a set of hydrogen bonds between the N—H groups of three cation complexes and two water molecules.

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Structure of Bis(1-ethyl-3-*p*-nitrophenyltriazene 1-oxide)nickel(II)

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Abstract. $C_{16}H_{18}N_8NiO_6$, $M_r = 477 \cdot 08$, monoclinic, $P2_1/c$, $a = 9 \cdot 200$ (1), $b = 8 \cdot 658$ (1), $c = 12 \cdot 654$ (1) Å, $\beta = 98 \cdot 82$ (1)°, $V = 996 \cdot 0$ (2) Å^3, $Z = 2$, $D_x = 1 \cdot 591$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1 \cdot 5418$ Å, $\mu = 1 \cdot 726$ mm^{-1}, $F(000) = 492$, $T = 295$ K, $R = 0 \cdot 0438$ for 1398 unique reflections with $I > 3\sigma(I)$. The molecule displays square-planar N_2O_2 coordination about Ni^{II}. Ligand phenyl rings are stacked $3 \cdot 426$ (2) Å apart.

Introduction. 1-Alkyl(aryl)-3-(*X*-phenyltriazene) 1-oxides {henceforth abbreviated as H[*R*(Ar);*X*]} belong to a wide class of ligands forming 'inorganic' (carbon-free) chelate rings (Haiduc & Silaghi-Dumitrescu, 1986). To date, three molecular structures of the free ligands, *i.e.* H[Me;4-CONH₂] (Kuroda & Wilman, 1985), H[*φ*;2-OH] (Samanta, De, Sarkar, Saha & Talapatra, 1985) and H[*φ*;2-CO₂H] (Sarkar, Khalil, Saha & Talapatra, 1983) have been reported. Of the metal complexes of these ligands the structures of Pd[*φ*;H]₂ (Meyer, 1965), Co[Me;2-Cl]₂, Ni[Me;2-Cl]₂ (Dwivedi & Srivastava, 1971, 1976), Ni[Me;2-Cl,6-Me]₂, Ni[Me;2-Cl,6-Me]₂-C₆H₆ (Rajasekharan, Varughese & Manoharan, 1979) and Ru[Et;4-Me]₂Cl₂ (Bhattacharya, Chakravorty, Cotton, Mukherjee & Schwotzer, 1984) are known. In addition, the structure of a dinuclear copper complex of the 3,3'-dimethoxy-4,4'-benzidine based ligand has been published (Hodgson, 1983).

Recently, we reported the formation of both high-spin and low-spin complexes of Co^{II}, together with the molecular structure of the low-spin, square-planar Co[Et;H]₂ (Rudolf, Wolny, Ciunik & Chmielewski, 1988). In contrast the Ni^{II} complexes

have been found to be diamagnetic as solids, but displayed different types of high-spin–low-spin equilibria in CHCl₃ solutions (Rudolf, 1979).

The crystal structure determination of the title complex was undertaken to verify whether the four-coordinate planar structure of Ni^{II} triazene 1-oxide complexes is retained for ligands bearing the strongly electron-withdrawing NO_2 group in the phenyl ring.

Experimental. The ligand was prepared by condensation of diazotized 4-nitroaniline with N-ethylhydroxylamine at pH $\simeq$ 4, according to the method of Bamberger & Busdorf (1897). The crude product was dried in air and recrystallized from toluene. The title complex was obtained by adding a methanolic solution of nickel acetate to a hot methanolic solution of the ligand. Recrystallization of the complex from CH_2Cl_2/acetone yielded suitable crystals. Space group was determined from oscillation and Weissenberg photographs. All intensity data were measured on a Kuma KM4 computer-controlled four-circle κ-axis diffractometer with graphite-monochromated Cu $K\alpha$ radiation. Stability of crystal monitored by measurements of standards every 50 reflections. Data were corrected for Lorentz and polarization effects but not for absorption. Details of the data collection and structure determination are given in Table 1.

The structure was solved by direct methods and refined on F by full-matrix least-squares methods, initially with isotropic and finally with anisotropic displacement parameters for non-H atoms. At an intermediate stage in the refinement, $\Delta\rho$ maps showed the positions of all H atoms. H-atom parameters were refined with isotropic displacement parameters. The neutral-atom scattering factors and anomalous-dispersion correction were those incorporated in programs. Final atom parameters are presented in Table 2.* During the structure calculations the following programs were used: $SHELX76$ (Sheldrick, 1976), $SHELXS86$ (Sheldrick, 1990), and $ORTEP$ (Johnson, 1971).

