

Bis(*N,N'*-diethylethylenediamine)(nitrito-*O,O'*)nickel(II) Nitrite*

BY MARTIN J. GOLDBERG† AND RICHARD E. MARSH

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA

(Received 14 September 1978; accepted 5 December 1978)

Abstract. $[\text{C}_{12}\text{H}_{32}\text{N}_5\text{NiO}_2][\text{NO}_2]$, $[\text{Ni}(\text{C}_{12}\text{H}_{32}\text{N}_4)(\text{NO}_2)][\text{NO}_2]$, triclinic, $P\bar{1}$, $Z = 4$, $a = 12.643$ (3), $b = 9.210$ (3), $c = 18.110$ (6) Å, $\alpha = 101.46$ (2), $\beta = 86.18$ (2), $\gamma = 108.86$ (2)°, $V = 1956$ Å³, $D_x = 1.276$, $D_m = 1.28$ (1) Mg m⁻³ (neutral buoyancy). One of the nitrite groups is coordinated through both O atoms completing a distorted octahedron about the Ni atom; the second nitrite group is attached to the cation through weak N–H···O hydrogen bonds. The two cations in the asymmetric unit have essentially identical conformations, including a 60%–40% disorder between two sites occupied by one of the terminal methyl groups. The stereochemistry is $\Delta\delta\delta$ for two of the cations and $\Delta\lambda\lambda$ for their inversion-related counterparts.

Introduction. Blue and green crystals (of which it appears that only the green are monocrystalline) were prepared by A. B. P. Lever and I. M. Walker of the Department of Chemistry, York University, Ontario, Canada, as follows. 0.02 mol (4.8 g) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 ml CH_3OH ; 15 ml of triethyl formate was added and the mixture was warmed for 1 h. The resulting solution was then chilled to 273 K. A solution of 0.04 mol of AgNO_2 in 50 ml Cl_3CN , also at 273 K, was added with stirring for 30 min, the AgCl precipitate was filtered off, and the $\text{Ni}(\text{NO}_2)_2$ filtrate was treated with 4.8 g *N,N'*-diethylethylenediamine. The product was crystallized by evaporation and recrystallized from ethanol.

The crystal used for data collection was needle-shaped, about $0.2 \times 0.2 \times 0.4$ mm, mounted along its long dimension (*b*). Preliminary oscillation and Weissenberg photographs suggested triclinic symmetry. Cell dimensions and intensity data were collected on a Syntex $P2_1$ diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) monochromatized by a graphite crystal, the cell dimensions being based on 15 reflections having

2θ values between 17.5 and 26°. The scan speed was 2° min^{-1} over a range extending 0.7° to either side of the $K\alpha_1$ – $K\alpha_2$ doublet; backgrounds were collected for one half of the scan time. Three check reflections showed an approximately uniform decay in intensity, reaching 13%; intensities of all reflections were corrected for this decay. Absorption effects were neglected ($\mu = 1.0 \text{ mm}^{-1}$); polarization corrections were based on an ideally imperfect monochromator crystal (Miyake, Togawa & Hosoya, 1964). The final data set included all 3827 reflections out to $2\theta = 40^\circ$, of which 687 had negative net intensities.

Positions of the Ni atoms were determined from a Patterson map, and the remaining atoms were located from subsequent electron-density and difference maps. H atoms were placed in tetrahedral positions, staggered with respect to the adjacent methylene group in the case of the terminal methyl groups, with $\text{C–H} = \text{N–H} = 0.95$ Å; they were given isotropic temperature parameters with *B* values one unit greater than those of their parent atoms.

At a late stage in the refinement, a difference map indicated that one of the methyl groups in each of the cations is disordered between two sites; both sites, and a relative population parameter, were included in subsequent refinements. H atoms were assigned to these partial sites, with corresponding population numbers; however, the H atoms attached to the adjacent methylene groups were positioned in a single set of sites only, so as to complete tetrahedra including the higher populated sites of the methyl groups.

