Filtered copper *K*α radiation was used and the preliminary studies were done photographically with a Weissenberg camera. From the systematic absences, the space group was determined as $P2_1/c$.

The density was measured by flotation in an aqueous solution of $ZnCl_2$. Accurate cell parameters measured on a G.E. diffractometer are listed in Table 1.

Table 1. *Crystal data of bis-*(1-*methyl-3-o-chloro-phenyltriazene* 1-*oxide*)*nickel*(II)

$a = 12\cdot189 \pm 0\cdot005$ Å	$C_{14}H_{14}N_6O_2Cl_2Ni$
$b = 6\cdot434 \pm 0\cdot004$	Melting point 175 °C
$c = 13\cdot316 \pm 0\cdot006$	M.W. 427·91
$\beta = 123\cdot1 \pm 0\cdot2°$	Space group $P2_1/c$ (No. 14)
$D_m = 1\cdot59 \pm 0\cdot02$ g cm^{-3}	$U = 874\cdot8$ Å^3
$D_c = 1\cdot62$ g cm^{3}	$\mu = 45\cdot32$ cm^{-1} (Cu $K\alpha$)
$Z = 2$	

Intensity data were collected from a crystal approximately 0·2 × 0·4 × 0·1 mm in size. It was mounted with the [010] axis parallel to the φ axis of a G.E. diffractometer equipped with a quarter-circle single crystal orienter. The stationary-crystal stationary-counter technique and filtered Cu *K*α radiation were used. Reflexions with $I > \sigma(I)$ were coded as 'observed'. The data were collected up to $2\theta = 120°$ beyond which the intensities were falling off so rapidly that it was not considered worthwhile to collect data. A total of 1113 reflexions were measured, of which 901 were coded as observed.
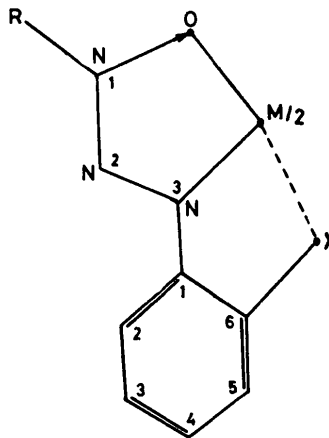

Fig. 1. Triazene 1-oxide complexes, Zacharias & Chakravorty (1971). Dotted line indicates that donor group X may or may not be coordinated with the metal atom. M = Ni, Co; X = Cl, Br, I, OCH_3, OC_2H_5, SCH_3; R = CH_3, C_2H_5, n-C_3H_7.

The intensity of 010 reflexions ($\chi=90°$) was plotted with φ varying from 0 to 360°. An approximate empirical absorption correction (Furnas, 1956) as a function of φ and 2θ was determined on the basis of these plots and applied to all reflexions. Owing to the small size and regular shape of the crystal such corrections were small, the maximum being 1·25.

Unobserved reflexions were given half the intensity of the weakest observed reflexion and the data were corrected for Lorentz and polarization factors.

Structure determination

With two molecules in a unit cell of space group $P2_1/c$ Ni^{2+} ions were located at the special positions $(0,0,0)$ and $(0,\frac{1}{2},\frac{1}{2})$. Other atoms were found by a series of three-dimensional Fourier and difference syntheses.

The structure was refined by the full-matrix least-squares technique using the adapted version of *ORFLS* (Busing, Martin & Levy, 1962). All observed reflexions were given unit weights, and the unobserved zero

weights; however, the structure factors for unobserved reflexions were also calculated at all stages and scrutinized for any serious discrepancy. Anisotropic temperature factors were introduced in the last three cycles of refinement and the R, on observed reflexions only, was 0·093. The positional and thermal parameters are listed in Table 2.[*]

Atomic form factors for Ni^{2+}, Cl, N, O and C were taken from *International Tables for X-ray Crystallography* (1968).

Discussion of the structure

(i) *Bond lengths and angles*

A molecule in (010) projection is shown in Fig. 2.

