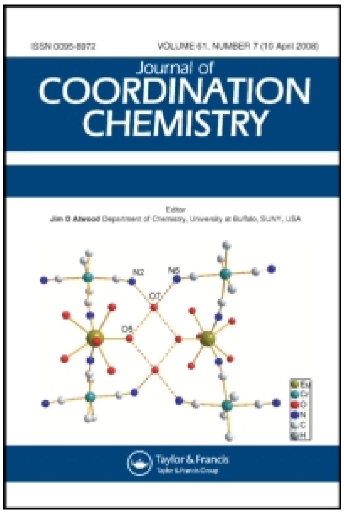

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and Characterization of Nitrato-Triamine-Metal(II) Complexes. Conglomerate Crystallization Part 55. Crystal Structure of [Ni(dien)(O_2NO)(ONO_2)] (I), {[Cu(dien)-(μ-ONO_2)]NO_3}$_\infty$ (II), [Zn(dien)(O_2NO)(ONO_2)] (III), [Ni(Medpt)(O_2NO)(ONO_2)] (IV) and [Cu(Medpt)$(ONO_2)_2$] (V)

Salah S. Massoud[a]; Hyunphil Chun[a]; Ruiwu Wen[a]; Ivan Bernal[a]
[a] Department of Chemistry, University of Houston, Houston, TX, USA

To cite this Article Massoud, Salah S. , Chun, Hyunphil , Wen, Ruiwu and Bernal, Ivan(2002) 'Synthesis and Characterization of Nitrato-Triamine-Metal(II) Complexes. Conglomerate Crystallization Part 55. Crystal Structure of [Ni(dien)(O_2NO)(ONO_2)] (I), {[Cu(dien)-(μ-ONO_2)]NO_3}$_\infty$ (II), [Zn(dien)(O_2NO)(ONO_2)] (III), [Ni(Medpt)(O_2NO)(ONO_2)] (IV) and [Cu(Medpt)$(ONO_2)_2$] (V)', Journal of Coordination Chemistry, 55: 9, 1065 — 1078

To link to this Article: DOI: 10.1080/0095897021000010026

URL: http://dx.doi.org/10.1080/0095897021000010026

J. Coord. Chem., 2002, Vol. 55(9), pp. 1065–1078

SYNTHESIS AND CHARACTERIZATION OF NITRATO-TRIAMINE-METAL(II) COMPLEXES. CONGLOMERATE CRYSTALLIZATION PART 55. CRYSTAL STRUCTURE OF $[Ni(dien)(O_2NO)(ONO_2)]$ (I), $\{[Cu(dien)\text{-}(\mu\text{-}ONO_2)]NO_3\}_\infty$ (II), $[Zn(dien)(O_2NO)(ONO_2)]$ (III), $[Ni(Medpt)(O_2NO)(ONO_2)]$ (IV) AND $[Cu(Medpt)(ONO_2)_2]$ (V)

SALAH S. MASSOUD, HYUNPHIL CHUN,
RUIWU WEN and IVAN BERNAL*

Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA

(Received 9 January 2001; Received 13 August 2001; In final form 16 December 2001)

In absolute ethanol and in the presence of triethylorthoformate, reactions of metal(II) nitrates with linear tridentate amines afforded metal complexes of the formula $M(NNN)(NO_3)_2$, where $M = Ni^{2+}$, Cu^{2+} and Zn^{2+}, and NNN = dien and Medpt. The compounds fall into three categories in accordance with their stereochemistry and mode of binding of the nitrato ligands. Compounds **I**, $[Ni(dien)(O_2NO)(ONO_2)]$ and **III**, $[Zn(dien)(O_2NO)(ONO_2)]$ are isomorphous and isostructural. They crystallize in the monoclinic space group $P2_1/n$ with nearly identical cell constants. The stereochemistry of these two compounds is such that the terdentate dien ligand forms a *fac* MN_3 moiety with the two oxygens of the bidentate nitrato ligand *trans* to the terminal NH_2. These ligands form the base of the octahedral arrangement in which the sixth position, *trans* to the secondary nitrogen of the dien, is an oxygen of the monodentate nitrato ligand. Compound **IV**, $[Ni(Medpt)(O_2NO)(ONO_2)]$ falls into the same category as **I** and **III** despite the fact that the two rings in the Ni-Medpt moiety are six-membered rings, unlike those in compounds **I** and **III** which are five-membered rings. Nevertheless, the nickel-amine arrangement is *fac*. The bidentate nitrato-oxygens are *trans* to the terminal NH_2 of the amine ligand, and the oxygen of the monodentate nitrato ligand is *trans* to the tertiary amine-nitrogen. Such stereochemistry is prevalent for nickel and zinc compounds. Interestingly, compound **IV** crystallizes as a conglomerate (space group $P2_12_12_1$).

Compound **II**, $\{[Cu(dien)(\mu\text{-}ONO_2)]NO_3\}_\infty$ belongs to the second category and has a polymeric structure. The repeating fragment in the polymeric chain is a Cu(dien)–O fragment with the monodentate nitrato ligand occupying an equatorial position of the base. A second oxygen of the equatorial nitrate becomes an axial ligand for an adjacent $Cu–N_3O$ fragment. In this way the substance propagates into an infinite chain. The repeating unit has an effective square pyramidal, five-coordinate, configuration. Finally, the compound crystallizes as a racemate. The second nitrate necessary for charge compensation of this copper(II) compound is ionic and its function is to hold the infinite chains of the lattice.

The third category represented by compound **V**, $[Cu(Medpt)(ONO_2)_2]$ contains two molecules in the asymmetric unit of the racemic lattice (monoclinic, space group $P2_1/a$). The structure of Cu-Medpt is unlike that of **IV** in that both species present in the asymmetric unit have the amine ligand in a *mer* configuration which together with a monodentate oxygen of a nitrato ligand form a base plane of a square pyramid. The fifth ligand of both Cu^{2+} ions is a second monodentate nitrato ligand. The stereochemical differences between

---

*Corresponding author. E-mail: ibernal@uh.edu

ISSN 0095-8972 print: ISSN 1029-0389 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/0095897021000010026

the two Cu^{2+} ions are insignificant for the Cu-Medpt fragment, which share the same conformation and configuration. The major difference between the two species is the torsional angles defined by the Cu–O–N–O angles. The difference arises from variation in the hydrogens of the primary amine moieties selected by nitrato-oxygens to form intramolecular hydrogen bonds. Finally, there is a little variation in the equatorial $Cu–ONO_2$ stereochemistry because of steric hindrance, imposed by the Medpt, preventing large torsional angles by these nitrato ligands. This is evident by comparing the two copper species shown in Fig. 5.

Finally, nitrate-to-Br ligand exchange was found to take place when KBr pellets are prepared for IR spectral measurements.

