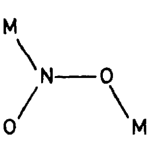
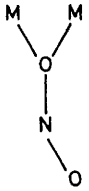
Steric Factors in Nitrite Co-ordination. Part 1. Crystal Structure of Bis(*NN'*-diethylethylenediamine)(nitrito-*OO'*)nickel(II) Tetrafluoroborate

By **Roshun Birdy, David M. L. Goodgame,* James C. McConway,** and **Donald Rogers,*** Chemistry Department, Imperial College, London SW7 2AY

The preparations and electronic and i.r. spectra are reported for the complexes $[NiL_2(NO_2)]X$ (X = BF_4 or ClO_4; L = $RHNCH_2CH_2NHR$ or $R_2NCH_2CH_2NH_2$, R = Me or Et). The structure of the title complex has been determined from three-dimensional *X*-ray diffractometer data. The crystals are monoclinic, with unit-cell dimensions *a* = 11.338(1), *b* = 16.291(2), *c* = 11.934(1) Å, and β = 112.015(8)°, space group $P2_1/c$, and *Z* = 4. The structure has been refined by least squares to *R* 0.053 for 2 522 independent reflections. The complex is monomeric with a chelating nitrite group forming part of a distorted-octahedral environment about nickel. The diethylethylenediamine ligands are arranged in *cis* positions and there is an approximation to a diad in the cation. The steric factors leading to this geometry, as distinct from M–ONO–M bridging, are discussed.

THE nitrite ion is an extremely versatile ligand. As a unidentate ligand it can co-ordinate either *via* nitrogen forming a nitro-complex or *via* oxygen giving a nitrito-complex. Alternatively it can use both oxygen atoms to form a chelate ring, or it can bridge two metal atoms as in (1)—(3). Although examples of bridges (1) and (2) have been demonstrated by *X*-ray structural studies,[1,2] there are no proven examples of type (3) bridges.


(1)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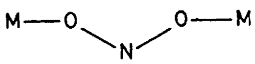
(3)

Earlier work had shown that with nickel nitrite complexes the mode of nitrite co-ordination depended on the steric influences of other ligands present. In complexes of the type $NiL_2(NO_2)_2$ (L = a substituted ethylenediamine), nitrite co-ordinates *via* nitrogen for ethylenediamine and *N*-monoalkylethylenediamines,[3] but *via* one oxygen atom as the extent of substitution of the amino- and/or methylene hydrogens is increased.[4] Very heavily substituted diamines, such as *NNN'N'*-tetra-alkylethylenediamines give only $NiL(O_2N)_2$ complexes in which the anions are chelating.[5,6] These observations suggested that the type (1) bridge, known to be present in $[Ni(en)_2(NO_2)][BF_4]$,[1] would be less favoured as alkyl substitution on the diamine was increased, and that, by a suitable choice of diamine, complexes of stoicheiometry $[NiL_2(NO_2)][BF_4]$ containing type (3) bridges might be obtained.

We report here the preparation and properties of the complexes $[NiL_2(NO_2)]X$ (X = BF_4 or ClO_4; L = $RHNCH_2CH_2NHR$ or $R_2NCH_2CH_2NH_2$, R = Me or Et), and the results of a single-crystal *X*-ray study of $[Ni(EtHNCH_2CH_2NHEt)_2(NO_2)][BF_4]$.

EXPERIMENTAL

Preparation.—All the complexes except $[Ni(EtHNCH_2CH_2NHEt)_2(NO_2)][BF_4]$ were prepared by the following method. A methanolic solution of nickel(II) nitrite[5] was heated under reflux with an equimolar quantity of hydrated nickel(II) perchlorate (or tetrafluoroborate) after the addition of 2,2-dimethoxypropane. This solution was added dropwise and with stirring to a methanolic solution of the appropriate amount of the diamine. After concentration and cooling, crystals formed and these were collected and dried *in vacuo*.

The complex $[Ni(EtHNCH_2CH_2NHEt)_2(NO_2)][BF_4]$ was obtained by a modification of the above procedure. A concentrated aqueous solution of $Ni[NO_2]_2$ and $Ni[BF_4]_2$ was prepared by adding solid potassium nitrite (0.85 g) to an aqueous solution of nickel(II) tetrafluoroborate hexahydrate (3.4 g) and filtering off the precipitated potassium tetrafluoroborate. This solution was added dropwise, with stirring, to a methanolic solution of the diamine. Large green crystals of the complex separated after the solution had been cooled for several hours.

