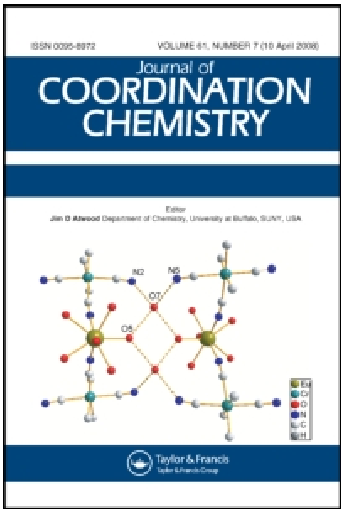

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CRYSTAL STRUCTURES OF [Ni(en)$_2$(NO$_2$)]Cl (I) AND [*cis*-β-Ni(trien)(NO$_2$)]ClO$_4$ (II)

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Compound (I) [Ni(en)$_2$(NO$_2$)]Cl, NiC$_4$ClH$_{16}$N$_5$O$_2$, has been synthesized and its crystal structure determined at 100 K. This compound crystallizes from a deionized water solution at 25°C, in the orthorhombic system space group Fdd2 (No. 43) with lattice constants: $a = 18.219(3)$, $b = 8.841(2)$, $c = 12.924(1)$ Å, $V = 2081.6(5)$ Å^3 and MW = 260.37, $Z = 8$ $d = 1.662$ mg m^{-3}. A total of 3239 data were recorded over the range of $4° \leq 2\theta \leq 60°$; of these, 3086 (unique and with $I > 1\sigma(I)$) were used in the structural analysis. Data were corrected for absorption. The final discrepancies in the refinement of the structure are RF = 0.057 and Rw = 0.072.

Compound (II) [Ni(trien)(NO$_2$)]ClO$_4$, NiC$_6$ClH$_{18}$N$_5$O$_6$, has been synthesized and its crystal structure determined at room temperature. This compound crystallizes from a deionized water solution at 25°C, in the monoclinic system space group P2$_1$/n (No. 14) with lattice constants: $a = 8.934(3)$, $b = 12.705(8)$, $c = 12.522(9)$ Å, $\beta = 90.33(4)$, $V = 1421.4(14)$ Å^3, MW = 350.40, $Z = 4$, $d = 1.637$ mg m^{-3}. A total of 4367 data were collected over the range of $4° \leq 2\theta \leq 60°$; of these, 4131 (unique and with $I > 2.5\sigma(I)$) were used in the structural analysis. Data were corrected for absorption. The final refinement of the structure produced discrepancies of RF = 0.041 and Rw = 0.044.

Keywords: Nickel amine complexes; nickel nitrite complexes; crystal structures; trien; en

INTRODUCTION

The nitrite anion coordinates to a metal in a number of different ways.[1] Inter-ligand repulsion is well accepted as an important factor that influences the nitrite coordination types,[1,2] however the counter anion could also be a factor. For example, in the series of compounds with general formula

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TABLE I Nitrite coordination modes of various nickel amine complexes

Compound	*Space group*	*Nitrite coordination mode*	*Ref.*
$[Ni(en)_2(NO_2)]ClO_4$	Pnma	*trans* μ-nitro(N,O)[b]	6–8
$[Ni(en)_2(NO_2)]PF_6$	Pnma[a]	*trans* μ-nitro(N,O)	6
$[Ni(en)_2(NO_2)]BF_4$	Pnma[a]	*trans* μ-nitro(N,O)	9
$[Ni(en)_2(NO_2)]I_3$	Pmma	*trans* μ-nitro(N,O)	6
$[Ni(en)_2(NO_2)]Cl$	Fdd2[a]	nitro(O,O′)	3
$[Ni(en)_2(NO_2)]Br$	?[a]	nitro(O,O′)	?[e]
$[Ni(en)_2(NO_2)]I$	A2/a	nitro(O,O′)	4
$[Ni(en)_2(NO_2)]NO_3$	B2/b	nitro(O,O′)[c]	5
$[Ni(en)_2(NO_2)]_2(BPh_4)_2$	$P2_1/n$	nitro(O), tridentate	10
$[Ni(tn)_2(NO_2)]ClO_4$	?[a]	*trans* μ-nitro,(N,O)[d]	12
$[Ni(tn)_2(NO_2)]BPh_4$	$P2_12_12_1$[a]	nitro(O,O′)	11