Keywords: Nickel complexes; Copper complexes; Zinc complexes; Amines; Nitrato complexes; Modes of crystallization; Racemates; Conglomerates; Ligand exchange in KBr pellets

INTRODUCTION

The nitrate ion can coordinate to a metal ion in many ways [1,2] and most nitrate complexes contain only one, or in some cases two, coordination modes. The presence of several nitrate modes within one compound is very rare [1,3]. To our knowledge, there are 38 complexes in the literature, where a single 3*d*-metal complex contains mono- ($O–NO_2$; nitrato–O) and bidentate (O_2NO; nitrato–O,O′) nitrates [4–41].

The crystal structures of $[M(py)_3(NO_3)_2]$, where $M = Co^{2+}$, Cu^{2+} and Zn^{2+} were shown to exhibit seven-coordinate geometry, with both nitrates coordinating in a bidentate fashion [42]. When $M = Ni^{2+}$, *fac*-octahedral geometry was obtained, with one bidentate and one monodentate nitrato ligands [31]. Seven-coordinate geometry was also observed in a Co(II) complex with NNO donor ligand, $[Co(O(CH_2CH_2pzR_2)_2)(NO_3)_2]$, where the two nitrato groups were acting as bidentate ligands [9]. Variation in the coordination mode of the $X(CH_2CH_2pzMe_2)_2$ ligands with X = S or NEt was accompanied by a change in the nitrate coordination modes, and the isolated complexes, $[Co(X(CH_2CH_2pzR_2)_2)(NO_3)_2]$ crystallized in nearly *fac*-octahedral geometry with the nitrate ligands exhibiting both unidentate and bidentate coordination modes [21,25]. Similar modes of coordination were adopted by the two nitrato ligands in $[Zn(O(CH_2CH_2pzR_2)_2)(NO_3)_2]$ (R = isopropyl) and in some other related dinitrato–Zn(II) systems [15,18,26,32,35].

The dinitrato–Cu(II) complexes, $[Cu(L)(NO_3)_2]$, where L represents a variety of linear tridentate NNN, NNO and NNS donor ligands displayed distorted octahedral geometry with three sites in the complexes occupied by two nitrato ligands, one as a bidentate and the other as a monodentate ligand [4,19,29,30,38]. A similar coordination environment was obtained with $L = NH(CH_2CH_2pzMe_2)_2$, [13] and was also proposed for L = 2,6-diacetyl- pyridinebis(anil), based on the IR assignment in the 1200–1500 cm^{-1} region, attributable to the nitrate ion [39]. Interestingly, when $NH(CH_2CH_2pzMe_2)_2$ was benzylated to produce $BzN(CH_2CH_2pzMe_2)_2$, the resulting Cu(II) complex had a distorted square-pyramidal geometry, where the Cu^{2+} ion is five-coordinate with three nitrogen donors from the amine and two oxygen atoms, one from each nitrate ligand [13].

The dinitrato–Ni(II) complexes, $[Ni(L)(NO_3)_2]$, with L = NNN and tris(N-donor) ligands are of special interest, since six coordination might be attained by the presence of both monodentate and bidentate nitrato groups. A few nickel(II) complexes of this type were observed based on x-ray analyses [6,20,31,34,39,41]. With $L = EtN(CH_2CH_2pzMe_2)_2$ [34] and monoimine-benzaldehyde of *cis*,*cis*-1,3,5-triaminocyclohexane, [6] the same coordination modes for the nitrato ligands were demonstrated [6,34]. Although the steric interaction between ethyl or benzyl group in this ligand

and the nitrate anions played no role in adoption of the six-coordinate environment for the nickel complexes, it significantly distorted and altered the coordination geometry in the corresponding Cu(II) and Zn(II) compounds [6,13].

In this paper, we report x-ray analyses and IR spectral measurements for the complexes [M(NNN)$(NO_3)_2$], where M = Ni^{2+}, Cu^{2+} and Zn^{2+} and NNN = dien and Medpt. In the latter case, the flexibility in the triamine ligand and the steric hindrance introduced at the tertiary amine nitrogen allow us to test the geometry adopted by these metal ions. Also, these substances will illustrate how the coordinating abilities of the NO_3^- ligands vary as a function of the aliphatic chain length of the amines. Finally, they are useful to demonstrate how the coordination environment is achieved with ligands capable of adopting meriditional "T-shaped", and facial geometry.

Ligand abbreviations: dien = diethylenetriamine, Medpt = 3,3′-diamino-*N*-methyldipropylamine, py = pyridine, $O(CH_2CH_2pzMe_2)_2$ = bis[(3,5-dimethyl-1-pyrazolyl) ethyl]ether, $S(CH_2CH_2pzMe_2)_2$ = bis[(3,5-dimethyl-1-pyrazolyl)ethyl]sulfide, $NH(CH_2CH_2pzMe_2)_2$ = bis[(3,5-dimethyl-1-pyrazolyl)ethyl]amine, $EtN(CH_2CH_2pzMe_2)_2$ = bis[(3,5-dimethyl-1-pyrazolyl)ethyl]ethylamine, $BzN(CH_2CH_2pzMe_2)_2$ = bis[(3,5-dimethyl-1-pyrazolyl)ethyl]benzylamine, $O(CH_2CH_2pz^{Pri2})_2$ = bis[(3,5-diisopropyl-1-pyrazolyl)ethyl]ether, bdmpae = *N*,*N*-bis(3,5-dimethypyrazol-1-ylmethyl)aminoethane.

EXPERIMENTAL

Materials

Diethylenetriamine (dien), 3,3′-diamino-*N*-methyl-dipropylamine (Medpt) and triethylorthoformate (anhydrous, 98%) were purchased from Aldrich Chem. Co. Commercially available $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ of sufficient purity (~98%) were used without further purification. Absolute ethanol was dried over 4 Å molecular sieves (8–12 mesh beads).

Synthesis of the Complexes

Dinitrato(dipropylenetriamine)nickel(II), [Ni(dien)(O₂NO)(ONO₂)] (I)

A hot solution of $Ni(NO_3)_2 \cdot 6H_2O$ (1.46 g, 5 mmol) dissolved in 40 mL of absolute ethanol, previously dehydrated by refluxing it for 15 min with 4 mL of triethylorthoformate, was added drop by drop to a hot solution of diethylenetriamine (0.57 g, 5 mmol) in absolute ethanol (20 mL) and triethylorthoformate (2 mL). The light-purple precipitate, which formed immediately, was filtered off. The filtrate was then allowed to crystallize at room temperature. Well-developed, light-blue, single crystals, suitable for x-ray diffraction were separated out after *ca.* 2 h. These were collected by filtration, washed with ether and air-dried (yield: 0.46 g, 16%). Anal. Calcd. for $C_4H_{13}N_5O_6Ni$ (%): C, 16.80; H, 4.58; N, 24.50. Found: C, 16.31; H, 4.55; N, 23.95.