Microanalytical results are given in Table 1 together with relevant spectral data and ligand abbreviations. Physical measurements were carried out as described previously.[5]

X-Ray Studies.—The dark green crystals of $[Ni(s\text{-}deen)_2(NO_2)][BF_4]$ were rather irregular in shape. They were stored in their mother liquor as they tended to powder on prolonged exposure to air. Crystals used for *X*-ray study were coated with varnish.

Crystal data. $C_{12}H_{32}BF_4N_5NiO_2$, $M = 433.9$, Monoclinic, $a = 11.338(1)$, $b = 16.291(2)$, $c = 11.934(1)$ Å, $\beta = 112.015(8)°$, $U = 2\,043.6$ Å^3, $D_m = 1.42$, g cm^{-3} $Z = 4$, $D_c = 1.41$ g cm^{-3}, $F(000) = 896$, $\mu = 18.13$ cm^{-1} for Cu-K_α radiation (λ 1.541 8 Å). Space group $P2_1/c$ (no. 14) uniquely from systematic absences.

Intensity data were collected by means of filtered Cu-K_α radiation for a crystal of dimensions *ca.* 0.2 × 0.2 × 0.3 mm mounted about the *b* axis on a Siemens off-line automatic four-circle diffractometer. The θ—2θ scan technique was employed, with the 'five-value' measuring procedure,[7] to give 2 522 independent reflections (to θ 60°) of which 140 were judged to be unobserved.[7] The net count of the reference reflection did not vary significantly during the

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[1] M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Chem. Comm.*, 1965, 477.

[2] D. M. L. Goodgame, M. A. Hitchman, D. F. Marsham, P. Phavanantha, and D. Rogers, *Chem. Comm.*, 1969, 1383.

[3] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1966, **5**, 1303.

[4] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1964, **3**, 1389.

[5] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1965, **4**, 721.

[6] M. G. B. Drew and D. Rogers, *Chem. Comm.*, 1965, 476.

[7] F. H. Allen, D. Rogers, and P. G. H. Troughton, *Acta Cryst.*, 1971, **B27**, 1325.

data collection (*ca.* 6 d). The data were scaled using the reference reflection, and Lorentz and polarisation corrections were applied.

The structure was determined in a straightforward way *via* a three-dimensional Patterson function and the heavy-atom method. Full-matrix least-squares refinement of the non-hydrogen atoms, initially isotropically but later anisotropically, gave R 0.095. At this stage the data were corrected for absorption effects according to the method of Busing and Levy,[8] using a 10 × 10 × 10 grid, with crystal pathlengths determined by the procedure of Coppens *et al.*[9] Further anisotropic refinement reduced R to 0.087. An anomalous-dispersion correction for nickel was then applied (R 0.076). Two misprocessed reflections and three reflections suffering from extinction were removed during the refinement procedure. When the hydrogen atoms, located from the latest difference-Fourier map, were included in the refinement as fixed-atom contributions R decreased to the final value of 0.053. The scattering factors used were those tabulated by Cromer and Waber,[10] and the values of $\Delta f'$ and $\Delta f''$ were those given by Cromer.[11] A final difference map was relatively featureless.

TABLE 1

Characterisation data

Complex[a]	Colour	Analysis (%)[b]			Nitrite i.r. bands (cm^{-1})	Electronic spectral bands (cm^{-1})[c]
		C	H	N		
[Ni(s-dmen)$_2$(NO$_2$)][ClO$_4$]	Dark purple	25.45	6.2	18.5	1 300m, 1 230s[d]	18 180, *ca.* 14 900w (sh),
		(25.25)	(6.4)	(18.4)		10 500, *ca.* 8 300br (sh)
[Ni(s-dmen)$_2$(NO$_2$)][BF$_4$]	Dark purple	26.3	6.2	19.1	1 300m, 1 215s[d]	18 000, 10 500[e]
		(26.1)	(6.6)	(19.0)		
[Ni(a-dmen)$_2$(NO$_2$)][ClO$_4$]	Bright green	25.3	6.25	18.45	1 295mw, 1 215vs,	16 800, *ca.* 12 500w (sh),
		(25.25)	(6.4)	(18.4)	857ms	10 050
[Ni(a-dmen)$_2$(NO$_2$)][BF$_4$]	Bright green	26.5	6.3	19.3	1 295mw, 1 217s,	16 650, *ca.* 12 400w (sh),
		(26.1)	(6.6)	(19.0)	859m	10 000
[Ni(s-deen)$_2$(NO$_2$)][ClO$_4$]	Blue-green	33.2	7.1	16.3	1 315m,[f] 1 210vs,	17 350, *ca.* 12 500w (sh),
		(33.0)	(7.4)	(16.0)	861m, 829w	10 250[e]
[Ni(s-deen)$_2$(NO$_2$)][BF$_4$]	Blue-green[g]	34.15	7.2	16.6	1 295mw,[f] 1 210vs,	17 400, *ca.* 14 700w (sh),
		(34.0)	(7.6)	(16.5)	861m	12 500w (sh), 10 250[e]

