in these compounds. The dihedral angle between the planes O(7)—Mo(1)—S(1) and O(7)—Mo(2)—S(1) is 145°, a value which is usual for five-coordinated Mo^V dimers. The Mo—S$_L$ bond lengths vary between 2·474 (3) and 2·495 (3) Å (mean 2·486 Å). Only at Mo(1) is there a significant difference between the bond lengths *cis* and *trans* to the μ-S bond, 2·474 (3) and 2·495 (2) Å respectively. This shows the greater *trans* effect of a μ-MoS bond relative to a μ-MoO bond, as already mentioned by Mennemann & Mattes (1979). The mean Mo—S$_L$ bond length is significantly longer (0·04 to 0·08 Å) than in other Mo^V complexes with uni- and bidentate S donor ligands (Newton, McDonald, Yamanouchi & Enemark, 1979; Dance, Wedd & Boyd, 1978). dts is obviously a rather poor ligand towards Mo^V.

The six π electrons in the free ligand are at least partially delocalized (D. Altmeppen & R. Mattes, in preparation). The delocalization is removed to a great extent in the complex. This is reflected by the decrease from 1·43 (1) to 1·38 (1) Å of the C—C bond between the two C—S bonds; d(CO) and d(CS) in the complex may be compared with the structure of the free ligand as well. But, unfortunately, it has not so far been possible for us to determine the structure of K$_2$dts.H$_2$O completely. A comparison of these parameters with those of the 1,2-dithiooxalate ion (Mattes & Meschede, 1976) or the S-methyl-1,2-dithiooxalate ion (Mattes, Meschede & Niemer, 1977) seems to be adequate. Here d(CS) and d(CO) vary between 1·69–1·70 Å and 1·21–1·22 Å respectively. In the present complex d(CS) (mean 1·718 Å) has slightly increased and d(CO) (mean 1·200 Å) has slightly decreased. This trend in molecular geometry of the ligand is also indicated by the increase of the C—O stretching vibrations from 1620 and 1700 cm^{-1} in the free ligand to 1700 and 1730 cm^{-1} in the complex.

One of the two symmetrically independent $[N(C_4H_9)_4]^+$ ions is strongly disordered. Already in the first coordination sphere around the N atom eight C atoms were found at the corners of a distorted cube [C(25), C(25A), C(29), C(29A), C(33), C(33A), C(37) and C(37A)]. They could be refined well with site-occupation factors of 0·5. Their B values range from 4·9 (4) to 7·6 (6) Å^2. Further splitting was necessary at the periphery of both cations. In total, 43 C atoms for both cations have been included in the refinement, with site-occupation factors ranging from 0·33 to 0·67 and isotropic temperature factors ranging from 5·1 to 16·6 Å^2.

References

Coucouvanis, D., Holah, D. G. & Hollander, F. J. (1975). *Inorg. Chem.* **14**, 2657–2665.

Coucouvanis, D. & Hollander, F. J. (1974). *J. Am. Chem. Soc.* **96**, 3006–3008.

Dance, I. G., Wedd, A. G. & Boyd, I. W. (1978). *Aust. J. Chem.* **31**, 519–526.

Dirand-Colin, J., Ricard, L. & Weiss, R. (1976). *Inorg. Chim. Acta*, **18**, L21–L23.

Hollander, F. J. & Coucouvanis, D. (1977). *J. Am. Chem. Soc.* **99**, 6268–6280.

Mattes, R. & Meschede, W. (1976). *Chem. Ber.* **109**, 1832–1836.

Mattes, R., Meschede, W. & Niemer, U. (1977). *Chem. Ber.* **110**, 2584–2587.

Mennemann, K. & Mattes, R. (1979). *J. Chem. Res. (M)*, pp. 1343–1371; *J. Chem. Res. (S)*, p. 100.

Newton, W. E., McDonald, J. W., Yamanouchi, K. & Enemark, J. H. (1979). *Inorg. Chem.* **18**, 1621–1626.

Stiefel, E. I. (1976). *Prog. Inorg. Chem.* **22**, 1–223.