Discussion. The numbering scheme and overall conformation of the title complex are presented in Figs. 1 and 2 with bond lengths and angles, and selected torsion angles in Table 3. Although our preliminary results from susceptibility measurements of $CDCl_3$ solutions of Ni^{II} complexes of the 4-nitro substituted triazene 1-oxides reveal that for those systems the highest fraction of high-spin species is observed, the

* List of structure factors, anisotropic temperature factors and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54321 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental data*

Crystal size (mm)	0·20 × 0·20 × 0·25
No. of reflections	25
θ range (°)	15–20
Intensity data collection	
Scan type	$\omega/2\theta$
Scan width, $\Delta\omega$ (°)	$1·2 + 0·35\tan\theta$
Scan range, 2θ (°)	4–120
Scan speed (° min⁻¹)	0·9–9
No. of check reflections	3
Crystal decay (%)	<3
Ranges of h, k, l	−10→10, 0→9, 0→14
Total reflections	1535
Unique reflections	1459
Observed reflections, $F > 6\sigma(F)$	1398
R_{int}	0·0282
Structure refinement (on F)	Full matrix
No. of parameters	179
Weighting scheme (w)	$[\sigma^2(F) + 0·0088F^2]^{-1}$
Secondary-extinction parameter (x)	0·036
R	0·0438
wR	0·0567
S	1·22
Max. shift to e.s.d. (Δ/σ)	0·033
Min./max. final $\Delta\rho$ map (e Å⁻³)	−0·46/0·39

Table 2. *Positional and thermal parameters* ($\times 10^4$) *for* non-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å²)
Ni	5000	0	5000	403 (2)
O(1)	4829 (2)	38 (2)	6420 (2)	525 (6)
O(2)	11628 (2)	2196 (3)	2538 (2)	776 (5)
O(3)	12289 (3)	3837 (3)	3796 (2)	998 (7)
N(1)	6053 (2)	615 (2)	6994 (1)	475 (5)
N(2)	7130 (2)	1024 (2)	6553 (1)	454 (4)
N(3)	6878 (2)	775 (2)	5498 (1)	423 (4)
N(4)	11486 (2)	2781 (2)	3390 (2)	605 (5)
C(1)	8049 (2)	1284 (2)	4984 (2)	385 (4)
C(2)	8963 (2)	2488 (3)	5409 (2)	481 (5)
C(3)	10107 (2)	2950 (3)	4886 (2)	520 (6)
C(4)	10313 (2)	2262 (2)	3954 (2)	487 (5)
C(5)	9404 (2)	1070 (2)	3513 (2)	489 (5)
C(6)	8280 (2)	573 (3)	4040 (2)	469 (5)
C(7)	6061 (3)	759 (4)	8163 (2)	592 (7)
C(8)	5640 (4)	−698 (4)	8634 (2)	726 (9)

solid Ni[Et;4-NO₂]₂ is diamagnetic. The molecule exhibits square-planar, four-coordinate N_2O_2 geometry about the metal ion. Metal–ligand bond lengths are somewhat larger than those found for low-spin Co[Et;H]₂. The exact symmetry of the molecule is C_i, whereas the symmetry of the coordination core is C_{2h}. The phenyl ring of the ligand is twisted 27·5 (3)° towards the NNNO plane with the nitro group lying in the plane of the aromatic ring. The absolute value of the torsion angle N(2)—N(3)—C(1)—C(2) [τ = −27·5 (3)°] is appreciably lower than that determined for Co[Et;H]₂ [τ = 39·2 (5)°]. This decrease of $|\tau|$ may be ascribed to the strong π-bond acceptor character of the NO_2 group, which may result in an increase of conjugation between NNNO and phenyl moieties. The intermolecular stacking interactions involve the parallel phenyl rings

of adjacent molecules (see Fig. 2), the distance between the planes being 3·426 (2) Å. The nitro group is involved in some contact with the NNNO linkage of an adjacent molecule – the distance between one of the NO₂ O atoms [the O(2) atom in the equivalent position $2 - x$, $-y$, $1 - z$] and the N(2) atom being 3·162 (3) Å (no contact involving the central ion was found, however). The presence of a nitro group may be of importance, as no stacking interactions were found in the Co[Et;H]₂ complex, which on the basis of a powder diffraction pattern was found to be isomorphic with Ni[Et;H]₂.