Refinement was by full-matrix least-squares minimization of $\sum w(F_o^2 - F_c^2)^2$, with $w = \sigma^{-2}(F_o^2)$; the observational variances $\sigma^2(F_o^2)$ were based on counting statistics plus a term $(0.02S)^2$, where *S* is the scan count. Scattering factors for Ni, C, N, and O were from *International Tables for X-ray Crystallography* (1962) and for H from Stewart, Davidson & Simpson (1965); values for Ni were incremented by 0.37 e to account for the in-phase component of anomalous dispersion (Cromer, 1965). In the final cycles, 206 parameters were adjusted: coordinates for the 48 Ni, C, N, and O atoms in the asymmetric unit (including the two pairs of disordered methyl C atoms), anisotropic temperature parameters for the two Ni atoms, isotropic temperature

* Contribution No. 5883 from the Arthur Amos Noyes Laboratory of Chemical Physics. This investigation was supported in part by Public Health Service Research Grant No. GM 16966 from the National Institute of General Medical Sciences, National Institutes of Health.

† Present address: Chemistry Department, Carnegie–Mellon University, Pittsburgh, Pennsylvania 15213.

Table 1. *Final coordinates* ($\times 10^4$) *and their e.s.d.'s* (in parentheses)

	Molecule A			Molecule B		
	x	y	z	x	y	z
Ni	7510 (1)	6407 (1)	804 (1)	2613 (1)	5857 (1)	3958 (1)
C(1 ^a)	6179 (15)	9518 (22)	886 (11)	1235 (18)	8794 (25)	3755 (15)
C(1 ^b)	6005 (25)	9358 (37)	-139 (19)	953 (29)	9570 (47)	4578 (23)
C(2)	6194 (10)	8363 (13)	270 (8)	1156 (11)	8111 (16)	4330 (9)
N(3)	7207 (6)	7875 (8)	121 (4)	2116 (6)	7787 (9)	4588 (4)
C(4)	7244 (8)	7098 (11)	-660 (5)	1997 (9)	7547 (13)	5345 (7)
C(5)	8134 (8)	6347 (10)	-747 (5)	2878 (9)	6975 (12)	5551 (6)
N(6)	7950 (5)	5276 (8)	-219 (4)	2889 (6)	5517 (8)	5024 (4)
C(7)	7063 (8)	3739 (10)	-463 (5)	2038 (8)	4100 (11)	5199 (5)
C(8)	7319 (9)	2719 (12)	-1184 (6)	2210 (9)	3646 (13)	5919 (7)
C(1')	7585 (10)	2874 (14)	2191 (7)	3012 (10)	1394 (14)	2588 (7)
C(2')	7126 (8)	3899 (12)	1826 (6)	2472 (8)	2647 (11)	2932 (5)
N(3')	7997 (5)	4976 (8)	1427 (4)	3255 (5)	4026 (8)	3414 (4)
C(4')	8893 (8)	6057 (11)	1922 (5)	4255 (8)	4800 (11)	3012 (5)
C(5')	9643 (8)	7195 (11)	1497 (5)	4895 (7)	6267 (10)	3508 (5)
N(6')	9053 (5)	8034 (8)	1172 (4)	4210 (5)	7310 (8)	3745 (4)
C(7')	8888 (9)	9396 (12)	1693 (6)	4183 (8)	8236 (10)	3184 (5)
C(8')	9920 (11)	10675 (16)	1947 (8)	5283 (9)	9485 (12)	3060 (6)
O(1)	5758 (5)	5121 (7)	835 (3)	883 (5)	4459 (7)	3808 (4)
O(1')	6472 (5)	6944 (7)	1743 (3)	1721 (5)	5650 (7)	2954 (3)
N(2)	5602 (7)	5913 (10)	1465 (5)	821 (7)	4766 (9)	3174 (5)
O(9)	9109 (5)	946 (8)	-7 (4)	5860 (6)	9078 (8)	5121 (4)
O(9')	9343 (5)	3332 (7)	294 (3)	5523 (5)	6883 (8)	5418 (4)
N(10)	8774 (6)	1992 (10)	344 (4)	6166 (7)	8274 (11)	5477 (5)