Wentworth, R. A. D. (1976). *Coord. Chem. Rev.* **18**, 1–27.

{2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}-nitritonitronickel(II) Hemihydrate

By Michael G. B. Drew and Stephen Hollis†

Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, England

Abstract. $C_{15}H_{26}N_6NiO_4.\frac{1}{2}H_2O$, $M_r = 421·9$, monoclinic, $a = 11·450$ (8), $b = 11·677$ (8), $c = 14·490$ (9) Å, $\beta = 91·1$ (1)°, $U = 1937·0$ Å^3, $Z = 4$, $D_m = 1·45$, $D_c = 1·45$ Mg m^{-3}, $F(000) = 892$, Mo $K\alpha$ radiation, $\lambda = 0·7107$ Å, $\mu = 1·041$ mm^{-1}; space group $P2_1/a$ from the systematic absences $h0l$, $h = 2n + 1$, $0k0$, $k = 2n + 1$. The Ni atom in the complex occupies an approximately octahedral environment with the four

† Deceased.

macrocycle N atoms in an approximate plane [Ni—N 2·081 (10), 1·970 (9), 2·085 (9), 2·048 (9) Å]. In axial positions are two nitrite ions, one coordinated through O [2·111 (10) Å] and the other through N [2·217 (8) Å]. 1643 independent reflections above background have been refined to $R = 0.049$.

Introduction. Two forms of the complex $[NiL]^{2+}$ have been prepared by Karn & Busch (1969), namely a red β form and a yellow α form. These have been characterized by single-crystal structure determinations as being respectively a *meso* isomer in which the methyl groups are on the same side of the ring (Drew & Hollis, 1980) and a racemic form in which the methyl groups are on opposite sides of the ring (Dewar & Fleischer, 1969). β-$[NiL(NO_2)_2] \cdot H_2O$ has been prepared by Karn & Busch (1969) and its IR spectrum indicated the presence of both N- and O-coordinated nitrite ions. In order to confirm this and to investigate the steric relationships between these ions and the β macrocycle, the crystal structure of this complex has been determined.

L
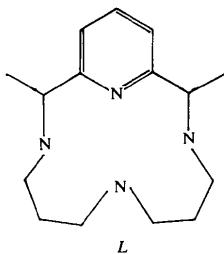
Crystals of the title compound were prepared using the published method and recrystallized from water. A crystal of approximate size 0·2 × 0·5 × 0·7 mm was mounted with the (110) planes perpendicular to the instrument axis of a General Electric XRD 5 diffractometer. 2544 independent reflections with $2\theta < 45°$ were measured by the stationary-crystal–stationary-counter method and, of these, 1689 with $I > 2\sigma(I)$ were used in subsequent calculations.

The positions of the Ni atoms were located from the Patterson map and those of all other atoms except H were obtained from Fourier maps. Ni, O, N, and C atoms were refined anisotropically. The water molecule was given an occupancy factor of 0·5.* H atoms bonded to C were fixed in trigonal or tetrahedral positions but their thermal parameters were refined successfully. The two sets of methyl H atoms were located as rigid groups and their thermal parameters were also refined. H atoms on N were allowed to refine freely. The final R obtained after full-matrix least-squares refinement was 0·049. The weighting scheme used was $w^{1/2} = 1$ for $F_o < 75$ and $75/F_o$ for $F_o > 75$.

---

* We tried several occupancy factors and this value of 0·5 gave the lowest R. With an occupancy factor of 1·0, the R value increased dramatically to 0·056.