[a] Ligand abbreviations: s-dmen = *NN'*-dimethylethylenediamine; a-dmen = *NN*-dimethylethylenediamine; and s-deen = *NN'*-diethylethylenediamine. [b] Calculated values are in parentheses. [c] Reflectance spectra. [d] Amine bands in the region of $\delta(NO_2)$. [e] Asymmetric to lower energy. [f] Assignment uncertain because of amine band. [g] When powdered; dark green when crystalline.

TABLE 2

Fractional co-ordinates of the non-hydrogen atoms (× 10^5 for Ni, × 10^4 for all others) with standard deviations in parentheses

	x	*y*	*z*
Ni	23 274(6)	9 381(4)	23 013(6)
O(1)	491(3)	877(2)	961(3)
N(2)	694(5)	1 403(3)	282(4)
O(1′)	1 808(3)	1 686(2)	734(3)
C(1)	3 261(7)	−756(4)	−272(5)
C(2)	2 647(5)	−60(3)	164(4)
N(3)	2 960(3)	−59(2)	1 485(3)
C(4)	2 513(5)	−806(3)	1 906(4)
C(5)	2 814(4)	−715(3)	3 246(4)
N(6)	2 172(3)	18(2)	3 473(3)
C(7)	817(4)	−158(3)	3 333(5)
C(8)	695(5)	−738(3)	4 271(5)
C(1′)	−430(6)	2 053(4)	2 798(6)
C(2′)	747(5)	2 456(3)	2 737(5)
N(3′)	1 898(3)	1 935(2)	3 282(3)
C(4′)	3 045(5)	2 465(3)	3 630(5)
C(5′)	4 220(5)	1 942(3)	4 122(4)
H(6′)	4 243(3)	1 337(2)	3 206(3)
C(7′)	4 740(5)	1 678(3)	2 317(5)
C(8′)	6 145(5)	1 885(4)	2 854(6)
B	6 458(6)	−693(4)	3 318(5)
F(1)	5 537(4)	−1 225(3)	2 706(4)
F(2)	6 912(7)	−313(4)	2 619(5)
F(3)	5 957(3)	−153(2)	3 929(3)
F(4)	7 403(3)	−1 109(2)	4 148(3)

TABLE 3

Fractional co-ordinates (× 10^3) of the hydrogen atoms which were located from the difference map and unrefined

	x	*y*	*z*
H(11)	429	−70	14
H(12)	300	−135	−1
H(13)	300	−77	−125
H(21)	288	53	−14
H(22)	158	−12	−28
H(31)	400	−1	191
H(41)	151	−90	145
H(42)	301	−135	176
H(51)	250	−127	358
H(52)	384	−67	371
H(61)	269	22	441
H(71)	38	43	339
H(72)	34	−41	244
H(81)	116	−133	424
H(82)	120	−49	519
H(83)	−27	−88	418
H(1′1)	−59	148	232
H(1′2)	−28	195	373
H(1′3)	−127	244	240
H(2′1)	90	303	321
H(2′2)	60	256	180
H(3′1)	187	163	408
H(4′1)	303	290	431
H(4′2)	303	280	284
H(5′1)	423	162	491
H(5′2)	505	232	435
H(6′1)	481	82	365
H(7′1)	422	224	195
H(7′2)	458	124	161
H(8′1)	630	233	357
H(8′2)	666	133	322
H(8′3)	652	213	221