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Table 2. *The final atomic parameters in the structure of* bis-(1-methyl-3-o-chlorophenyltriazene 1-oxide)nickel(II)

Numbers in parentheses are standard deviations. Anisotropic temperature factors are of the form
$\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)]$. All parameters have been multiplied by 10^4.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	0	0	0	100 (3)	225 (10)	97 (3)	−16 (5)	57 (3)	−11 (5)
Cl	2395 (4)	5299 (6)	54 (3)	147 (6)	244 (16)	105 (5)	−20 (8)	53 (4)	34 (7)
O	−120 (7)	−757 (11)	−1392 (7)	72 (10)	168 (32)	83 (9)	−35 (13)	56 (8)	−19 (13)
N(1)	989 (9)	−186 (15)	−1308 (8)	104 (14)	137 (38)	82 (12)	−1 (19)	61 (11)	9 (17)
N(2)	1905 (8)	752 (14)	−373 (8)	57 (12)	169 (40)	70 (11)	−27 (16)	41 (10)	−16 (16)
N(3)	1619 (8)	1015 (15)	444 (8)	70 (13)	195 (40)	67 (10)	−29 (16)	50 (10)	−25 (16)
C(1)	2602 (11)	2134 (19)	1476 (11)	82 (16)	141 (49)	103 (16)	2 (21)	61 (14)	−24 (21)
C(2)	3116 (11)	1138 (27)	2633 (11)	46 (15)	586 (80)	68 (14)	−6 (27)	36 (13)	−40 (27)
C(3)	4095 (14)	2268 (25)	3644 (13)	121 (22)	318 (69)	111 (19)	58 (30)	74 (18)	32 (28)
C(4)	4544 (13)	4101 (24)	3556 (12)	127 (22)	333 (71)	97 (18)	−5 (30)	68 (17)	−67 (28)
C(5)	4059 (11)	5105 (25)	2453 (13)	60 (15)	353 (63)	141 (20)	−42 (26)	75 (15)	−52 (30)
C(6)	3049 (13)	4042 (19)	1418 (11)	129 (20)	138 (50)	95 (16)	−4 (23)	84 (16)	−7 (21)
C(7)	1095 (10)	−718 (20)	−2304 (9)	69 (15)	274 (57)	64 (13)	29 (22)	42 (12)	−3 (20)

(a)   (b)
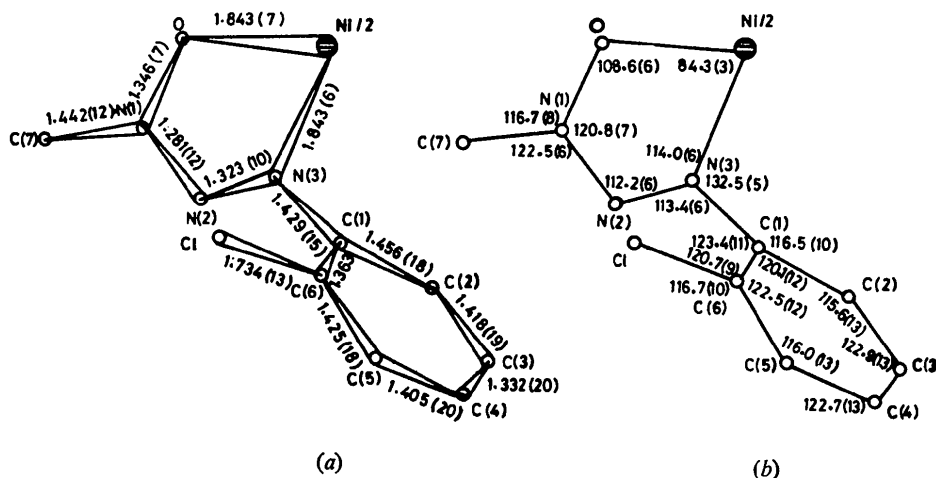
Fig. 2. (a) Bond lengths in Å. Numbers in brackets give standard deviations $\times 10^3$ Å. (b) Angles with standard deviations (°) in bis-(1-methyl-3-o-chlorophenyltriazene 1-oxide)nickel(II).

The Ni^{2+} ion forms a square planar arrangement with one O and one N atom of a ligand and the two corresponding atoms of the other ligand. The metal ion lies exactly on the plane formed by the four coordinating atoms. The Ni–Cl distance is 4·42 Å, showing almost no interaction between the Ni and Cl atoms. In the cobalt complex (Dwivedi & Srivastava, 1971) such an interaction, though weak, was observed. The Ni–N and Ni–O distances are 1·84 and 1·85 Å respectively, which may be compared with those observed in other similar diamagnetic nickel(II) complexes: 1·83 and 1·86 Å in bis(salicylaldoximato)nickel (Merritt, Guare & Lessor, 1956); 1·87 and 1·90 Å in bis(dimethylglyoximato)nickel (Godycki & Rundle, 1953) and 1·84 Å in bis(salicylaldiminato)nickel(II) (Stewart & Lingafelter, 1959). The N–Ni–O angle is 84·4°, thus the coordination around nickel is somewhat distorted square planar.

