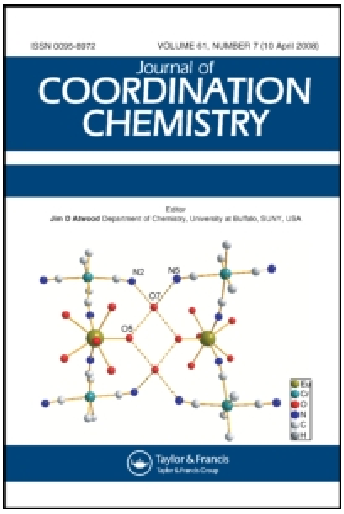


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses and structures of cobalt(II), nickel(II), and copper(II) complexes with *N,N,N',N'*-tetraalkylpyridine-2,6-dicarboxamides (O-daap) containing nitrate as the counter ion

Pratibha Kapoor[a]; Ajay Pal Singh Pannu[b]; Mukesh Sharma[a]; Geeta Hundal[b]; Ramesh Kapoor[c]; Maninder Singh Hundal[b]
[a] Department of Chemistry, Panjab University, Chandigarh 160014, India [b] Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India [c] Indian Institute of Science Education and Research, Mohali, Chandigarh 160 019, India

To cite this Article Kapoor, Pratibha , Pannu, Ajay Pal Singh , Sharma, Mukesh , Hundal, Geeta , Kapoor, Ramesh and Hundal, Maninder Singh(2011) 'Syntheses and structures of cobalt(II), nickel(II), and copper(II) complexes with *N,N,N',N'*-tetraalkylpyridine-2,6-dicarboxamides (O-daap) containing nitrate as the counter ion', Journal of Coordination Chemistry, 64: 2, 256 — 271

To link to this Article: DOI: 10.1080/00958972.2010.542237

URL: http://dx.doi.org/10.1080/00958972.2010.542237

Journal of Coordination Chemistry
Vol. 64, No. 2, 20 January 2011, 256–271

Syntheses and structures of cobalt(II), nickel(II), and copper(II) complexes with *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dicarboxamides (O-daap) containing nitrate as the counter ion

PRATIBHA KAPOOR†, AJAY PAL SINGH PANNU‡, MUKESH SHARMA†,
GEETA HUNDAL‡, RAMESH KAPOOR§ and MANINDER SINGH HUNDAL*‡

†Department of Chemistry, Panjab University, Chandigarh 160014, India
‡Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India
§Indian Institute of Science Education and Research, Mohali, Chandigarh 160 019, India

(*Received 9 August 2010; in final form 13 October 2010*)

Reactions of $M(NO_3)_2 \cdot xH_2O$ [M = Co(II), Ni(II), and Cu(II)] with *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dicarboxamides(O-daap) in CH_3CN yield [Co(O-dmap)$(NO_3)_2$] (**1**), [Co(O-deap)$(NO_3)_2$] (**2**), [Co(O-dpap)$(NO_3)_2$] (**3**), [Ni(O-dmap)$(H_2O)_3$]$(NO_3)_2$] (**4**), [Ni(O-deap)$(H_2O)_2(NO_3)$](NO_3)] (**5**), [Cu(O-deap)$(NO_3)_2$] (**6**), and [Cu(O-dpap)$(NO_3)_2$] (**7**). X-ray crystal structures of **1**, **2**, **4**, **5**, and **7** reveal that O-daap ligands coordinate tridentate to each metal, O–N–O, with nitrate playing a vital role in molecular and crystal structures of all the complexes. The coordination geometry in the two Co(II) complexes, **1** and **2**, is approximately pentagonal bipyramidal with nitrate bonded in a slightly unsymmetrical bidentate chelating mode. [Ni(dmap)$(H_2O)_3$]$(NO_3)_2$ (**4**) and [Ni(deap)$(H_2O)_2(NO_3)$](NO_3) (**5**) exhibit octahedral geometry, the former containing uncoordinated nitrate while the latter has one nitrate coordinated unidentate and the other nitrate outside the coordination sphere. The Cu(II) in [Cu(dpap)$(NO_3)_2$] (**7**) occupies a distorted square pyramidal geometry and is linked to two unidentate nitrates, although one nitrate is also involved in a weak interaction with the metal through its other oxygen. IR spectra and other physical studies are consistent with their crystal structural data. O-dmap = *N*,*N*,*N*′,*N*′-tetramethylpyridine-2,6-dicarboxamides; O-deap = *N*,*N*,*N*′,*N*′-tetraethylpyridine-2,6-dicarboxamides; and O-dpap = *N*,*N*,*N*′,*N*′-tetraisopropylpyridine-2,6-dicarboxamides.