Analysis of the available structural data (Kuroda & Wilman, 1985; Samanta, De, Sarkar, Saha & Talapatra, 1985; Sarkar, Kalil, Saha & Talapatra, 1983; Dwivedi & Srivastava, 1976; Rajasekharan, Varughese & Manoharan, 1979; Bhattacharya, Chakravorty, Cotton, Mukherjee & Schwotzer, 1984; Hodgson, 1983; Rudolf, Wolny, Ciunik & Chmielewski, 1988; Rudolf, Ciunik & Wolny, 1991) gave the following values of mean bond lengths and angles of an NNNO moiety for triazene 1-oxide complexes (corresponding values for free ligands are given in square brackets): N(1)—N(2) 1·281 (12) [1·278 (5)], N(2)—N(3) 1·325 (12) [1·331 (8)], N(1)—O(1) 1·329 (16) [1·290 (7)], N(3)—C(1) 1·421 (10) [1·400 (3)] Å, O(1)—N(1)—N(2) 122 (1) [123 (1)], N(1)—N(2)—N(3) 112·0 (1) [112 (1)]°. Thus, the most important effect of ligand coordination is the lengthening of N(1)—O(1) and N(3)—C(1) bonds. For coordinated ligands the NNNO fragment remains essentially planar, displaying rather small alterations of bond lengths and angles for different
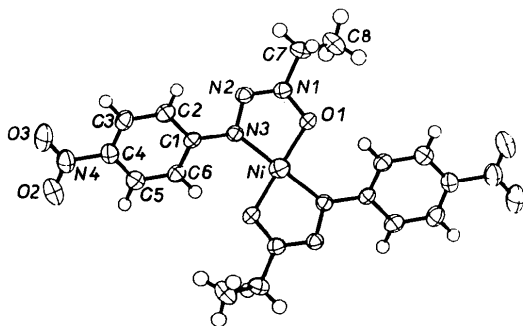

Fig. 1. *ORTEP* (Johnson, 1971) drawing showing atom numbering. The non-H atoms are represented by 50% probability ellipsoids.
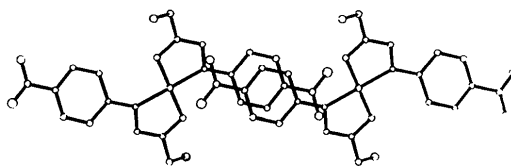

Fig. 2. Intermolecular stacking in the unit cell. The hydrogen atoms have been removed for clarity.

Table 3. *Bond lengths* (Å) *and angles* (°), *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

Ni—O(1)	1·828 (3)	N(4)—C(4)	1·453 (3)
Ni—N(3)	1·871 (2)	C(1)—C(2)	1·394 (3)
O(1)—N(1)	1·340 (3)	C(1)—C(6)	1·389 (4)
O(2)—N(4)	1·216 (4)	C(2)—C(3)	1·385 (3)
O(3)—N(4)	1·237 (3)	C(3)—C(4)	1·360 (4)
N(1)—N(2)	1·260 (3)	C(4)—C(5)	1·390 (3)
N(1)—C(7)	1·483 (3)	C(5)—C(6)	1·382 (3)
N(2)—N(3)	1·337 (2)	C(7)—C(8)	1·472 (5)
N(3)—C(1)	1·412 (3)		

O(1)—Ni—N(3)	82·9 (1)	N(3)—C(1)—C(2)	120·9 (2)
Ni—O(1)—N(1)	110·4 (1)	N(3)—C(1)—C(6)	119·1 (2)
O(1)—N(1)—N(2)	121·2 (2)	C(2)—C(1)—C(6)	120·0 (2)
O(1)—N(1)—C(7)	116·6 (2)	C(1)—C(2)—C(3)	119·3 (2)
N(2)—N(1)—C(7)	122·3 (2)	C(2)—C(3)—C(4)	120·3 (2)
N(1)—N(2)—N(3)	111·7 (2)	N(4)—C(4)—C(3)	120·2 (2)
Ni—N(3)—N(2)	113·8 (1)	N(4)—C(4)—C(5)	118·6 (2)
Ni—N(3)—C(1)	133·4 (1)	C(3)—C(4)—C(5)	121·2 (2)
N(2)—N(3)—C(1)	112·5 (2)	C(4)—C(5)—C(6)	119·1 (2)
O(2)—N(4)—O(3)	122·5 (2)	C(1)—C(6)—C(5)	120·1 (2)
O(2)—N(4)—C(4)	119·7 (2)	N(1)—C(7)—C(8)	111·7 (2)
O(3)—N(4)—C(4)	117·8 (2)		

O(1)—N(1)—N(2)—N(3)	−1·2 (3)	N(1)—N(2)—N(3)—C(1)	177·6 (2)
O(2)—N(4)—C(4)—C(5)	1·8 (3)	N(2)—N(3)—C(1)—C(2)	−27·5 (3)

complexes, the differences concerning mainly the N(1)—O(1) bond length. Double-bond character is more pronounced for the N(1)—N(2) bond, both for metal complexes and free ligands.

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