Bis(diethylenetriamine)nickel(II) nitrate, [Ni(dien)₂](NO₃)₂

The light-purple compound, isolated from the reaction of $Ni(NO_3)_2$ and dien was dissolved into the minimum amount of water in a 10 mL beaker and put into a closed jar containing about the same amount of ethanol. After 1 week of standing at room temperature, single crystals of x-ray quality were obtained by diffusion. These were collected by filtration, washed with ethanol and ether, and air-dried.

Nitrato(diethylenetriamine)copper(II) nitrate, $\{[Cu(dien)(\mu\text{-}ONO_2)]NO_3\}_\infty$ (II)

Diethylenetriamine (0.51 g, 5 mmol) was added dropwise over a period of 5 min to a well stirred, absolute ethanolic (60 mL) solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1.21 g, 5 mmol) previously dehydrated by refluxing for 15 min with 6 mL of triethylorthoformate. The resulting blue precipitate, which was formed immediately, was heated at 60°C with stirring for *ca.* 5 min and the product was collected by filtration. Single light-blue crystals suitable for x-ray diffraction were obtained when the volume of the filtrate was reduced to *ca.* 20 mL by heating at 60°C, and then allowed to crystallize at room temperature (yield: 1.45 g, 96%). Anal. Calcd. for $C_4H_{13}N_5O_6Cu$(%): C, 16.52; H, 4.51; N, 24.09. Found: C, 16.57; H, 4.67; N, 24.21.

Dinitrato(diethylenetriamine)zinc(II), $[Zn(dien)(O_2NO)(ONO_2)]$ (III)

The procedure for (I) was repeated with $Zn(NO_3)_2 \cdot 6H_2O$. White needles (yield: 0.6 g, 82%). Anal. Calcd. for $C_4H_{13}N_5O_6Zn$(%): C, 16.42; H, 4.48; N, 23.94. Found: C, 16.54; H, 4.65; N, 24.08.

Dinitrato(3,3′-diamino-N-methyl-tripropylamine)nickel(II), $[Ni(Medpt)(O_2NO)(ONO_2)]$ (IV)

The ligand Medpt (0.73 g, 5 mmol), dissolved in absolute ethanol (10 mL) was added dropwise to an absolute ethanolic (40 mL) solution of $Ni(NO_3)_2 \cdot 6H_2O$ (1.46 g, 5 mmol) previously dehydrated by refluxing for 15 min with 4 mL of triethylorthoformate. After *ca.* 2 h of standing at room temperature, the green precipitate, which separated, was collected by filtration, washed with acetone and air-dried. Crystallization from absolute ethanol pretreated with triethyorthoformate, afforded green single crystals suitable for x-ray diffraction (yield: 1.5 g, 91%). Anal. Calcd. for $C_7H_{19}N_5O_6Ni$(%): C, 25.64; H, 5.84; N, 21.35. Found: C, 25.57; H, 5.94; N, 21.21.

Dinitrato(3,3′-diamino-N-methyl-tripropylamine)copper(II), $[Cu(Medpt)(ONO_2)_2]$ (V)

This was prepared as described above for **IV** in 78% yield as a deep-blue crystalline solid. Anal. Calcd. for $C_7H_{19}N_5O_6Cu$(%): C, 25.26; H, 5.75; N, 20.04. Found: C, 25.27; H, 5.83; N, 21.20.

Dinitrato(3,3′-diamino-N-methyl-tripropylamine)zinc(II), $[Zn(Medpt)(NO_3)_2]$

The complex was prepared in a similar manner as that described for **IV** in 80% yield as a white solid. Anal. Calcd. for $C_7H_{19}N_5O_6Zn$(%): C, 25.12; H, 5.72; N, 20.93. Found: C, 25.06; H, 5.63; N, 19.95.

Physical Measurements

Elemental analyses were performed at Galbraith Laboratory, Knoxville, TN USA.

Infrared spectra for the dinitrato complexes were recorded in the range 4000–400 cm^{-1} using KBr discs and as Nujol mulls.

X-ray Crystallography

For all five compounds, the intensity data were collected with an Enraf-Nonius CAD-4 diffractometer at room temperature and SHELXS-86 [43] and SHELXL-93 [44] were used to solve and refine the structures. All the hydrogen atoms of **I** and **III** were located from difference maps and refined isotropically; those of **II**, **IV** and **V** were placed in their geometrically ideal positions with isotropic temperature factors 1.2 times those of the attached non-hydrogen atoms. The Flack x parameter [45] was refined at a late stage of refinement of **IV** to determine the absolute structure. Tables I and II summarize the parameters for data collection and structure refinements and selected bond lengths and angles are shown in Tables III–V.

TABLE I Crystal data and structure refinement for [Ni(dien)(ONO_2)(O_2NO)] (**I**), {[Cu(dien)(ONO_2)]NO_3}$_\infty$ (**II**) and [Zn(dien)(O_2NO)(ONO_2)] (**III**)[a]

	I	**II**	**III**
Formula	$C_4H_{13}N_5NiO_6$	$C_4H_{13}CuN_5O_6$	$C_4H_{13}N_5O_6Zn$
F.w.	285.90	290.74	292.56
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pmnb$	$P2_1/n$
a (Å)	7.904(4)	9.0602(13)	7.9624(12)
b (Å)	11.786(4)	9.071(2)	11.8560(13)
c (Å)	11.619(8)	12.9681(14)	11.652(2)
α (°)	90	90	90
β (°)	100.54(5)	90	99.95(2)
γ (°)	90	90	90
v (Å^3)	1064.1(10)	1065.8(3)	1083.5(3)
Z	4	8	4
D_{calc} (g/cm^3)	1.785	1.812	1.794
μ (mm$-^1$)	1.848	2.074	2.292
$F(000)$	592	596	600
2θ range (°)	2–30	2–26	2–25
Index ranges (h, k, l)	$\pm 11, +16, +12$	$+11, +11, +15$	$\pm 9, +14, +13$
Reflections collected	2984	1115	1991
Independent (R_{int})	2857 (0.0312)	1115 (0.0000)	1900 (0.0186)
observed [$I > 2\sigma(I)$]	2048	671	1469
Transmission	0.9849–0.8063	0.9846–0.8934	0.9945–0.9045
Data/restraints/parameters	2857/0/197	1115/0/85	1900/0/197
GOF on F^2 [b]	0.998	0.963	1.049
Final R indices[c] [$I > 2\sigma(I)$]	$R_1 = 0.0356$ $wR_2 = 0.0774$	$R_1 = 0.0274$ $wR_2 = 0.0638$	$R_1 = 0.0221$ $wR_2 = 0.0537$
R indices (all data)	$R_1 = 0.0643$ $wR_2 = 0.0820$	$R_1 = 0.0768$ $wR_2 = 0.0711$	$R_1 = 0.0391$ $wR_2 = 0.0571$
Largest diff. peak/hole (e/Å^3)	0.916/−0.493	0.385/−0.361	0.275/−0.302

[a] Common for all structures: room temperature, $\lambda = 0.71073$ Å (Mo K_α), absorption correction by ψ-scans, refinements by full-matrix least-squares on F^2.