All other bond lengths and angles in the structure are in good agreement with those of the cobalt complex and other related complexes (Dwivedi & Srivastava, 1971).

(ii) *Geometry of the molecule and packing*

The five-membered ring consisting of the three nitrogens, one oxygen and the metal ion as well as the phenyl ring are good planes with no constituent atom more than 0·034 Å away from its least-squares plane. The equations of the least-squares planes through these rings and the deviations of the constituent atoms are listed in Table 3. The dihedral angle between these planes is 55·4° whereas similar planes in the cobalt complex were roughly coplanar. The methyl carbon and the chlorine atoms are on the same side of the ligand unlike the cobalt complex where they were on opposite sides. It may also be noted that the N(3)–C(1) bond connecting the two rings is in the plane of both rings and the chlorine is in the plane of the phenyl ring. These geometrical features show that in the cobalt complex the phenyl ring rotates about the N(3)–C(1) bond so as to bring the chlorine into a position appropriate for octahedral coordination.

The packing of the molecules in the crystal as viewed along the *b* axis is illustrated in Fig. 3. All short (< 4 Å) intermolecular distances are shown in the figure. The

Table 3. *Equations of the best planes and deviations of constituent atoms from them*

Equation of the plane $lx + my + nz = p$, where x, y, z are the coordinates in Å, p is the perpendicular distance of the plane from the origin and l, m, n are direction cosines of the normal.

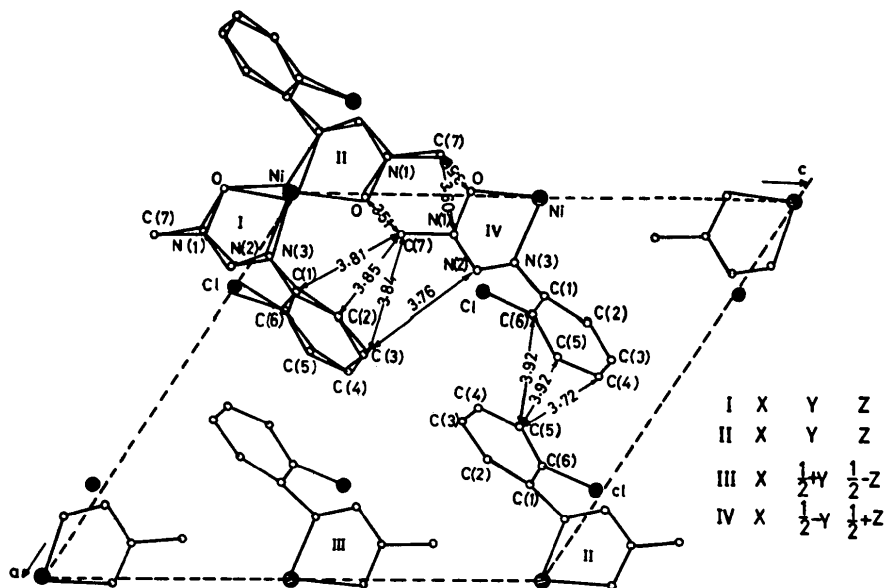| Plane through	l	m	n	p	Constituent atoms and their deviations in Å
Ni, O, N(1), N(2), N(3), C(1), C(7)	0·2284	−0·8799	0·4166	0·0072 Å	Ni −0·007, N(1) −0·031, N(2) −0·008, N(3) 0·001, O −0·028, C(1) −0·051, C(7) 0·0017
C(1), C(2), C(3), C(4), C(5), C(6), Cl, N(3)	0·8890	−0·4478	−0·0947	1·0718	C(1) 0·020, C(2) −0·005, C(3) −0·034, C(4) −0·005, C(5) 0·001, C(6) −0·005, Cl −0·028, N(3) 0·055