Table 2 lists the final co-ordinates of the non-hydrogen atoms and their standard deviations which were obtained

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[8] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[9] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[10] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[11] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

TABLE 4

Bond lengths (Å) with estimated standard deviations in parentheses

Ni–N(3)	2.151(4)	Ni–N(3′)	2.161(4)
Ni–N(6)	2.102(4)	Ni–N(6′)	2.132(3)
Ni–O(1)	2.099(3)	Ni–O(1′)	2.123(3)
N(2)–O(1)	1.258(7)	N(2)–O(1′)	1.261(6)
C(1)–C(2)	1.521(9)	C(1′)–C(2′)	1.513(9)
C(2)–N(3)	1.481(6)	C(2′)–N(3′)	1.487(6)
N(3)–C(4)	1.477(6)	N(3′)–C(4′)	1.484(6)
C(4)–C(5)	1.513(7)	C(4′)–C(5′)	1.503(7)
C(5)–N(6)	1.476(6)	C(5′)–N(6′)	1.479(7)
N(6)–C(7)	1.509(6)	N(6′)–C(7′)	1.483(7)
C(7)–C(8)	1.511(8)	C(7′)–C(8′)	1.515(7)
B–F(1)	1.342(7)	B–F(2)	1.292(11)
B–F(3)	1.392(8)	B–F(4)	1.338(6)

TABLE 5

Selected bond angles (°) with estimated standard deviations in parentheses

O(1)–Ni–O(1′)	59.2(1)	O(1′)–Ni–N(6)	158.6(1)
N(6)–Ni–N(6′)	101.8(1)	O(1)–Ni–N(3′)	95.1(1)
N(3)–Ni–N(3′)	173.6(1)	O(1′)–Ni–N(3)	93.7(1)
O(1)–Ni–N(3)	91.3(1)	N(3)–Ni–N(6)	83.6(1)
O(1′)–Ni–N(3′)	90.1(1)	N(3′)–Ni–N(6′)	83.7(1)
O(1)–Ni–N(6)	99.6(1)	N(3)–Ni–N(6′)	90.6(1)
O(1′)–Ni–N(6′)	99.5(1)	N(3′)–Ni–N(6)	94.8(1)
O(1)–Ni–N(6′)	158.6(1)	O(1)–N(2)–O(1′)	111.7(4)

TABLE 6

Deviations (in Å × 10^3) of various atoms from the planes (1)—(4) defined by the atoms marked with asterisks

	Plane			
	(1)	(2)	(3)	(4)
Ni	*	*	*	*
N(2)	−1 973	1 973	−16	−94
O(1)	−2 070	764	*	−18
O(1′)	−770	2 093	*	−96
C(1)	−471			
C(2)	−716			
N(3)	*			−2 137
C(4)	−458			
C(5)	280			
N(6)	*		−102	*
C(7)	−1 279			514
C(8)	−1 233			686
C(1′)		38		
C(2′)		771		
N(3′)		*		2 144
C(4′)		474		
C(5′)		−244		
N(6′)		*	20	*
C(7′)		1 283		−626
C(8′)		1 314		−821

Equations of each plane, in the form $Px + Qy + Rz + S = 0$

Plane	P	Q	R	S
(1)	8.731 3	2.794 8	3.352 6	−3.065 8
(2)	2.278 2	10.113 4	−9.282 9	0.657 3
(3)	−5.866 8	11.657 2	7.506 9	−1.455 7
(4)	−6.053 7	11.108 4	7 920.1	−1.455 8