[a]Not in CSD (Cambridge Structural Database (Ref. 13)) or it is in CSD but 3D structure not available; [b]all *trans* μ-nitro(N,O) bridges are disordered; [c]3D structure in CSD is not complete; [d]coordination mode was suggested by magnetic studies; [e]no publication could be found.

$[Ni(en)_2(NO_2)]X$ (for this manuscript en = 1,2-ethylenediamine, tn = 1,3-diaminopropane, trien = 1,4,7,10-tetraazadecane) the coordination mode of nitrite group varies with changes in X. A chelating nitro(O,O) mode occurs when $X = Cl^-$, Br^-, I^- or NO_3^-.[3–5] When $X = ClO_4^-$, BF_4^-, PF_6^- or I_3^-, linear polymeric chains of Ni(II) ions are formed, bridged by the *trans* μ-nitro (N,O) groups.[6–9] The coordination to Ni(II) is summarized in Table I. When tetraphenylborate is the counter anion, a dimer cation, $[Ni(en)_2(NO_2)]_2^{2+}$, is formed.[10] There are two nitrite groups in the dimer cation, one nitrite functions as monodentate nitro(O) ligand and bonds to one nickel, the other nitrite functions as tridentate ligand with one oxygen bonding to the second nickel and the other oxygen bonding to both, nickels. At the same time, a chelating nitro(O,O′) group was reported to occur in $[Ni(tn)_2(NO_2)]BPh_4$,[11] while a μ-nitro(N,O) group was suggested to exist in $[Ni(tn)_2(NO_2)]ClO_4$ by magnetic studies.[12] We report two crystal structures here to better understand nickel amine nitrite chemistry and the function of the counter ion.

EXPERIMENTAL

Preparation of the Compounds

Compound (I), $[Ni(en)_2(NO_2)]Cl$, was prepared by addition of en and $NaNO_2$ to an aqueous solution of $NiCl_2 \cdot 6H_2O$ in a 2 : 2 : 1 ratio, stirring for half an hour and slowly evaporating at room temperature. Besides the two other major products (which are believed to be *trans*-$[Ni(en)_2(NO_2)_2]$ and *cis*-$[Ni(en)_2(NO_2)_2]$), reddish, well defined single crystals suitable for X-ray diffraction were obtained. These were filtered, dried and used for X-ray data collection.

Compound (II), [Ni(trien)(NO_2)]ClO_4, was prepared by addition of the trien and $NaNO_2$ to an aqueous solution of $NiCl_2 \cdot 6H_2O$ in a 1 : 2 : 1 ratio, stirring for half an hour and slowly evaporating at room temperature. A small amount of well defined, blue, single crystals suitable for X-ray diffraction were obtained and used for data collection.

X-ray Crystallography

Data for compound (I) were collected with an Enraf-Nonius CAD-4 diffractometer at LSU at 100 K. A crystal was centered with data from 25 reflections. Examination of the cell constants, absences, and Niggli matrix[14] clearly showed the compound to crystallize in a orthorhombic lattice whose systematic absences belong to Fdd2 (No. 43). Data were corrected for absorption using empirical curves derived from Psi scan of suitable reflections, and were processed with an Enraf-Nonius program package (MolEN).