Table 1. *Atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	$\bar{U}$ (Å²)
Ni	1087 (1)	58 (1)	2124 (1)	47 (1)
N(3)	−36 (9)	−1205 (8)	2596 (6)	50 (6)
C(4)	−479 (10)	−854 (9)	3525 (7)	55 (7)
C(5)	−482 (9)	426 (9)	3613 (7)	49 (6)
N(6)	306 (7)	974 (7)	3072 (6)	47 (6)
C(7)	534 (10)	2068 (10)	3154 (8)	55 (7)
C(8)	1518 (10)	2506 (9)	2551 (8)	58 (8)
N(9)	1742 (8)	1672 (8)	1800 (6)	57 (6)
C(10)	2958 (10)	1667 (11)	1487 (8)	75 (8)
C(11)	3105 (11)	843 (11)	681 (8)	79 (9)
C(12)	3108 (10)	−415 (10)	931 (9)	66 (8)
N(13)	1933 (8)	−882 (8)	1149 (6)	55 (6)
C(14)	2035 (10)	−2123 (10)	1400 (8)	79 (8)
C(15)	873 (11)	−2673 (10)	1605 (8)	75 (8)
C(16)	388 (10)	−2387 (9)	2542 (8)	67 (8)
C(17)	−1645 (12)	−1403 (13)	3763 (10)	92 (10)
C(18)	−1119 (11)	1063 (9)	4220 (7)	77 (9)
C(19)	−916 (12)	2224 (12)	4282 (8)	81 (10)
C(20)	−83 (11)	2760 (11)	3759 (9)	70 (9)
C(21)	1316 (13)	3719 (10)	2180 (11)	107 (11)
O(1)	2486 (8)	−405 (8)	3019 (7)	95 (7)
N(1)	2581 (12)	−98 (15)	3748 (10)	133 (13)
O(2)	3391 (10)	−409 (10)	4250 (8)	109 (10)
N(2)	−341 (7)	488 (8)	1128 (5)	58 (6)
O(3)	−254 (6)	1294 (6)	570 (5)	66 (5)
O(4)	−1287 (6)	−57 (7)	1106 (5)	64 (5)
O(5)	4323 (17)	564 (17)	5826 (14)	129 (16)

This gave satisfactory values of $w\Delta^2$ over groups of F_o and $\sin \theta/\lambda$. The calculations were carried out on a CDC 7600 computer at the University of Manchester Computer Centre using the *SHELX* 76 package (Sheldrick, 1976). Atomic scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The final
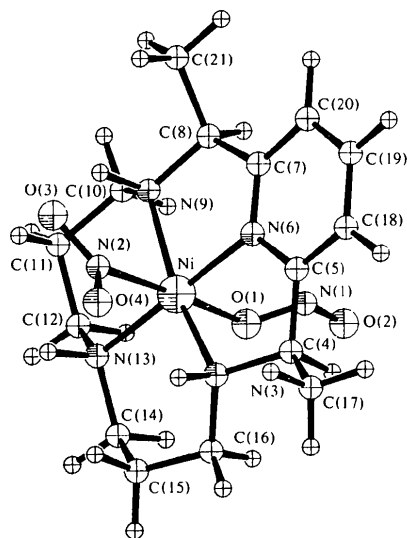

Fig. 1. Atom numbering for $[NiL(NO_2)(ONO)]$.