Angles (°) between the planes

	(2)	(3)	(4)
(1)	78.2	89.3	89.3
(2)		89.1	86.4
(3)			2.8

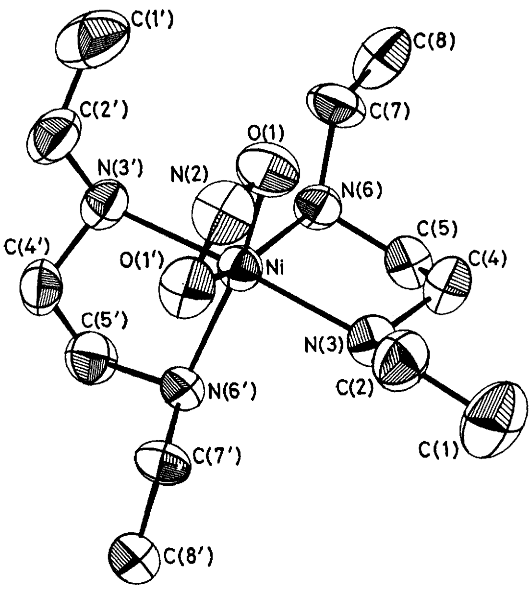

FIGURE 1 Structure of the cation $[Ni(EtHNCH_2CH_2NHEt)_2(O_2N)]^+$

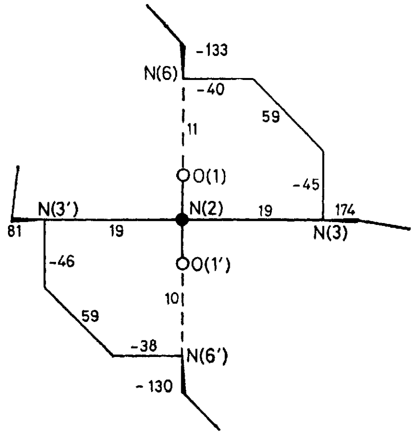

FIGURE 2 Some torsion angles (°) in the cation

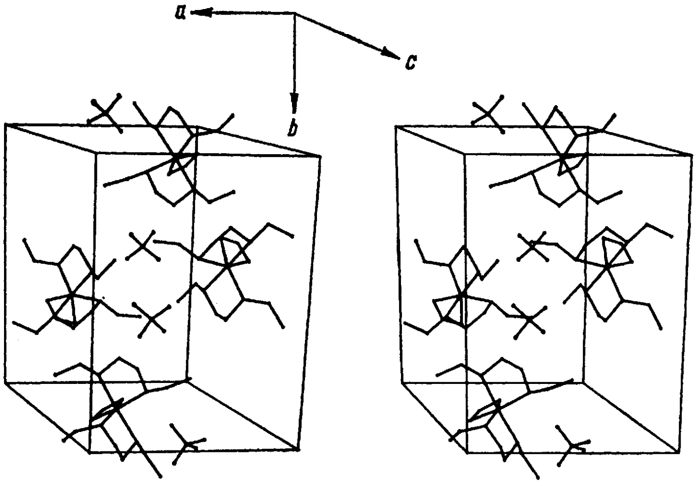

FIGURE 3 Stereodiagram of the molecular packing

using the full-matrix least-squares refinement procedure ORFLS of '*X*-Ray '70.' The co-ordinates of the hydrogen atoms are given in Table 3. The bond lengths and some angles are given in Tables 4 and 5, details of best planes in Table 6, and of some torsion angles in Figure 2. The structure of the cation $[Ni(s\text{-}deen)_2(O_2N)]^+$ is shown in Figure 1 and the molecular packing in Figure 3 (both drawn using the program ORTEP[12]). All the intermolecular contacts are of the van der Waals type. The cation approximates fairly closely to C_2 symmetry, and the numbering scheme adopted (see Figure 1) indicates symmetry-related atoms. Only the peripheral atoms C(1) and C(1′) depart substantially from diad symmetry (see Figure 2).

Observed and calculated structure factors and the anisotropic temperature factors for all the non-hydrogen atoms are deposited in Supplementary Publication No. SUP 22077 (14 pp.).*

DISCUSSION

Complexes of the type $[Ni(diamine)_2(NO_2)]X$ (X = BF_4 or ClO_4) were readily obtained with a-dmen, s-dmen, and s-deen. The electronic spectra of the solid complexes (Table 1) indicate the absence of type (1) bridges, as the spin-allowed *d-d* bands are at much lower energies than in $[Ni(en)_2(NO_2)]X$. For the last complexes the two lowest-energy bands were observed[13] at *ca.* 20 000 and *ca.* 12 000 cm^{-1}, whereas the corresponding bands in the spectra of the complexes described here are at 16 600—18 200 and 10 000—10 500 cm^{-1} respectively. The absence of type (1) bridging is supported by the nitrite band frequencies in the i.r. spectra (Table 1), particularly by the absence of an N–O stretch in the 1 390—1 440 cm^{-1} region. Instead, the ν(NO) bands are at 1 210—1 230 and 1 295—1 315 cm^{-1}. These results also show the absence of a single oxygen bridge [type (2)].