[b] $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(\text{no. of reflections} - \text{no. of parameters refined})\}^{1/2}$.

[c] $R_1 = \sum ||F_o| - |F_c|/\sum |F_o|$, $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4\right]^{1/2}$, $w = 1/[\sigma^2 F_o^2 + (aP)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

TABLE II Crystal data and structure refinement for [Ni(Medpt)(O_2NO)(ONO_2)] (**IV**) and [Cu(Medpt)$(ONO_2)_2$] (**V**)[a]

	IV	V
Formula	$C_7H_{19}N_5NiO_6$	$C_7H_{19}CuN_5O_6$
F.w.	327.98	332.81
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/a$
a (Å)	8.182(2)	15.362(4)
b (Å)	10.623(4)	11.703(3)
c (Å)	15.387(5)	16.599(6)
β (°)	90	115.61(3)
v (Å^3)	1337.4(7)	2691.1(14)
Z	4	4
D_{calc} (g/cm^3)	1.629	1.643
μ (mm^{-1})	1.482	1.654
F(000)	688	1384
2θ range (°)	2–30	2–24
Index ranges (h, k, l)	$+11, +14, +21$	$\pm 17, +13, +18$
Reflections collected	2228	4370
Independent (R_{int})	2228 (0.0000)	4218 (0.0234)
Observed [$I > 2\sigma(I)$]	1360	3166
Transmission	0.9962–0.9075	0.9997–0.8565
Data/restraints/parameters	2228/0/172	4218/0/343
GOF on F^2 [b]	1.005	1.041
Final R indices[c] [$I > 2\sigma(I)$]	$R_1 = 0.0426$, $wR_2 = 0.1079$	$R_1 = 0.0285$, $wR_2 = 0.0727$
R indices (all data)	$R_1 = 0.0879$, $wR_2 = 0.1212$	$R_1 = 0.0495$, $wR_2 = 0.0774$
Absolute structure parameter	0.00(3)	–
Largest diff. peak/hole (e/Å^3)	0.760/$-$0.556	0.401/$-$0.283

[a] Common for all structures: room temperature, $\lambda = 0.71073$ Å (Mo K_α), absorption correction by ψ-scans, refinements by full-matrix least-squares on F^2.

[b] $\text{GOF} = \{\sum[w(F_o^2 - F_c^2)^2]/(\text{no. of reflections} - \text{no. of parameters refined})\}^{1/2}$:

[c] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4\right]^{1/2}$, $w = 1/[\sigma^2 F_o^2 + (aP)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

RESULTS AND DISCUSSION

The reactions of $M(NO_3)_2$, where $M = Ni^{2+}$, Cu^{2+} and Zn^{2+} with linear tridentate ligands (NNN) such as dien and Medpt, in absolute ethanol and in presence of triethylorthoformate afforded metal complexes with the general formula [M(NNN)$(NO_3)_2$]. The elemental analyses of all the complexes were identical except for the nature of the metal. Good crystals, suitable for x-ray diffraction, were obtained by slow crystallization of the compounds at ambient temperature. During the preparation of [Ni(dien)$(NO_3)_2$] (**I**), a light purple product first separated. The crystal structure determination of this compound, obtained by aqueous ethanol diffusion, indicated that it has an octahedral geometry with the composition mer-[Ni$(dien)_2$]$(NO_3)_2$. With the exception of [Zn(Medpt)$(NO_3)_2$], we were able to determine the molecular structures of five of these compounds. However, as we shall see the molecular structure of **II** and **V** are totally different from **I**, **III** and **IV**. Compound **II** is a polymer, whereas **I**, **III**, **IV** and **V** are discrete molecules. In these complexes, the stereochemistry and the mode of binding of the nitrate ions depend entirely on the nature of the metal ion and the coordinating amine.

Compounds **I** and **III** are isomorphous and isostructural. Figs. 1 and 2 show the bonding of **I** and **III**, respectively, in which there is a central metal surrounded by

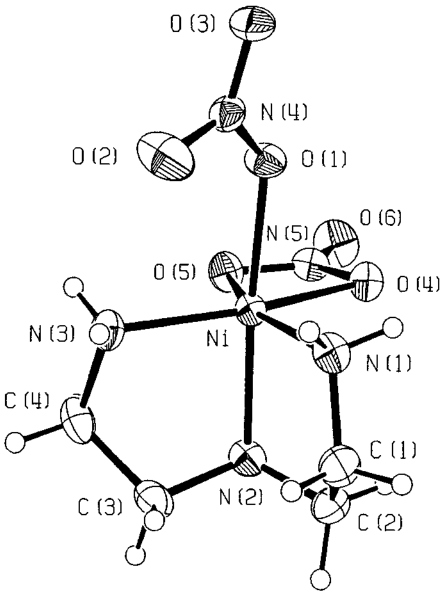

FIGURE 1 Molecular structure of [Ni(dien)(O_2NO)(ONO_2)] (**I**) shown in 40% probability level.

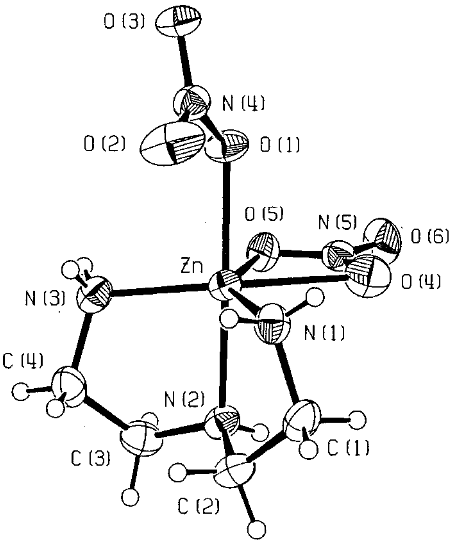

FIGURE 2 Molecular structure of [Zn(dien)(O_2NO)(ONO_2)] (**III**) shown in 40% probability level.

the dien in a *fac*-arrangement, a bidentate nitrato, whose oxygens are *trans* to terminal NH_2 moieties of the triamine. An oxygen of a monodentate nitrato ligand occupies the *trans* position opposite to the secondary nitrogen of the dien. The stereochemistry of compounds **I** and **III** (Figs. 1 and 2) happened accidentally to be enantiomorphic to one another as shown by the fact that the configuration of the two five-membered rings are of opposite chirality (the two rings in compound **I** are $\lambda\lambda$ whereas for **III**, they are $\delta\delta$).

