

trans-Bis[1-methyl-3-(*p*-nitrophenyl)-triazenido 1-oxide- $\kappa^2 N^3, O$]dipyridine-nickel(II)

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Received 24 September 2002

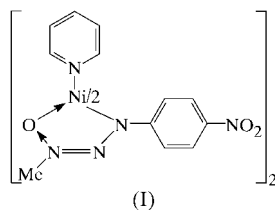
Accepted 30 October 2002

Online 20 November 2002

In the centrosymmetric title complex, $[\text{Ni}(\text{C}_7\text{H}_7\text{N}_4\text{O}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$, the coordination geometry about the Ni^{2+} ion is octahedral, with two deprotonated 1-methyl-3-(*p*-nitrophenyl)triazenido 1-oxide ions, *viz.* $[\text{O}_2\text{NC}_6\text{H}_4\text{NNN}(\text{O})\text{CH}_3]^-$, acting as bidentate ligands (four-electron donors). Two neutral pyridine (py) molecules complete the coordination sphere in positions *trans* to each other. The triazenido 1-oxide ligand is almost planar, the largest interplanar angle of $8.80(12)^\circ$ being between the phenyl ring of the *p*-nitrophenyl group and the plane defined by the N_3O moiety. The $\text{Ni}-\text{N}_{\text{triazenido}}$, $\text{Ni}-\text{O}$ and $\text{Ni}-\text{N}_{\text{py}}$ distances are 2.0794 (16), 2.0427 (13) and 2.1652 (18) Å, respectively.

Comment

Despite the fact that complexes of triazene *N*-oxides have been widely investigated in recent decades, the structure of nickel(II) complexes involving deprotonated 1,3-disubstituted triazenido 1-oxide ligands, *viz.* $[\text{RNNN}(\text{O})\text{R}]^-$, continue to attract interest (Dutta & Sharma, 1981; Ciunik *et al.*, 1991). However, only two examples of six-coordinate nickel(II) complexes with triazenido 1-oxide as a ligand have been reported in the literature. In these examples, the triazenido 1-oxide ligand is incorporated as part of a larger chelating group (Karmakar *et al.*, 1993*a,b*). As part of our investigations



of the synthesis and characterization of metal complexes incorporating triazene 1-oxide derivatives, we report here the structure of the title complex, (I), which is a centrosymmetric

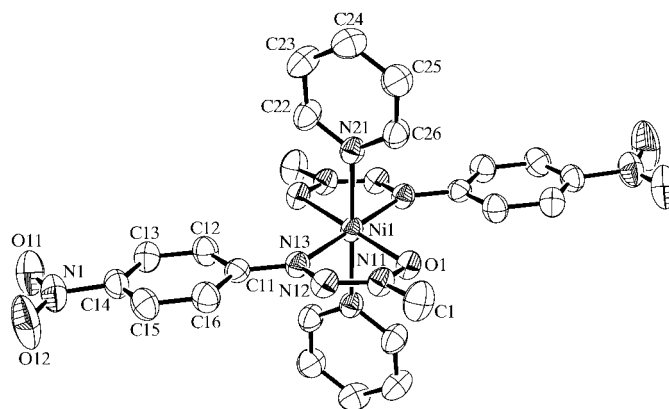


Figure 1

Perspective view of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

hexacoordinated mononuclear Ni^{II} complex, with deprotonated 1-methyl-3-(*p*-nitrophenyl)triazenido 1-oxide ions and neutral pyridine molecules as ligands. Compound (I) is the first example of a triazenido 1-oxide complex with a hexacoordinated Ni^{2+} ion and two different kinds of ligands (Fig. 1).

Deviations from normal N—N and N—C_{aryl} bond lengths (Table 1) underline the delocalization of the π electrons over the N—N—N chain of the $\text{N13}-\text{N12}-\text{N11}-\text{O1}$ group and the *p*-nitrophenyl substituent. The $\text{N13}-\text{N12}$ [1.332 (2) Å] bond length is longer than a normal double bond (1.24 Å), $\text{N12}-\text{N11}$ [1.273 (2) Å] is shorter than a normal single bond (1.44 Å) (*International Tables for X-ray Crystallography*, 1985, Vol. III, p. 270) and $\text{N13}-\text{C11}$ [1.391 (3) Å] is shorter than expected for an N—C_{aryl} single bond. The N—N bond lengths in complex (I) are almost identical to those of non-coordinated triazene 1-oxide molecules, where $\text{N13}-\text{N12} = 1.323$ (2), 1.327 (4) and 1.332 (4) Å, and $\text{N12}-\text{N11} = 1.263$ (2), 1.264 (3) and 1.270 (4) Å (Samanta *et al.*, 1997, 1998).