Fig. 3. Packing of the molecules of bis-(1-methyl-3-*o*-chlorophenyltriazene 1-oxide)nickel(II) in the crystal. Short intermolecular approach distances are shown in Å.
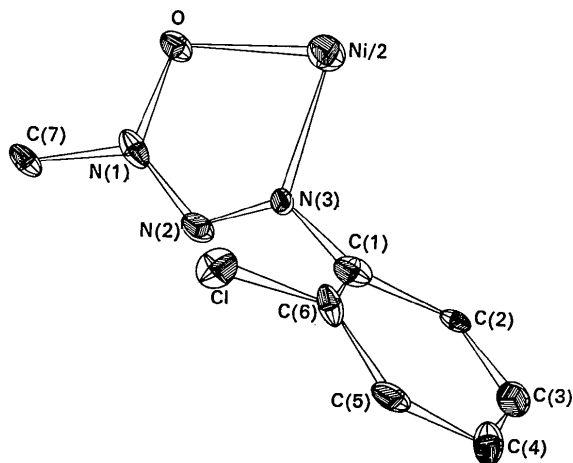
Fig. 4. Anisotropic thermal vibrations in bis-(1-methyl-3-*o*-chlorophenyltriazene 1-oxide)nickel(II).

packing is good and the shortest intermolecular distance of 3·51 Å is between the O of molecule II and the C(7) of molecule IV.

(iii) Thermal vibrations

The anisotropic thermal parameters are listed in Table 3. From these parameters, the magnitudes and the directions of the principal axes of thermal ellipsoids have been calculated using the program *ANTEMP* (Dwivedi, 1970) and are listed in Table 4. It may be noticed that the chlorine atom has the largest isotropic B in the present complex whereas in the cobalt complex it was among the atoms with a smaller B. This is also indicative of the fact that the chlorine atom is coordinated in the cobalt complex and not in the present complex. The relative magnitudes of vibration amplitudes and the orientation of thermal ellipsoids are shown in Fig. 4.

Table 4. *Principal axes of thermal ellipsoids*

The root mean square displacement U_i corresponds to the *i*th principal axis of the ellipsoid, and $\theta_{ia}, \theta_{ib}, \theta_{id}$ are angles between the *i*th axis and the crystallographic axes, a, b and an axis d normal to a and b. $B_i = 8\pi^2 U_i^2$.

Atom	i	B_i (Å²)	U_i (Å)	θ_{ia} (°)	θ_{ib} (°)	θ_{id} (°)
Ni	1	4·9	0·2492	91·3	74·9	164·8
	2	4·14	0·2290	148·4	59·9	81·1
	3	3·46	0·2095	58·4	34·4	77·8
Cl	1	7·85	0·3153	151·6	68·5	72·4
	2	5·27	0·2585	65·8	74·8	29·1
	3	3·28	0·2040	76·0	26·8	112·4
O	1	4·47	0·2381	105·1	66·4	151·4
	2	2·89	0·1914	117·3	41·5	61·4
	3	1·59	0·1421	31·8	58·2	90·7

Table 4 (cont.)

N(1)	1	4·53	0·2396	55·7	87·4	34·4
	2	3·24	0·2026	142·9	73·3	58·0
	3	2·17	0·1659	77·7	16·9	101·4
N(2)	1	3·73	0·2177	97·1	60·9	149·8
	2	2·87	0·1910	119·5	43·4	61·4
	3	1·66	0·1450	30·5	61·0	81·4
N(3)	1	4·24	0·2318	107·4	50·2	135·1
	2	2·57	0·1803	86·9	41·2	49·0
	3	1·80	0·1510	17·7	80·9	105·1
C(1)	1	5·28	0·2588	86·5	76·3	165·8
	2	3·30	0·1960	30·5	61·4	80·2
	3	1·86	0·1539	120·3	32·3	79·9
C(2)	1	9·94	0·3549	85·9	10·9	100·1
	2	3·17	0·2003	94·2	79·6	11·2
	3	1·51	0·1384	174·2	86·7	94·8
C(3)	1	6·84	0·2943	65·3	47·4	52·7
	2	4·81	0·2468	64·3	64·0	142·0
	3	3·46	0·2094	143·0	53·7	96·3
C(4)	1	7·23	0·3028	77·2	38·0	125·1
	2	5·28	0·2587	31·6	82·5	59·5
	3	2·57	0·1806	118·4	53·0	50·1
C(5)	1	8·05	0·3194	88·1	56·2	146·2
	2	4·91	0·2495	98·4	34·4	56·9
	3	1·14	0·1200	8·6	84·1	83·8
C(6)	1	5·80	0·2712	125·3	87·4	144·5
	2	2·65	0·1834	38·8	71·0	122·4
	3	2·23	0·1684	104·0	19·2	77·1
C(7)	1	4·91	0·2494	68·4	21·6	89·9
	2	3·21	0·2016	100·4	85·8	168·8
	3	2·04	0·1610	155·8	68·8	78·8

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