As expected, the major difference between compounds **I** and **III** is in the stereochemical parameters that in some cases are rather large. This is true for both bond lengths and bond angles. As an example, the M–O(4) bond distance in **I** is 2.169(2) Å, whereas for **III** it is 2.396(2) Å. Among the large differences in bond angles is the case of N(1)–M–N(3), which in **I** is 105.93(10)°, whereas in **III** it has a value of 115.95(10)°. Other bond lengths and angles that differ by large amounts are listed in Table III.

Interestingly, we noted that the bidentate nitrate M–O bonds are asymmetric, for example for compounds **I** and **III**, the values are 2.169(2) and 2.396(2) Å, respectively, whereas for **III** they are 2.157(2) and 2.220(2) Å. At first these appear to be unusual since these two oxygens are *trans* to two terminal NH_2 groups. However, close inspection of Figs. 1 and 2, and of the H-bonds between amines and adjacent oxygens show that O(4) has shorter H-bonds than those of O(5). This phenomenon is a result of the helical arrangement of the five-membered rings that results in a twist about the Ni–N vector such as the H of N(1) comes closer to non-bonded electron pairs of the O(4) atom. Also the stereochemistry of the monodentate nitrato ligand is similarly affected by H-bonds, i.e., O(2) is pointing directly to the H of N(3). Naturally, this is a solid state effect, which does not persist in solution. In this conformation, the non-bonding pairs of O(2) and O(5) are kept as large as possible as well, thus, minimizing the non-bonding pair repulsion, while maximizing the intramolecular H-bonds. Surprisingly, we noted that despite the differences in bond distances observed above, the bond angles at N(4) and N(5) are essentially identical within experimental error.

TABLE III Selected bond lengths (Å) and angles (°) for **I**, **III** and **IV**

	I	III	IV
M–N(1)	2.057(3)	2.056(2)	2.030(4)
M–N(2)	2.068(2)	2.136(2)	2.100(4)
M–N(3)	2.047(2)	2.066(2)	2.005(5)
M–O(1)	2.074(2)	2.115(2)	2.269(4)
M–O(4)	2.169(2)	2.396(2)	2.194(4)
M–O(5)	2.157(2)	2.220(2)	2.108(4)
N(4)–O(1)	1.282(2)	1.284(2)	1.258(6)
N(4)–O(2)	1.224(3)	1.218(3)	1.241(7)
N(4)–O(3)	1.239(3)	1.232(2)	1.223(6)
N(5)–O(4)	1.262(3)	1.245(2)	1.271(6)
N(5)–O(5)	1.272(3)	1.251(2)	1.277(6)
N(5)–O(6)	1.225(3)	1.230(2)	1.215(6)
N(1)–M–N(2)	83.93(10)	83.35(8)	97.0(2)
N(1)–M–N(3)	105.93(10)	115.95(10)	102.8(2)
N(1)–M–O(4)	98.56(9)	89.60(9)	98.6(2)
N(2)–M–N(3)	83.74(9)	83.28(9)	94.4(2)
N(2)–M–O(1)	175.70(8)	175.15(7)	169.6(2)
N(3)–M–O(5)	95.58(9)	99.18(8)	96.1(2)
O(4)–M–O(5)	59.70(7)	54.73(6)	59.9(2)
O(1)–N(4)–O(2)	120.5(2)	119.6(2)	119.1(5)
O(1)–N(4)–O(3)	117.8(2)	118.0(2)	118.1(5)
O(2)–N(4)–O(3)	121.7(2)	122.4(2)	122.8(5)
O(4)–N(5)–O(5)	116.4(2)	116.9(2)	115.0(4)
O(4)–N(5)–O(6)	122.2(2)	122.0(2)	122.2(5)
O(5)–N(5)–O(6)	121.4(2)	121.1(2)	122.8(5)

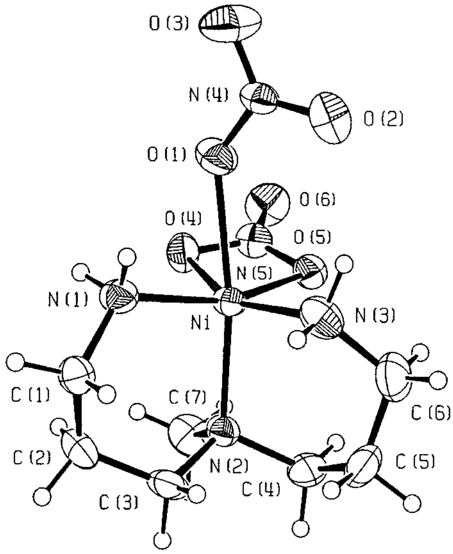

FIGURE 3 Molecular structure of [Ni(Medpt)(O_2NO)(ONO_2)] (**IV**) shown in 40% probability level.

Compound **IV** (Fig. 3) has a stereochemistry that closely resembles **I** and **III** despite the change in the number of methylene carbons of the two rings of the triamine (3 and 3 *vs*. 2 and 2 in **I** and **III**). In all three cases, the conformation of the nitrogen ligand is *fac*, irrespective of the metal. There is a bidentate nitrato ligand whose oxygens are also *trans* to the terminal NH_2's and an axial oxygen of a monodentate NO_3^- *trans* to the central nitrogen of the triamine, which in this case is a tertiary nitrogen. Note in Fig. 3, as is the case of **I** and **III**, O(2) of the monodentate nitrato ligand is so oriented to be in a favorable position for making H-bonds with the oxygen at N(3). Therefore, the stereochemistry of **IV** is remarkably close to that observed for **I** and **III**. As a result, it is not surprising that the bidentate nitrato ligand is asymmetrically bonded to the metal as well. In this case the Ni–O distances are 2.194(4) and 2.108(4) Å. This difference is about 21σ. Finally, the bond angles for the monodentate and bidentate nitrato ligands are remarkably close for all compounds (Table III).

Concerning the stereochemical parameters of related compounds reported earlier with comparable precision, we note the following: (1) In the case of [Ni(bdmpae)(NO_3)$_2$], the Ni–O distances of the bidentate nitrate differ by very little (2.157(5) and 2.145(5) Å) [34]. This difference is less than 3σ; and, there are no H-bonds that may affect the M–O distances which we believe is the origin of the asymmetry noted above. (2) Another interesting example for M–O asymmetry was observed by Parkin *et al.* [9] who reported the stereochemistry of [Zn(η^3–O($CH_2CH_2pzR_2$)$_2$)(NO_3)$_2$], the two values observed in this case for the bidentate nitrate ligand are 2.183(3) and 2.397(4) Å. The longer of the two distances is of O13, which is nearest to the ether-oxygen of the ligand backbone [9]. This observation is consistent with ours; namely, that the M–ligand distances in compounds containing bidentate nitrato ligands can be affected by non-bonding electron pair repulsion and/or H-bonds.