parameters for the C, N, and O atoms, population parameters for the two pairs of disordered atoms, a scale factor and a secondary-extinction parameter (Larson, 1967). Final values of the population parameters for the major sites were 0.59 (2) and 0.60 (3) and, for the extinction parameter, $0.25 (6) \times 10^{-6}$. The final R index $\sum |AF|/\sum F_o$ was 0.081 for the 3140 reflections with positive net intensity and 0.056 for the 2311 reflections with $F_o^2 > 3\sigma(F_o^2)$; the goodness-of-fit, $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, was 1.97 for $n = 3827$ observations and $p = 206$ parameters. Atomic parameters are given in Table 1.*

Discussion. The purpose of this investigation was to determine the nature of the coordination between the Ni atom and the nitrite group, as an aid to the interpretation of the electronic and vibrational spectra (Lever, McCarthy & Walker, 1979). During the course of our work Birdy, Goodgame, McConway & Rogers (1977; hereinafter, BGMR) reported the crystal structure of the tetrafluoroborate salt of this same cation, which showed the nitrite group to be coordinated as a bidentate group to a single Ni atom. We have found the same coordination geometry. Perspective drawings of

the two monocations in the asymmetric unit are shown in Fig. 1. The structures of the two cations are essentially identical, even including the relative populations of the two sites of the disordered methyl groups C(1). (This latter coincidence, in particular, has led us to spend many hours in vain attempts to find a higher-symmetry space group in which the two cations would be structurally equivalent.) The cations have approximate C_2 symmetry, the twofold axis passing through the Ni atom and the N atom of the nitrite group. Of the two N atoms in each diethylethylenediamine ligand, one [N(3),N(3')] is *trans* to a N atom of the other ligand while the second [N(6),N(6')] is *cis* to the other N atoms and approximately *trans* to a nitrito O atom.

Bond distances and selected angles are given in Tables 2 and 3, together with the values reported by BGMR. While the general agreement between the two

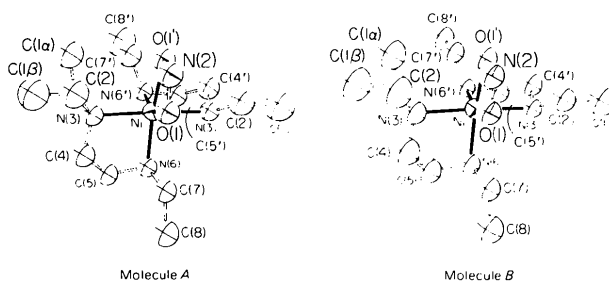


Fig. 1. Views (Johnson, 1965) of the two independent cations. H atoms are omitted.

* Lists of structure factors, thermal parameters and hydrogen coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34132 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å)

	Molecule A*	Molecule B*	BGMR†
Ni—N(3)	2.138	2.162	2.151
—N(3')	2.144	2.143	2.161
—N(6)	2.075	2.084	2.102
—N(6')	2.093	2.091	2.132
—O(1)	2.151	2.153	2.099
—O(1')	2.155	2.148	2.123
N(2)—O(1)	1.266	1.248	1.258
—O(1')	1.256	1.259	1.261
N(10)—O(9)	1.224	1.234	
—O(9')	1.229	1.264	
C(1)—C(2)	1.38, 1.37‡	1.30, 1.43‡	1.521
C(1')—C(2')	1.523‡	1.534‡	1.513
C(7)—C(8)	1.532	1.496‡	1.511
C(7')—C(8')	1.474‡	1.528	1.515
C(2)—N(3)	1.481‡	1.466‡	1.481
C(2')—N(3')	1.480	1.489	1.487
N(6)—C(7)	1.500	1.474	1.509
N(6')—C(7')	1.476	1.460	1.483
N(3)—C(4)	1.459	1.421	1.477
N(3')—C(4')	1.460	1.462	1.484
C(5)—N(6)	1.462	1.489	1.476
C(5')—N(6')	1.453	1.477	1.479
C(4)—C(5)	1.484	1.473	1.513
C(4')—C(5')	1.473	1.482	1.503

* This investigation; $\sigma \approx 0.007$ Å for bonds to Ni, 0.01–0.02 Å for others.