However, the spectral results do not permit a reliable differentiation between the presence of a type (3) bridge and a chelating nitrite group. Both types of nitrite co-ordination would be expected to affect the internal modes of the $[NO_2]^-$ group in a similar way. Moreover, the only significant difference in the electronic spectra would be differences in the splitting of the orbital-triplet levels between a *trans*-NiN_4O_2 chromophore [for the type (3) bridge] and a *cis*-NiN_4O_2 system for the chelating nitrite. As such differences are too ill defined for diagnostic purposes, one of the series of complexes was chosen for *X*-ray study, $[Ni(s\text{-}deen)_2(NO_2)][BF_4]$.

The structural study showed that in this complex the nitrite group acts as a chelate and not as a bridging group. The co-ordination about the nickel atom is distorted octahedral. Within each chelate ring formed by s-deen both ethyl groups point upward toward the nitrite groups. This arrangement allows the s-deen molecules to occupy *cis* positions without undue steric strain whilst leaving sufficient room for the nitrite group to chelate.† The atoms N(6) and N(6′) lie almost in the plane containing Ni, O(1), and O(1′) [deviations from this plane are 0.02 and 0.10 Å respectively; see plane (3), Table 6]. As expected, the constraint imposed on the angle O(1)–Ni–O(1′) by the 'bite' of the nitrite group permits the angle N(6)–Ni–N(6′) to open out from an ideal octahedral angle of 90 to 101.8°. However, the departure from linearity of N(3)–Ni–N(3′) is quite small (173.6°). The *trans*-Ni–N bonds to N(3) and N(3′) are significantly longer (2.15 and 2.16 Å) than those to N(6) and N(6′) (2.10 and 2.13 Å), and all are longer than the Ni–N bonds (2.09 Å) in $[Ni(tetmen)(O_2N)_2]$ (tetmen = *NNN′N′*-tetramethylethylenediamine).[6] The angles at the nitrite group [O(1)–N(2)–O(1′) and O(1)–Ni–O(1′)] are quite similar to those in the tetmen complex, but the nitrite chelation is more symmetric {Ni–O, 2.10 and 2.12 Å compared with 2.07 and 2.15 Å, and 2.06 and 2.12 Å for the two nitrites in $[Ni(tetmen)(O_2N)_2]$[6]}.

In conclusion, although the steric factors in $[Ni(s\text{-}deen)_2(ONO)_2]$ are sufficient to favour nitrito-[4] as compared with nitro-co-ordination, they are insufficient in the range of complexes reported here to prevent the *cis* chelation of the diamine required for nitrite chelation. In turn, the relatively small steric requirements of the chelating nitrite group facilitate this *cis* arrangement of the diamine co-ordination, as they permit any unfavourable diamine–diamine contacts to open out by distortion from octahedral geometry. The present results suggest that the type (3) bridging nitrite may be rather elusive, as the further increase in steric hindrance required to prevent a *cis* arrangement of two diamines would probably result in only one diamine molecule co-ordinating to the metal atom.

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

† We are indebted to a referee for drawing our attention to a paper[14] describing the structure of $[Ni(en)_2(O_2N)][NO_3]$ in which the complex ion is monomeric and, within the more limited accuracy of the work, very similar to the corresponding part of the present structure. The only noteworthy differences are in the torsion angles in the ethylenediamine rings. In the previous work, the rings, which are devoid of ethyl groups, are distinctly flatter. Our work was completed before that paper appeared, but, even if we had been able to take it into consideration before embarking on our study, we would still have felt it necessary to proceed, because, apart from its sensitivity to alkyl substitution, the co-ordination geometry is also dependent on the counter ion. For example, our earlier work[1] on $[Ni(en)_2(NO_2)][BF_4]$ showed it to be polymeric: it in no way resembles $[Ni(en)_2(O_2N)][NO_3]$.

[12] C. K. Johnson, ORTEP, 'A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations,' Oak Ridge National Laboratory, Oak Ridge, Tennessee, Report ORNL 3794, 1965.

[13] D. M. L. Goodgame, M. A. Hitchman, and D. F. Marsham, *J. Chem. Soc.* (*A*), 1971, 259.

[14] A. E. Shvelashvili, M. A. Porai-Koshits, A. I. Kvitashvili, and B. M. Shchedrin, *Zhur. strukt. Khim.*, 1974, **15**, 307.