$C_{15}H_{26}N_6NiO_4.\frac{1}{2}H_2O$

Table 2. *Interatomic distances (Å) and angles (°)*

Ni–N(3)	2·081 (10)	N(3)–Ni–N(6)	82·2 (4)
Ni–N(6)	1·970 (9)	N(3)–Ni–N(9)	160·3 (4)
Ni–N(9)	2·085 (9)	N(3)–Ni–N(13)	98·7 (4)
Ni–N(13)	2·048 (9)	N(3)–Ni–O(1)	94·8 (4)
Ni–O(1)	2·111 (10)	N(3)–Ni–N(2)	85·5 (3)
Ni–N(2)	2·217 (8)	N(6)–Ni–N(9)	80·6 (3)
N(3)–C(4)	1·50 (1)	N(6)–Ni–N(13)	178·8 (4)
N(3)–H(3)	0·77 (9)	N(6)–Ni–O(1)	93·4 (4)
N(3)–C(16)	1·47 (1)	N(6)–Ni–N(2)	89·5 (3)
C(4)–C(5)	1·50 (1)	N(9)–Ni–N(13)	98·7 (4)
C(4)–C(17)	1·53 (2)	N(9)–Ni–O(1)	95·6 (4)
C(5)–N(6)	1·37 (1)	N(9)–Ni–N(2)	85·0 (3)
C(5)–N(18)	1·37 (2)	N(13)–Ni–O(1)	85·6 (4)
N(6)–C(7)	1·31 (1)	N(13)–Ni–N(2)	91·4 (3)
C(7)–C(8)	1·53 (2)	O(1)–Ni–N(2)	177·0 (3)
C(7)–C(20)	1·39 (2)	Ni–N(3)–C(4)	108·8 (6)
C(8)–N(9)	1·49 (1)	Ni–N(3)–C(16)	116·3 (7)
C(8)–C(21)	1·53 (2)	C(4)–N(3)–C(16)	115·0 (8)
N(9)–C(10)	1·47 (1)	N(3)–C(4)–C(5)	110·4 (8)
N(9)·H(9)	0·88 (10)	N(3)–C(4)–C(17)	113·5 (9)
C(10)–C(11)	1·53 (2)	C(5)–C(4)–C(17)	113·3 (10)
C(11)–C(12)	1·51 (2)	C(4)–C(5)–N(6)	114·5 (9)
C(12)–N(13)	1·49 (1)	C(4)–C(5)–C(18)	126·6 (10)
N(13)–C(14)	1·50 (1)	N(6)–C(5)–C(18)	118·6 (10)
N(13)–H(13)	0·84 (8)	Ni–N(6)–C(7)	120·1 (7)
C(14)–C(15)	1·51 (2)	C(5)–N(6)–C(7)	122·5 (9)
C(15)–C(16)	1·51 (2)	Ni–N(6)–C(5)	117·4 (7)
C(18)–C(19)	1·38 (2)	N(6)–C(7)–C(8)	115·0 (10)
C(19)–C(20)	1·38 (2)	N(6)–C(7)–C(20)	121·3 (11)
C(8)–C(7)–C(20)	123·6 (10)	C(11)–C(12)–N(13)	114·1 (9)
C(7)–C(8)–N(9)	109·8 (9)	C(12)–N(13)–C(14)	109·8 (8)
C(7)–C(8)–C(21)	113·7 (10)	Ni–N(13)–C(12)	113·0 (7)
N(9)–C(8)–C(21)	112·1 (10)	Ni–N(13)–C(14)	112·7 (7)
Ni–N(9)–C(10)	114·3 (7)	N(13)–C(14)–C(15)	113·2 (9)
Ni–N(9)–C(8)	111·1 (7)	C(14)–C(15)–C(16)	115·0 (10)
C(8)–N(9)–C(10)	113·9 (9)	C(15)–C(16)–N(3)	112·5 (9)
N(9)–C(10)–C(11)	111·0 (10)	C(5)–C(18)–C(19)	118·9 (11)
C(10)–C(11)–C(12)	115·4 (10)	C(18)–C(19)–C(20)	121·9 (12)
		C(19)–C(20)–C(7)	116·5 (12)
N(1)–O(1)	1·119 (18)	N(2)–O(3)	1·246 (11)
N(1)–O(2)	1·222 (18)	N(2)–O(4)	1·256 (11)
Ni–O(1)–N(1)	123·8 (10)	Ni–N(2)–O(3)	121·7 (6)
O(1)–N(1)–O(2)	121·7 (15)	Ni–N(2)–O(4)	121·8 (6)
		O(3)–N(2)–O(4)	116·5 (8)

atomic positions are given in Table 1, bond lengths and angles in Table 2.*

Discussion. The molecule (I) is shown in Fig. 1, together with the atomic numbering scheme. The Ni atom is in an approximately octahedral environment with the macrocycle forming an equatorial plane and the two nitrites in axial positions. The Ni–N (macrocycle) bond lengths are 2·081 (10), 1·970 (9), 2·085 (9), 2·048 (9) Å; values *ca* 0·14 Å longer than those found in the four-coordinate [NiL]²⁺ (Drew & Hollis, 1980). This difference is commensurate with the increase in metal radius with coordination number. The conformation of the macrocycle in (I) is almost exactly the same as that observed in [NiL]²⁺ (Table 3) with a

maximum deviation of 10° in the torsion angle. The two six-membered-ring conformations are rather flattened chairs (planes 2 and 3, Table 4). The NiN₄ equatorial plane is planar to within 0·11 Å.