A typical feature of the coordinated deprotonated triazenido 1-oxide ligand is the lengthening of the N—O bond; $\text{N11}-\text{O1} = 1.329$ (2) Å [comparative values for neutral non-coordinated triazene 1-oxides are 1.288 (3) and 1.288 (2) Å; Samanta *et al.*, 1997, 1998]. The N—N and N—O bond lengths in (I) are also in good agreement with those found in bis[1-ethyl-3-(*p*-nitrophenyl)triazenido 1-oxide]nickel(II) (Ciunik *et al.*, 1991), hereafter (II) [$\text{N}-\text{N} = 1.260$ (3) and 1.337 (2) Å, and $\text{N}-\text{O} = 1.340$ (3) Å], while $\text{Ni1}-\text{N13}$ of 2.0794 (16) Å [1.871 (2) Å in (II)] and $\text{Ni1}-\text{O1}$ of 2.0427 (13) Å [1.828 (3) Å in (II)] are significantly longer (Ciunik *et al.*, 1991). These significant differences between the Ni—N and Ni—O bond distances of both complexes can be explained by the expansion of the coordination number of the Ni^{2+} ion from four in (II) to six in (I) and the steric demand of the two additional axial pyridine ligands in (I). This observation is in good agreement with the Ni—N and Ni—O bond distances observed in other Ni^{II} complexes with octahedral coordination, such as $[\{\text{H}_3\text{CN}(\text{O})\text{NNC}_6\text{H}_4\text{S}(\text{CH}_2)_3\text{SC}_6\text{H}_4\text{NN}(\text{O})\text{N}-\text{CH}_3\}\text{Ni}]$ [$\text{Ni}-\text{N} = 1.984$ (8) and 1.993 (8) Å, and $\text{Ni}-\text{O} = 2.060$ (7) and 2.075 (8) Å] and $[\{\text{PrN}(\text{O})\text{NNC}_6\text{H}_4\text{SMe}\}_2\text{Ni}]$

[Ni—N = 1.972 (4) and 1.970 (4) Å, and Ni—O = 2.048 (4) and 2.051 (4) Å] (Karmakar *et al.*, 1993*a,b*).

Due to the strong π -acidity of the nitro group, which favours the delocalization of the π electrons and the conjugation between the C11–C16 phenyl ring and the NNNO moiety, the triazenide 1-oxide ligand shows only a slight deviation from planarity [the angles between the C11–C16 phenyl ring and the O11/N1/O12 and N13/N12/N11/O1 planes are 5.5 (4) and 8.80 (12)°, respectively]. In addition to this electronic effect, steric interactions involving the axial pyridine ligands can also be associated with the small interplanar angle of 8.80 (12)°. In contrast, the related four-coordinated nickel complex, (II), shows a deviation from planarity for the ligand, characterized by an N12–N13–C11–C16 torsion angle of 27.5 (3)° (Ciunik *et al.*, 1991). The C11–C16 phenyl ring (r.m.s. deviation 0.0068 Å) and the N21/C22–C26 pyridine ring (r.m.s. deviation 0.0031 Å) are planar within experimental error. The Ni1–N21 bond distance of 2.1652 (18) can be compared with the values found in the related complex *cis*-[Ni{O₂NC₆H₄NC(OEt)NC(O)C₆H₅}₂(C₅H₅N)₂] (Ni–N_{py} = 2.150 and 2.131 Å; Beyer *et al.*, 1999). The nitro O atoms show a large thermal motion, indicated by their elongated displacement ellipsoids (Fig. 1). Split peaks for these atoms were not observed and consequently a disorder model was not used.