For compound (II), data were collected with an Enraf-Nonius CAD-4 diffractometer at UH. A crystal was centered with data in the $4° \leq 2\theta \leq 60°$ range and examination of the cell constants, absences, and Niggli matrix[14] clearly showed the compound to crystallize in a monoclinic lattice whose systematic absences belong to $P2_1/n$ (No. 14). Data were corrected for absorption using empirical curves derived from Psi scan of suitable reflections. The scattering curves were taken from Cromer and Waber's compilation.[15] Processing of the data was carried out with the PC version of the NRCVAX package.[16]

For compound (I), the structure was solved using direct methods. For compound (II) the structure was solved from the Patterson map, using the Ni as the heavy atom. After refinement the scale factor and the positional parameters of the Ni atoms, a difference Fourier map produced many of the non-hydrogen atoms. The remaining atoms were found in subsequent difference maps. The positions and anisotropic thermal parameters of heavy atoms were refined. For compound (II), all hydrogen atoms were found experimentally in the difference maps and used for least squares calculation. The final residuals are $RF = 0.057$, $Rw = 0.072$ for compound (I), and $RF = 0.041$, $Rw = 0.044$ for compound (II). The details of data collection for compounds (I) and (II) are summarized in Tables II and III and the results are presented in Tables IV–VII.

TABLE II Summary of data collection and processing parameter for compound (I)

	Compound (I)
Space group	Fdd2
Cell constants	$a = 18.219(3)$
	$b = 8.841(2)$
	$c = 12.924(1)$
Cell volume (Å^3)	2081.6(5)
Molecular formula	$NiC_4ClH_{16}N_5O_2$
Molecular weight	260.37
$F(000)$	1088
Z	8
Density (mg m^{-3})	1.662
Temperature (K)	100
Radiation employed	MoKα(0.71073 Å)
μ	2.112 mm^{-1}
h(min, max)	0, 15
k(min, max)	−23, 23
l(min, max)	−32, 32
Absorption correction	Yes
Relative transmission coefficients	0.9072, 1.0000
Data collection range	5–80
Total data collected	3239
Total unique data collected	3086
Data used in refinement	3086 ($I > 1\sigma(I)$)
Merging R-value	0.025
RF, Rw for significant reflections	0.057, 0.072
GoF	1.537
Max shif/sigma ratio	0.000
Deepest hole (e/Å^3)	−1.561
Highest peak (e/Å^3)	1.440
Weights used	$w = \sigma[(F_o)]^{-2}$

RF $= \sum(F_o - F_c)/\sum(F_o)$, Rw $= \left[\sum(w(F_o - F_c)^{**}2)/\sum(wF_o^{**}2)\right]^{1/2}$, GoF $= \left[\sum(w(F_o - F_c)^{**}2)/(\text{No. of reflns.} - \text{No. of params.})\right]^{1/2}$.

TABLE III Summary of data collection and processing parameter for compound (II)

	Compound (II)
Space group	$P2_1/n$
Cell constants	$a = 8.934(3)$
	$b = 12.705(8)$
	$c = 12.522(9)$
	$\beta = 90.33(4)$
Cell volume (Å^3)	1421.4(14)
Molecular formula	$NiC_6ClH_{18}N_5O_6$
Molecular weight	350.40
$F(000)$	730.08
Z	4
Density (mg m^{-3})	1.637
Radiation employed	MoKα(0.70930 Å)
μ	1.59 mm^{-1}
h(min, max)	−12, 12
k(min, max)	0, 17
l(min, max)	0, 17

TABLE III (*Continued*)

	Compound (II)
Absorption correction	Yes
Relative transmission coefficients	0.500291, 0.702423
Data collection range	4–60
Scan width	$0.80 + 0.3 \tan\theta$
Total data collected	4367
Total unique data collected	4131
Data used in refinement	2683 ($I > 2.5\sigma(I)$)
Merging R-value	0.017
RF, Rw for significant reflections	0.041, 0.044
RF, Rw for all reflections	0.041, 0.044
GoF	0.49
Max shift/sigma ratio	0.199
Deepest hole (e/Å^3)	−0.390
Highest peak (e/Å^3)	0.520
Weights used	$w = \sigma[(F_o)]^{-2}$

$\mathrm{RF} = \sum(F_o - F_c)/\sum(F_o)$, $\mathrm{Rw} = [\sum(w(F_o - F_c)^{**}2)/\sum(wF_o^{**}2)]^{1/2}$, $\mathrm{GoF} = [\sum(w(F_o - F_c)^{**}2)/(\text{No. of reflns.} - \text{No. of params.})]^{1/2}$.