As indicated by the IR spectrum, the two nitrite groups are coordinated differently to Ni, one through O [Ni–O 2·111 (10) Å] and the other through N [Ni–N 2·217 (8) Å]. The N–O distances are also as expected with O(1)–N(1) particularly short at 1·119 (18) Å. Karn & Busch (1969) considered it likely that the cause of the variation in the nitrite bonding was steric in that as the three N–H hydrogen atoms extend on the same side of the macrocycle they would prevent coordination of the nitrite ion through N on this side. However, as is clear from Fig. 1, the N-bonded nitrite is to be found on this very crowded side of the macrocycle.

The explanation of this unexpected result is straightforward. The N-bonded nitrite is stabilized by hydrogen bonding between the two O atoms and the two H atoms on N(3) and N(9). Thus, O(3)···N(9) is 2·90 (1) and

Table 3. *Torsion angles (°)*

Standard deviations of all angles in (I) are 1°.

	(I)	[NiL]²⁺
C(7)–C(8)–N(9)–C(10)	−151	−153
C(21)–C(8)–N(9)–C(10)	82	79
C(8)–N(9)–C(10)–C(11)	−177	−174
N(9)–C(10)–C(11)–C(12)	−74	−65
C(10)–C(11)–C(12)–N(13)	75	68
C(11)–C(12)–N(13)–C(14)	−179	172
C(12)–N(13)–C(14)–C(15)	−178	−179
N(13)–C(14)–C(15)–C(16)	−77	−73
C(14)–C(15)–C(16)–N(3)	72	70
C(15)–C(16)–N(3)–C(4)	−177	177
C(16)–N(3)–C(4)–C(17)	−72	−72
C(16)–N(3)–C(4)–C(5)	160	164
N(3)–C(4)–C(5)–N(6)	−26	−24
N(6)–C(7)–C(8)–N(9)	18	20

Table 4. *Least-squares planes*

Deviations of atoms from the planes are given in Å. Atoms not contributing to the calculation of the plane are marked by an asterisk.

Plane (1): Ni 0·06 (1), N(3) −0·10 (1), N(6) 0·09 (1), N(9) −0·11 (1), N(13) 0·06 (1)

Plane (2): Ni, N(9), N(13) 0·00, C(10)* 0·76 (1), C(11)* 0·30 (1), C(12)* 0·74 (1)

Plane (3): Ni, N(3), N(13) 0·00, C(14)* 0·72 (1), C(15)* 0·20 (1), C(16)* 0·65 (1)

Plane (4): Ni* −0·19 (1), N(3)* −0·33 (1), C(4)* 0·19 (1), C(5) 0·02 (1), N(6) −0·02 (1), C(7) 0·02 (1), C(8)* 0·09 (1), N(9)* −0·33 (1), C(10)* 0·31 (1), C(11)* −0·22 (1), C(12)* 0·29 (1), N(13)* −0·32 (1), C(14)* 0·26, C(15)* −0·33 (1), C(16)* 0·18 (1), C(17)* −0·37 (1), C(18) 0·00 (1), C(19) −0·01 (1), C(20) 0·00 (1), C(21)* −0·69 (1)
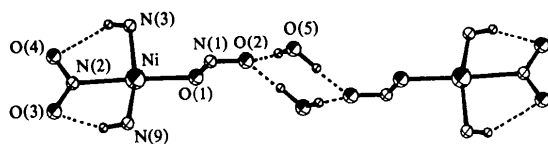
Fig. 2. Hydrogen-bond scheme in (I). Hydrogen bonds are indicated by broken lines.