Experimental

[NiCl₂(PPh₃)₂] (654 mg, 1 mmol) was dissolved, with heating, in a mixture of methanol (50 ml) and ethyl acetate (25 ml). A solution of 1-methyl-3-(*p*-nitrophenyl)triazene 1-oxide (392 mg, 2 mmol) in methanol (25 ml) and triethylamine (5 ml) was added under continuous stirring and heating. After 10 min, pyridine (5 ml) was added to the reaction mixture, which changed colour to deep red. Stirring was continued for 1 h. Red plate-shaped crystals of complex (I), suitable for X-ray analysis, were obtained by slow evaporation of the solvents at room temperature (yield: 91 mg, 15%; m.p. 498 K).

Crystal data

[Ni(C ₇ H ₇ N ₄ O ₃) ₂ (C ₅ H ₅ N) ₂]	$D_x = 1.506 \text{ Mg m}^{-3}$
$M_r = 607.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 10.473 (2) \text{ Å}$	$\theta = 2.0\text{--}25.0^\circ$
$b = 14.961 (3) \text{ Å}$	$\mu = 0.78 \text{ mm}^{-1}$
$c = 8.569 (2) \text{ Å}$	$T = 294 (1) \text{ K}$
$\beta = 94.028 (10)^\circ$	Prism, red
$V = 1339.4 (5) \text{ Å}^3$	$0.30 \times 0.20 \times 0.10 \text{ mm}$
$Z = 2$	

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.0427 (13)	N1—C14	1.449 (3)
Ni1—N13	2.0794 (16)	N11—N12	1.273 (2)
Ni1—N21	2.1652 (18)	N11—C1	1.455 (3)
O1—N11	1.329 (2)	N12—N13	1.332 (2)
O11—N1	1.226 (3)	N13—C11	1.391 (3)
O12—N1	1.225 (3)		
O1—Ni1—N13	76.73 (6)	O12—N1—O11	122.0 (2)
O1—Ni1—N21	89.12 (6)	N12—N11—O1	124.29 (16)
N13—Ni1—N21	87.59 (7)	N11—N12—N13	113.61 (17)
N11—O1—Ni1	109.92 (11)	N12—N13—Ni1	113.86 (13)

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.036$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: ψ scan (Spek, 1990)	$h = -12 \rightarrow 12$
$T_{\text{min}} = 0.799$, $T_{\text{max}} = 0.926$	$k = -15 \rightarrow 17$
8301 measured reflections	$l = -10 \rightarrow 10$
2373 independent reflections	3 standard reflections
1888 reflections with $I > 2\sigma(I)$	frequency: 60 min
	intensity decay: <1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.4419P]$
$R(F) = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.076$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.17 \text{ e Å}^{-3}$
2373 reflections	$\Delta\rho_{\text{min}} = -0.25 \text{ e Å}^{-3}$
188 parameters	
H-atom parameters constrained	

The positional parameters of the H atoms were obtained geometrically, the C—H distances fixed (0.93 Å for Csp^2 and 0.96 Å for Csp^3 H atoms), and the atoms refined as riding on their respective C atoms, with an isotropic displacement parameter of 1.2 times the U_{eq} value of the attached Csp^2 and 1.5 times the U_{eq} value of the attached Csp^3 atom. The methyl group was refined as a rigid group, with rotation around the N11—C1 bond as a free variable.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work has received partial support from CNPq (Proc. 475734/01-7) and FAPERGS. MH and JB thank CNPq, and JSO thanks CAPES for grants.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1398). Services for accessing these data are described at the back of the journal.

References

- Beyer, L., Richter, R., Wolf, R., Yaumseil, J., Lino-Pacheco, M. & Angulo Cornejo, J. (1999). *Inorg. Chem. Commun.* **2**, 184–187.
- Ciunik, Z., Wolny, J. A. & Rudolf, M. F. (1991). *Acta Cryst.* **C47**, 2539–2541.
- Dutta, R. L. & Sharma, R. (1981). *J. Sci. Ind. Res.* **40**, 715–737.
- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Karmakar, S., Choudhury, S. B., Ray, D. & Chakravorty, A. (1993*a*). *Polyhedron*, **12**, 291–296.
- Karmakar, S., Choudhury, S. B., Ray, D. & Chakravorty, A. (1993*b*). *Polyhedron*, **12**, 2325–2329.
- Samanta, C., Mukherjee, A. K. & Mukherjee, M. (1998). *Acta Cryst.* **C54**, 1544–1546.
- Samanta, C., Saha, S. C. & Mukherjee, A. K. (1997). *Acta Cryst.* **C53**, 1657–1658.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.