We accidentally made the same compound as the one made by Krestl *et al.* [46], namely nitrato(diethylenetriamine)copper(II) nitrate, $\{[Cu(dien)(\mu\text{-}ONO_2)]NO_3\}_\infty$ (**II**). Our synthetic procedure for **II** was different from that reported for a compound of the same composition. In both cases, the elemental analysis (see Experimental Section) corresponds to $C_4H_{13}CuN_5O_6$. However, the recorded IR spectrum does not correspond to the one described [46]. For more details, see below. Therefore, the only reasonable solution for this discrepancy is that compound **II** and its analog in the literature [46] differ by being polymorphic crystalline forms for the same compound. Such a phenomenon was observed and published in our group [47]. Consequently, this possibility resulted in determining the structure of our sample, shown in Fig. 4. Two facts were noted from the structure determination: (a) the crystals were identical with those reported in Ref. [46]; e.g., same space group and very similar cell constants (b) there were no extraneous molecules in the lattice, such as water of hydration, to provide some explanation for differences in the IR spectral bands, i.e., hydrogen bonding of the water to the presumed N–O oxygen which could provide a mechanism to account for the observed IR differences. However, this was not the case, as shown by the elemental analysis and by a final difference electron density map. We briefly provide a description for our structure in Table IV. The reason for presenting these data is that our structure is of superior quality than the preceding one [46].

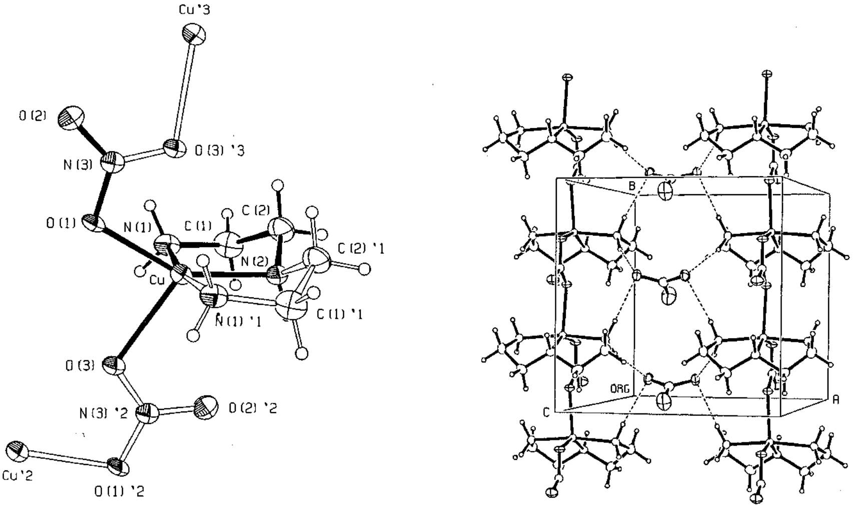

FIGURE 4 (a) Structure of the polymeric cation $\{[Cu(dien)(\mu\text{-}ONO_2)]^+\}_\infty$ (**II**). Crystallographically unique atoms are connected with filled bonds. (b) Composite packing structure showing the hydrogen bonds of nitrate anion [2.304(3) and 2.260(4) Å].

TABLE IV Selected bond lengths (Å) and angles (°) for **II**

Cu–N(1)	1.992(2)	N(1)–Cu–N(1)[b]	168.7(2)
Cu–N(2)	1.995(3)	N(1)–Cu–N(2)	85.23(8)
Cu–O(1)	2.115(3)	N(1)–Cu–O(1)	92.69(8)
Cu–O(3)	2.284(3)	N(1)–Cu–O(3)	95.11(7)
N(3)–O(1)	1.266(4)	N(2)–Cu–O(1)	150.75(12)
N(3)–O(2)	1.217(4)	N(2)–Cu–O(3)	123.11(12)
N(3)–O(3)[a]	1.266(4)	O(1)–Cu–O(3)	86.14(10)

[a] $0.5-x$, $0.5+y$, $1.5-z$.
[b] $0.5-x$, y, z.

Compound **V** has an interesting property as crystallized in space group $P2_1/a$. Its molecular structure, depicted in Fig. 5, shows that there are two molecules in the asymmetric unit ($z = 8$). As evident from the conformation of the two molecules, the helical chirality at the two metal-amine rings is essentially identical, and there are two nitrato ligands *cis* to each other and bound in the monodentate fashion. The coordination sphere for both Cu^{2+} ions is square pyramidal, in which one nitrate–oxygen, O(1) and O(7), occupy positions in the base, while O(4) and O(10) occupy the axial positions. Selected bond lengths and angles for compound **V** are given in Table V.

The Cu–O(1) and Cu–O(7) bond lengths have values, respectively, 2.131(2) and 2.129(2) Å that differs by only one σ. On the other hand, the Cu(1)–O(4) is 2.381(2) Å,

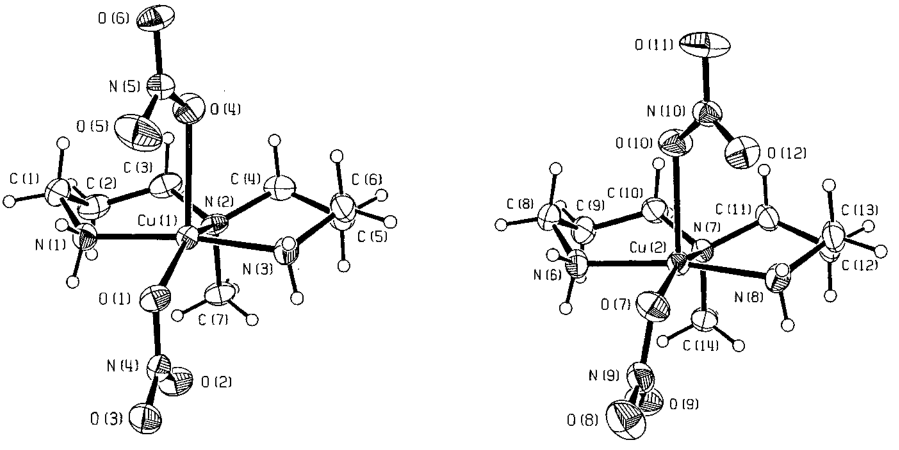

FIGURE 5 Structures of the two independent molecules in the asymmetric unit of $[Cu(Medpt)(ONO_2)_2]$ (**V**) (30% probability level).