TABLE IV Atomic parameters x, y, z for compound (I) (ESDs refer to the last digit printed)

	x	y	z
Ni	0.00000	0.00000	0.00000
Cl	0.00000	0.50000	−0.16095(3)
O1	−0.05061(5)	0.0572(1)	−0.14417(8)
N1	0.05278(5)	0.2082(1)	0.00203(9)
N2	−0.07055(5)	0.1026(1)	0.10651(8)
N3	0.00000	0.00000	−0.1984(1)
C1	0.02838(7)	0.2877(1)	0.0964(1)
C2	−0.05410(7)	0.2669(1)	0.1066(1)
H1NA	0.043(1)	0.254(2)	−0.050(2)
H1NB	0.0974(9)	0.200(2)	0.009(1)
H2NA	−0.0617(9)	0.067(2)	0.170(1)
H2NB	−0.119(1)	0.090(2)	0.098(2)
H1A	0.0409(8)	0.395(2)	0.089(1)
H1B	0.054(1)	0.245(2)	0.154(2)
H2A	−0.073(1)	0.321(2)	−0.165(2)
H2B	−0.083(1)	0.317(4)	0.047(2)

RESULTS AND DISCUSSION

The crystal structure of compound (I) is made up of a $[Ni(en)_2(NO_2)]^+$ cation and an uncoordinated chloride anion (Figure 1). In the unit cell, both the chloride anion and complex cation sit on the two-fold axes. Each nickel is coordinated by four nitrogens of the two en ligands and two oxygens of the chelating nitrite group, with an average Ni–N bond length 2.084(1) and Ni–O bond length 2.140(1) Å. The two-fold axis go through the nickel atom and the nitrogen of the nitrite group. For the structure of the

TABLE V Atomic parameters x, y, z for compound (II) (ESDs refer to the last digit printed)

	x	y	z
Ni	0.82331(5)	0.76243(4)	0.15987(4)
N1	1.0571(4)	0.7658(3)	0.1719(3)
N2	0.8644(4)	0.6972(3)	0.0120(3)
N3	0.5989(4)	0.7367(3)	0.1168(3)
N4	0.7767(4)	0.9169(3)	0.1237(3)
N5	0.7970(5)	0.6710(4)	0.3415(3)
O1	0.7857(4)	0.7700(3)	0.32610(24)
O2	0.8238(4)	0.6214(3)	0.2563(3)
C1	1.1185(5)	0.7322(5)	0.0676(4)
C2	1.0148(6)	0.6497(4)	0.0202(4)
C3	0.7383(6)	0.6239(4)	−0.0061(5)
C4	0.5957(6)	0.6854(5)	0.0103(5)
C5	0.5249(5)	0.8416(4)	0.1203(5)
C6	0.6270(5)	0.9236(4)	0.0736(4)
H1	1.127(10)	0.732(7)	0.259(7)
H2	1.082(6)	0.817(4)	0.191(4)
H3	1.228(6)	0.696(4)	0.082(4)
H4	1.127(8)	0.808(6)	0.019(6)
H5	1.006(5)	0.582(4)	0.074(4)
H6	1.044(6)	0.620(5)	−0.056(5)
H7	0.860(6)	0.738(5)	−0.050(4)
H8	0.745(5)	0.562(4)	0.045(3)
H9	0.736(6)	0.602(5)	−0.081(5)
H10	0.591(6)	0.745(5)	−0.053(4)
H11	0.504(7)	0.645(5)	−0.003(5)
H12	0.558(6)	0.690(4)	0.164(4)
H13	0.515(5)	0.861(4)	0.200(4)
H14	0.424(5)	0.841(4)	0.078(4)
H15	0.636(5)	0.912(4)	0.000(4)
H16	0.587(5)	1.000(4)	0.085(4)
H17	0.836(5)	0.946(3)	0.086(3)
H18	0.787(6)	0.968(5)	0.184(4)
O3	0.3588(6)	0.6729(3)	0.3036(4)
O4	0.4441(5)	0.5264(3)	0.2125(3)
O5	0.3906(6)	0.5148(4)	0.3936(3)
O6	0.1984(5)	0.5389(5)	0.2711(4)
Cl	0.34768(12)	0.56181(8)	0.29598(9)

four-membered nitro chelating ring, the O1–Ni–O1 angle is 58.88(3)° and the O1–N3–O1 angle is 112.6(1)°, which are in the range of the literature data.[1]