$O(4) \cdots N(3)$ 2·90 (1) Å with the $O \cdots H$ distances 2·1, 2·2 Å. Indeed, the orientation of the NO_2 group around the $Ni-N(3)$ bond facilitates formation of these hydrogen bonds as N(3), N(9) are as close as possible to the plane of the $Ni-NO_2$ fragment with deviations of only 0·05, 0·58 Å. It is clear then that Karn & Busch (1969) were correct in their view that the nitrite ion would find it difficult to N-bond to this side of the macrocycle. It is only the formation of the hydrogen bonds that permits this.

The O-bonded nitrite occupies the opposite less crowded* side of the macrocycle. N(1) takes up the least crowded positions over the pyridine ring [the $N(6)-Ni-O(1)-N(1)$ torsion angle is $-2 \cdot 0°$]. Thus the planes of the two nitrites are almost perpendicular,

---

* Models indicate that this side also is too crowded to permit nitrite to bond through N.

the angle of intersection being 85·5°. O(2) is hydrogen bonded to two water molecules [O(5) at 2·75 (2) Å, $O(5)(\frac{1}{2} - x, -y, \frac{1}{2} - z)$ at 2·63 (2) Å] related by a centre of symmetry. It is surprising that despite these short distances the occupancy factor of the water molecule is only 0·5. This pattern of hydrogen bonding in the unit cell is illustrated in Fig. 2. Apart from this, there is one other short intermolecular distance that could represent a hydrogen bond – albeit a very weak one: $N(13) \cdots O(3)(-x, -y, -z)$ 3·15 Å, with an $N-H \cdots O$ angle of 163°. There are no other intermolecular distances less than the sum of the van der Waals radii.

References

DEWAR, R. & FLEISCHER, E. (1969). Nature (London), 222, 372–373.
DREW, M. G. B. & HOLLIS, S. (1980). Acta Cryst. B36, 718–720.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
KARN, J. L. & BUSCH, D. H. (1969). Inorg. Chem. 8, 1149–1153.
SHELDRICK, G. M. (1976). SHELX 76. Program for crystal structure determination. Univ. of Cambridge. England.

The Structure of Anhydrous Cadmium Formate

By Gabriela Weber

Anorganisch-Chemisches Institut der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

Abstract. $Cd(CHO_2)_2$, $2CHO_2^- \cdot Cd^{2+}$, $M_r = 202 \cdot 44$, $C2/c$, $a = 11 \cdot 614$ (4), $b = 6 \cdot 185$ (3), $c = 12 \cdot 409$ (5) Å, $\beta = 112 \cdot 51$ (5)°, $Z = 8$, $D_c = 3 \cdot 266$ Mg m^{-3}. $R = 0 \cdot 053$ for 1634 independent reflexions. Formate ion (1) is tridentate and bridges symmetry-related cations. Both O atoms of the quadridentate formate ion (2) chelate one Cd atom and are also in bridging positions to two symmetry-related cations. Four-membered rings are a significant feature of the polymeric lattice thus formed. Cd is seven-coordinate in pseudo-octahedral geometry with Cd–O distances in the range 2·259 (4)–2·599 (7) Å.

Introduction. The isomorphism of the formate dihydrates of Ni^{II}, Cd, Zn, Mg, Mn^{II}, Fe^{II} and Cu^{II} has

been proved by investigations of the pure formates (Krogmann & Mattes, 1963; Post & Trotter, 1974a; Burger & Fuess, 1977; de With, Harkema & van Hummel, 1976; Osaki, Nakai & Watanabé, 1963, 1964; Kay, Almodovar & Kaplan, 1968; Bukowska-Strzyżewska, 1965; Hoy, de S. Barros, de S. Barros & Friedberg, 1965; Malard & Pascal, 1966a) as well as mixed formates (Ogata, Taga & Osaki, 1977a,b; March, Weber & Nagorny, 1973). Heating leads to dehydration by a mechanism which is similar for all the formates mentioned above (Masuda & Shishido, 1979). This might indicate isomorphism of the anhydrous formates, some of which are reported to exist in an unstable α and a stable β form (Malard & Pascal, 1966b; Dollimore, Gupta & Nowell, 1979). The