TABLE V Selected bond lengths (Å) and angles (°) for **V**

Cu(1)–N(3)	1.964(2)	Cu(2)–N(6)	1.972(3)
Cu(1)–N(1)	1.976(2)	Cu(2)–N(8)	1.974(3)
Cu(1)–N(2)	2.083(2)	Cu(2)–N(7)	2.085(2)
Cu(1)–O(1)	2.131(2)	Cu(2)–O(7)	2.129(2)
Cu(1)–O(4)	2.381(2)	Cu(2)–O(10)	2.263(2)
N(4)–O(3)	1.226(3)	N(9)–O(8)	1.217(4)
N(4)–O(2)	1.241(3)	N(9)–O(9)	1.239(4)
N(4)–O(1)	1.278(3)	N(9)–O(7)	1.279(4)
N(5)–O(5)	1.222(4)	N(10)–O(11)	1.219(3)
N(5)–O(6)	1.232(3)	N(10)–O(12)	1.231(3)
N(5)–O(4)	1.253(3)	N(10)–O(10)	1.269(3)
N(1)–Cu(1)–N(2)	95.63(11)	N(6)–Cu(2)–N(7)	93.93(11)
N(1)–Cu(1)–N(3)	167.82(11)	N(6)–Cu(2)–N(8)	168.81(12)
N(1)–Cu(1)–O(1)	82.37(10)	N(6)–Cu(2)–O(7)	86.59(11)
N(1)–Cu(1)–O(4)	91.26(10)	N(6)–Cu(2)–O(10)	91.19(10)
N(2)–Cu(1)–N(3)	95.01(10)	N(7)–Cu(2)–N(8)	94.45(11)
N(2)–Cu(1)–O(1)	156.08(9)	N(7)–Cu(2)–O(7)	165.48(9)
N(2)–Cu(1)–O(4)	87.90(9)	N(7)–Cu(2)–O(10)	96.47(10)
N(3)–Cu(1)–O(1)	85.50(9)	N(8)–Cu(2)–O(7)	83.44(11)
N(3)–Cu(1)–O(4)	95.03(10)	N(8)–Cu(2)–O(10)	95.22(10)
O(1)–Cu(1)–O(4)	115.92(9)	O(7)–Cu(2)–O(10)	98.02(9)

while Cu(2)–O(10) is 2.263(3) Å. Therefore, for both molecules in the asymmetric unit the axial bond is significantly longer than the equatorial one, as expected. An interesting stereochemical feature of both molecules is the fact that a non-bonded oxygen of the axial nitrato ligand is clearly oriented in the direction of terminal amino hydrogens. Consequently, this observation is consistent with remarks made previously with respect to the orientation of the plane of the axial nitrato ligand present in compounds **I** and **III**, both of which are octahedral. Since both molecules of compound **V** are square pyramidal, it is interesting to note that the H-bonding orientation of the axial nitrato ligands is not influenced by the coordination nature around the central metal ion. Similar coordination involving two mono-nitrato ligands with Cu^{2+} ions are available in the literature [41,48].

UNEXPECTED NITRATO LIGAND EXCHANGE OBSERVED IN KBr PELLETS

In as much as our compounds contained nitrate anions in a variety of environments, we decided to record their infrared spectra and compare our results with those of Krestl *et al.* [46] who synthesized a crystalline species similar to our compound $\{[Cu(dien)(\mu\text{-}ONO_2)]NO_3\}_\infty$ (**II**). They recorded bands at 735, 810, 1320 cm^{-1} for unidentate ligands, at 820 and 1360 cm^{-1} for ionic nitrate and a split band (20 cm^{-1} split) assigned to bridging or bidentate nitrato ligands. These results are in reasonable agreement with those described for such species by Nakamoto [49]. During the course of recording our data in KBr pellets, we noted that the most prominent band for all five complexes of them was at 1385.0 cm^{-1}. It is well known [49] that this band corresponds to ionic nitrate, such as found in the lithium, sodium and potassium salts. Those corresponding to unidentate were either obscured by the large band due to free nitrate or are present as very weak bands compared to the former. We found this behavior odd since we had expected a free nitrate IR band only for compound (**II**), whose structure we determined to contain such ionic nitrate, all four other complexes contain bound nitrato ligands (*vide supra*).

The only sensible explanation for our observations was that we had experienced exchange of nitrate ligands for bromide during the course of preparing the wafers for IR measurements. In order to prove this, we gently powdered crystals of all five species, placed them between NaCl flat plates and recorded their IR spectra. Now, the free nitrate band disappeared in four of the five compounds, but remained clearly visible in the case of (**II**) where it appeared at 1346.2 cm^{-1}, a shift no doubt caused by hydrogen bonding differences, see Fig. 4 and its caption.

Although the powdered spectra are rather busy in the NO stretching frequency region (roughly 800–1400 cm^{-1}) compounds (**I**), (**III**) and (**V**), containing both mono- and bi-dentate nitrato ligands, show bands at the expected places for such moieties; thus, our suspicion of ligand exchange in the KBr pellets was confirmed.

SUPPLEMENTARY DATA

All structural and spectral data are available from the authors in magnetic media. Requests should be sent to Ivan Bernal.

Acknowledgements

We thank the Robert A. Welch foundation for support of this research (Grant E-594 to I. Bernal) and for fellowship granted to H. Chun. IB also thanks the National Science Foundation for the funds used in purchasing the diffractometer.