The structure of the $[Ni(en)_2(NO_2)]^+$ cation in compound (I) is very similar to the structure of $[Ni(en)_2(NO_2)]^+$ in $[Ni(en)_2(NO_2)]I$, which also has a two-fold axis going through the nickel atom and nitrogen atom of NO_2. But, interestingly, these two compounds crystallize in different space groups. Usually structural analogs crystallize in the same space group, i.e. compounds $[Co(en)_2(NO_2)_2]X$ ($X = Cl^-$, Br^-, I^-) all crystallize as space group $P2_1$.[17]

TABLE VI Bond lengths and selected bond angles for compound (I)

Bond lengths			
Ni-O1	2.140(1)	N2-H2NA	0.89(2)
Ni-N1	2.077(1)	N2-H2NB	0.89(2)
Ni-N2	2.090(1)	C1-C2	1.520(2)
O1-N3	1.246(1)	C1-H1A	0.98(2)
N1-C1	1.477(2)	C1-H1B	0.96(2)
N1 H1NA	0.80(2)	C2-H2A	0.96(2)
N1-H1NB	0.82(2)	C2-H2B	1.03(2)
N2-C2	1.483(2)		
Selected bond angles			
O1-Ni-O1A	58.88(3)	N2-Ni-N2A	97.63(4)
O1-Ni-N1	90.06(4)	Ni-O1-N3	94.26(8)
O1-Ni-N1A	91.20(4)	Ni-N1-C1	107.04(7)
O1-Ni-N2	101.88(4)	Ni-N2-C2	107.52(7)
O1-Ni-N2A	160.22(4)	O1-N3-O1	112.6(1)
N1-Ni-N1A	178.55(4)	N1-C1-C2	108.1(1)
N1-Ni-N2	83.79(4)	N2-C2-C1	108.5(1)
N1-Ni-N2A	95.26(4)		

TABLE VII Bond lengths and selected bond angles for compound (II)

Bond lengths			
Ni-N1	2.093(4)	C1-C2	1.518(8)
Ni-N2	2.063(4)	C1-H3	1.10(5)
Ni-N3	2.099(4)	C1-H4	1.14(7)
Ni-N4	2.057(4)	C2-H5	1.10(5)
Ni-O1	2.113(3)	C2-H6	1.06(6)
Ni-O2	2.160(3)	C3-C4	1.510(8)
N1-C1	1.482(6)	C3-H8	1.01(5)
N1-H1	1.33(9)	C3-H9	0.97(6)
N1-H2	0.73(5)	C4-H10	1.10(6)
N2-C2	1.476(6)	C4-H11	0.97(6)
N2-C3	1.479(6)	C5-C6	1.505(7)
N2-H7	0.93(6)	C5-H13	1.04(5)
N3-C4	1.485(7)	C5-H14	1.04(5)
N3-C5	1.488(6)	C6-H15	0.93(5)
N3-H12	0.91(5)	C6-H16	1.04(5)
N4-C6	1.476(6)	O3-Cl	1.419(4)
N4-H17	0.80(4)	O4-Cl	1.431(4)
N4-H18	1.00(6)	O5-Cl	1.411(4)
N5-O1	1.276(6)	O6-Cl	1.398(5)
N5-O2	1.263(6)		
Selected bond angles			
N1-Ni-N2	83.68(16)	Ni-N3-C4	108.2(3)
N1-Ni-N3	166.61(16)	Ni-N3-C5	106.1(3)
N1-Ni-N4	101.36(16)	C4-N3-C5	114.4(4)
N1-Ni-O1	95.30(15)	Ni-N4-C6	109.3(3)
N1-Ni-O2	88.73(15)	O1-N5-O2	112.3(4)
N2-Ni-N3	83.22(16)	Ni-O1-N5	95.2(3)
N2-Ni-N4	102.85(16)	Ni-O2-N5	93.3(3)
N2-Ni-O1	158.85(15)	N1-C1-C2	108.4(4)
N2-Ni-O2	99.71(15)	N2-C2-C1	107.3(4)
N3-Ni-N4	84.27(15)	N2-C3-C4	107.2(4)