† Birdy *et al.* (1977); $\sigma \approx 0.004$ Å, 0.006–0.009 Å.

‡ At least one of the atoms involved in these bonds has a large *B* parameter (8 Å² or greater). We have not attempted to correct the bond lengths for the implied motions.

Table 3. Selected bond angles (°)

	Molecule A*	Molecule B*	BGMR†
N(3)—Ni—N(3')	173.4	173.8	173.6
N(3)—Ni—N(6)	82.9	83.7	83.6
N(3')—Ni—N(6')	83.3	83.7	83.7
N(3)—Ni—N(6')	92.6	92.8	90.6
N(3')—Ni—N(6)	92.8	91.9	94.8
N(6)—Ni—N(6')	101.3	99.1	101.8
O(1)—Ni—O(1')	58.7	58.5	59.2
O(1)—Ni—N(3)	91.6	90.0	91.3
O(1')—Ni—N(3')	88.7	90.5	90.1
O(1)—Ni—N(3')	94.1	95.0	95.1
O(1')—Ni—N(3)	97.1	95.2	93.7
O(1)—Ni—N(6)	100.1	100.0	99.6
O(1')—Ni—N(6')	99.8	102.4	99.5
O(1)—Ni—N(6')	158.5	160.9	158.6
O(1')—Ni—N(6)	158.9	158.5	158.6
O(1)—N(2)—O(1')	113.8	114.0	111.7
O(9)—N(10)—O(9')	116.3	114.3	

* This investigation; $\sigma \approx 0.3^\circ$ for angles at Ni, 0.7° for angles at N.

† Birdy *et al.* (1977); $\sigma \approx 0.15^\circ$, 0.4°.

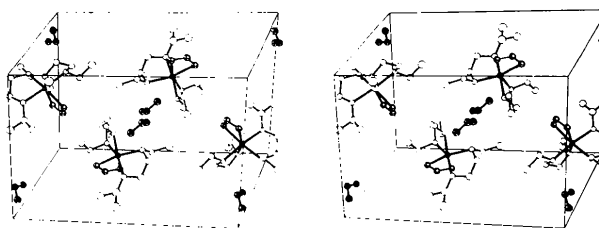


Fig. 2. A stereoview (Johnson, 1965) of the structure. The *c* direction runs from left to right, *a* is directed upward, and *b* runs out of the plane of the drawing toward the viewer.

different investigations is good, some of the details differ. In particular, our values of the Ni—O distances are significantly longer than BGMR's, and the Ni—N(*cis*) distances are marginally shorter, and we find statistical agreement within pairs of chemically equivalent bonds while BGMR report significant differences. In both compounds the Ni—N(*trans*) bonds are noticeably longer than the Ni—N(*cis*) bonds, an interesting and statistically significant *trans* effect.

A view of the crystal structure is shown in Fig. 2. The cations are connected to the nitrite anions through weak hydrogen bonds from all four coordinated N atoms in each cation; the N...O distances range from 3.06 to 3.23 Å, the H...O distances from 2.17 to 2.46 Å (assuming N—H = 0.95 Å), and the N—H...O angles from 138 to 159°. The two cations have closely similar hydrogen-bond patterns, and each of the nitrite O atoms accepts two of these bonds.

The N—O distances in the coordinated nitrite group are marginally longer, by about 0.02 Å, than those in the uncoordinated nitrite anion (Table 2), and the O—N—O angles may be marginally smaller (Table 3).

We thank Professor Lever for providing the material, the incentive for the project, and continuing good counsel and cheer.

References

- BIRDY, R., GOODGAME, M. L., MCCONWAY, J. C. & ROGERS, D. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1730–1733.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–205. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- LEVER, A. B. P., MCCARTHY, P. J. & WALKER, I. M. (1979). To be submitted.
- MIYAKE, S., TOGAWA, S. & HOSOYA, S. (1964). *Acta Cryst.* **17**, 1083–1084.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.