References

[1] L.-W. Yang, S. Liu, S.J. Retting and C. Orvig (1995). *Inorg. Chem*,. **43**, 4921.
[2] F.A. Cotton, G. Wilkinson, C.A. Murillo and M. Bochmann (1999). *Advanced Inorganic Chemistry*, 6th edn., p. 489. John Wiley & Sons Inc., New York.
[3] N.W. Alcock and W.D. Harrison (1982). *J. Chem. Soc*., *Dalton Trans*., 1421.
[4] M. Kretschmann and U. Diefenbach (1998). *Z. Anorg. Allg. Chem*., **624**, 335.
[5] G. De Munno, T. Poerio, M. Julve, F. Lloret, G. Viau and A. Caneschi (1997). *J. Chem. Soc*., *Dalton Trans*., 601.
[6] L. Cornin, B. Greener, S.P. Foxon, S.L. Heath and P.H. Walton (1997). *Inorg. Chem*., **36**, 2594.
[7] Z. Xu, L.K. Thompson and D.O. Miller (1997). *Inorg. Chem*., **36**, 3985.
[8] S. Arrowsmith, M.F.A. Dove, N. Logan and A. Batsanov (1998). *Polyhedron*, **17**, 421.
[9] C. Dowling, V.J. Murphy and G. Parkin (1996). *Inorg. Chem*., **35**, 2415.
[10] S.T. Frey, H.H.J. Sun, N.N. Murthy and K.D. Karlin (1996). *Inorg. Chim. Acta*, **242**, 329.
[11] D.M. Hong, H.H. Wei, L.L. Gan, G.H. Lee and Y. Wang (1996). *Polyhedron*, **15**, 2335.
[12] K.K. Palkina, N.E. Kuz'mina, V.T. Orlova and I.V. Kondakova (1996). *Zh. Neorg. Khim*., **41**, 57.
[13] C.F. Martens, A.P.H.J. Schenning, M.C. Feiters, H.W. Berens, J.G.M. van der Linden, G. Admiral, P.T. Beurskens, H. Kooijman, A.L. Sek and R.J.M. Nolte (1995). *Inorg. Chem*., **34**, 4735.
[14] G.A. Doyle, D.M.L. Goodgame, S.P.W. Hill, S. Menzer, A. Sinden and D.J. Williams (1995). *Inorg. Chem*., **34**, 2850.
[15] C. Titze, J. Hermann and H. Vahrenkamp (1995). *Chem. Ber*., **128**, 1095.
[16] S.-N. Choi, M.-A. Kwon, Y. Kim, R.D. Bereman, P. Singh, B. Knight and K. Seff (1995). *J. Coord. Chem*., **34**, 241.
[17] S. Arrowsmith, M.F.A. Dove, M.N. Gibbons, N. Logan and A. Batsanov (1995). *J. Chem. Soc*., *Chem. Comm*., 1733.
[18] C. Kimblin, W.E. Allen and G. Parkin (1996). *Main Group Chemistry*, **1**, 297.
[19] L. Carlucci, G. Giani, M. Moret and A. Sironi (1994). *J. Chem. Soc*., *Dalton Trans*., 2397.
[20] E. Diamantopoulou, T.F. Zafiropoulos, S.P. Perplespes, C.P. Raptopoulou and A. Terzis (1994). *Polyhedron*, **13**, 1593.
[21] W.L. Driessen, R.A.G. de Graaff, F.J. Parlevliet, J. Reedijk and R.M. de Vos (1994). *Inorg. Chim. Acta*, **216**, 43.
[22] J.C. Plakatouras, T. Bakas, C.J. Huffman, J.C. Huffman, V. Papaefthymiou and S.P. Perlopes (1994). *J. Chem. Soc*., *Dalton Trans*., 2737.
[23] T. Otieno, S.J. Rettig, R.C. Thompson and J. Trotter (1993). *Acta Crystallogr*., *Sect. C*, **49**, 2067.
[24] G.A. Doyle, D.M.L. Goodgame, S.P.W. Hill and D.J. Williams (1993). *J. Chem. Soc*., *Chem. Comm*., 207.
[25] W.G. Haanstra, W.L. Driessen, M. van Roon, A.L. Stoffels and J. Reedijk (1992). *J. Chem. Soc*., *Dalton Trans*., 481.
[26] R. Gregorzik, J. Wirbser and H. Vahrenkamp (1992). *Chem. Ber*., **125**, 125.
[27] H. Paulus, H. Fuess, P. Baran and D. Valingura (1992). *Z. Kristallogr*., **202**, 140.
[28] K. Ruhlandt-Senge, A.D. Bacher and U. Muller (1992). *Z. Naturforsch*., *Teil B*, **47**, 31.
[29] M. Koman, D. Valigura, G. Ondrejovic, A. Goeminne, M. Herman and G.P. Van der Kelen (1991). *Acta Crystallogr*., *Sect. C*, **47**, 1202.
[30] J.C. Lockhart, W. Clegg, M.N.S. Hill and D.J. Rushton (1990). *J. Chem. Soc*., *Dalton Trans*., 3541.
[31] J.L. Atwood, S.G. Bott and R.L. Vincent (1990). *J. Crystallogr. Spectrosc. Res*., **20**, 631.
[32] K.R. Adam, K.P. Dancey, A.J. Leong, L.F. Lindoy, B.M. McCool, M. McPartlin and P.A. Tasker (1988). *J. Am. Chem. Soc*., **110**, 8471.
[33] K. Locher, H.L. Blonk, W.L. Driessen and J. Reedijk (1987). *Acta Crystallogr*., *Sect*. C, **43**, 651.
[34] J.W.F.M. Schoonhoven, W.L. Driessen, J. Reeddijk and G.C. Verschoor (1994). *J. Chem. Soc*., *Dalton Trans*., 1053.
[35] K.R. Adam, K.P. Dancey, B.A. Harrison, A.J. Leong, L.F. Lindoy, M. McPartlin and P.A. Tasker (1983). *J. Chem. Soc*., *Chem. Comm*., 1351.
[36] E.M. Holt, N.W. Alcock, R.R. Hendrixson, G.D. Malpass Jr., R.G. Ghirardelli and R.A. Palmer (1981). *Acta Crystallogr*., *Sect. B*, **37**, 1080.
[37] E.M. Holt, R.A. Palmer and T.B. Vance Jr. (1980). *Am. Cryst. Assoc*., *Ser*., **27**, 24.

[38] R.J. Restivo and G. Ferguson (1976). *J. Chem. Soc.*, *Dalton*, *Trans.*, 518.
[39] E.C. Alyea, G. Ferguson and R.J. Restivo (1975). *Inorg. Chem.*, **14**, 2491.
[40] M.J. Begley, M.J. Haley, T.J. King, A. Morris, R. Pike and B. Smith (1976). *Inorg. Nucl. Chem. Lett.*, **12**, 99.
[41] L. Yongxin, Y.-H. Lai, K.F. Mok and M.G.B. Drew (1998). *Inorg. Chim. Acta*, **279**, 221.
[42] A.F. Cameron, D.W. Taylor and R.H. Nuttall (1972). *J. Chem. Soc.*, *Dalton Trans.*, 1603 and 1608.
[43] G.M. Scheldrick (1990). *Acta Crystallogr.*, *Sect.* A, **46**, 467.
[44] G.M. Scheldrick (1993). SHELXL-93, *A Program for Crystal Structure Determination*. University of Göttingen, Germany.
[45] H.D. Flack (1983). *Acta Crystallogr.*, *Sect. A*, **39**, 876.
[46] R.A.M. Krestl, C.B. Manoussakis and G. St. Nikolov (1990). *Inorg. Chim. Acta*, **175**, 255.
[47] I. Bernal, F. Somoza, Y.-C. Chen and S.S. Massoud (1997). *J. Coord. Chem.*, **41**, 233.
[48] M.J. Begley, P. Hubberstey and J. Stroud (1997). *Polyhedron*, **16**, 805.
[49] K. Nakamoto (1997). *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. John Wiley & Sons, New York. For ionic nitrates, see Part A, pp. 181–182; for metal coordinated nitrato ligands, see Part B, pp. 87–89 and 273.