TABLE VII (*Continued*)

N3–Ni–O1	95.92(15)	N3–C4–C3	109.7(4)
N3–Ni–O2	90.76(14)	N3–C5–C6	109.8(4)
N4–Ni–O1	98.07(15)	N4–C6–C5	110.2(4)
N4–Ni–O2	156.12(15)	O3–Cl–O4	108.7(3)
O1–Ni–O2	59.14(14)	O3–Cl–O5	110.1(3)
Ni–N1–C1	107.8(3)	O3–Cl–O6	106.8(4)
Ni–N2–C2	105.6(3)	O4–Cl–O5	109.7(3)
Ni–N2–C3	104.5(3)	O4–Cl–O6	110.5(3)
C2–N2–C3	116.5(4)	O5–Cl–O6	111.0(3)

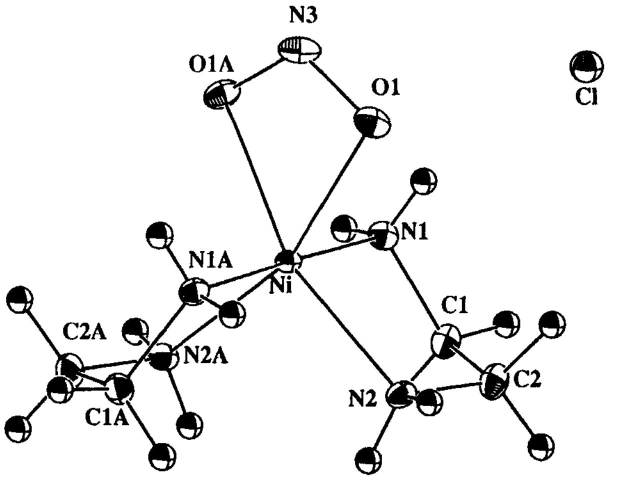

FIGURE 1 Zortep view of the molecular structure of $[Ni(en)_2(NO_2)]Cl$. Thermal ellipsoids are drawn at 40% probability level.

The crystal structure of $[Ni(tren)(NO_2)_2]$ has two *cis* nitrite groups coordinated to the central nickel atom.[18] However, in several tries, we failed to prepare that compound. Instead, compound (II) [*cis*-β-Ni(trien)(NO_2)]ClO_4] was obtained. The crystal structure of compound (II) is made up of [*cis*-β-Ni(trien)$(NO_2)]^+$ cations and uncoordinated perchlorate counter anions (Figure 2). Each nickel is coordinated by four nitrogens of the trien ligand and two oxygens of the chelating nitrite group. The average Ni–N bond length 2.078(4) and Ni–O bond length 2.137(3) Å, are similar to the bond lengths in compound (I). The trien ligand is in the *cis*-β conformation although *cis*-α is the most common geometry for 3*d* transition element derivatives of this ligand. For the structure of the nitro chelating ring, the O1–Ni–O2 angle is 59.14(14)° and the O1–N5–O2 angle is 112.3(4)°, similar to the values obtained for compound (I).

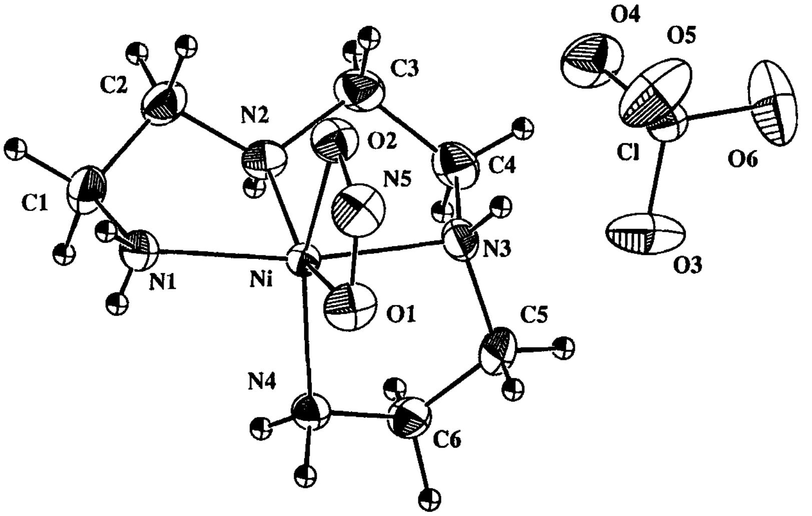

FIGURE 2 Zortep view of the molecular structure of [*cis*-β-Ni(trien)(NO_2)]ClO_4. Thermal ellipsoids are drawn at 30% probability level.

We have reported that the counter ion affects the crystallization pathway in cobalt amine complexes by competing for the hydrogens of the amino nitrogens to form hydrogen bonds.[19] It has been noted that halides act as weak hydrogen-bonding species primarily with basal plane hydrogens of the amine moieties. Thus, the oxygens of the nitro group in [Co(en)$_2$(NO_2)$_2$]X, or of the oxalato group in compounds [Co(en)$_2$(OX)]X, form inter-complex hydrogen bonds and helical cationic chains. When that occurs, compounds frequently crystallize as conglomerates. We define ClO_4^- and NO_3^- as strong hydrogen-bonding species which will compete for the hydrogens, while forming several hydrogen bonds per mole of anion. Thus, the desired inter-complex hydrogen bond pattern necessary for conglomerate crystallization could not form; so, the anions modify the crystallization pathway and racemate crystals are formed.

For compounds with general formula [Ni(en)$_2$(NO_2)]X, the coordination mode of the nitrite group is also affected by the counter anion. Chelating nitro(O,O) occurs when $X = Br^-$, I^-, NO_3^-, or Cl^-, while μ-nitro(N,O) occurs when $X = ClO_4^-$, BF_4^-, PF_6^- or I_3^-. In the compound [Ni(en)$_2$(NO_2)] NO_3, nitrate has the same effect as compounds with X = halides. In this case we may not say that the counter ion effect is due to their different hydrogen bond abilities. Thus, in the case of Ni complexes, the function of the counter ion is, and how it affects the coordination type of the nitrite group and the crystallization mode is uncertain. This study is an effort to define the role of counter ions.

In $[Ni(en)_2(NO_2)]X$ ($X = ClO_4^-$, BF_4^-, PF_6^- or I_3^-) the μ-nitro(N,O) bridges are *trans* to each other. In compound (II), $[Ni(trien)(NO_2)]ClO_4$, the nitrite group functions as a chelating nitro(O,O′) instead of a bridging μ-nitro(N,O) as in compound $[Ni(en)_2(NO_2)]ClO_4$. This might be due to the coordination preference of the ligand trien. In theory, the $[Ni(trien)X_2]$ complex can exist as three distinct geometric isomers, symmetrical *cis* (*cis*-α), unsymmetrical *cis* (*cis*-β) and *trans* forms. Although the *cis*-α is the most commonly observed, trien shows a preference for *cis*-β over *trans* form. Therefore, when occupying two *cis* positions, it is much easier for the chelating nitro to compete with the bridging mode, although *cis* μ-nitro (N,O) is also known in a nickel amine polymer.[20]

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Supplementary Material

Torsion angles, anisotropic thermal parameters, structure factor tables and packing diagrams for the compounds are available in hard copy or PC diskette format from I. Bernal.

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