Keywords: Thermogravimetric; Square pyramidal; Crystal structure; Counterion

1. Introduction

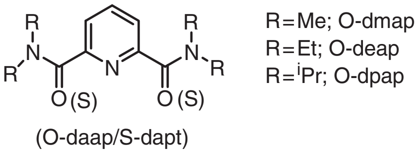
In continuation of our investigations on the coordination behavior of *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dicarboxamides (O-daap) and *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dithiocarboxamides (S-dapt) [1–7] (scheme 1) toward transition metals, we have now carried out the synthesis of complexes of O-daap ligands [R = Me, Et, ^{i}Pr] with Co(II), Ni(II), and Cu(II) using nitrate as the counter anion.

Structural adaptability on the part of these ligands and the counter ions play a significant role in determining the solid-state geometry of their complexes with

---

*Corresponding author. Email: mshundal@gmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2010.542237



Scheme 1. The *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-carboxamide ligands.

metal ions. In our previous communication [7], weakly electrophillic –$OClO_3$ and –OSO_2CF_3 ions were used to emphasize the counter ion effect on molecular and crystal structures. In this study, nitrate was used as a counter anion because it can adopt different coordination modes in unidentate or bidentate (chelating or bridging) fashion and even unidentate bridging, or be present as a free ion [8–17]. Furthermore, nitrate may be present in more than one coordination mode in the same complex.

2. Experimental

2.1. *Materials*

The synthetic procedures leading to the preparation of the ligands (O-daap) have been performed under dry N_2. Solvents and other reagents were dried using standard techniques [18]. $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ were used as such. Ligands were prepared as per the methods described earlier [1–7, 19].

2.2. *Syntheses*

Complexes **1–7** were prepared by reacting hydrated metal(II) nitrates with the appropriate ligand in 1 : 1 mole ratio in CH_3CN. The contents were refluxed for 8 h. On concentration, the solution yielded solid compounds which were recovered by filtration and dried *in vacuo*. Irrespective of whether the metal nitrate-to-ligand ratio was 1 : 1 or 1 : 2, the product was always the same.

2.2.1. [Co(O-dmap)(NO_3)$_2$] (1). [$Co(NO_3)_2 \cdot 6H_2O$, 2.90 g, 10 mmol; dmap, 2.21 g, 10 mmol; CH_3CN, 50 mL, yield, 3.24 g, 80%]. Dark pink, m.p. 216–220°C. Anal. Calcd for $C_{11}H_{15}N_5O_8Co$ (%) : C, 32.68; H, 3.74; N, 17.33. Found: C, 32.69; H, 3.66; N, 16.99. IR (KBr pellet, cm^{-1}) : 1615(ν_{CO}); molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$) : 28.5 ($CH_3CN$).

2.2.2. [Co(O-deap)(NO_3)$_2$] (2). [$Co(NO_3)_2 \cdot 6H_2O$, 2.90 g, 10 mmol; deap, 2.77 g, 10 mmol; CH_3CN, 50 mL, yield, 3.40 g, 74%]. Light red, m.p. 140°C. Anal. Calcd for $C_{15}H_{23}N_5O_8Co$ (%) : C, 39.14; H, 5.04; N, 15.21. Found: C, 38.96; H, 5.15; N, 15.16. IR (KBr pellet, cm^{-1}) : 1610(ν_{CO}); molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$) : 30.0 ($CH_3CN$).

2.2.3. [Co(O-dpap)(NO_3)$_2$] (3). [Co(NO_3)$_2 \cdot 6H_2O$, 2.90 g, 10 mmol; dpap, 3.30 g, 10 mmol; CH_3CN, 50 mL, yield, 4.0 g, 77%]. Light red, m.p. 160°C. Anal. Calcd for $C_{19}H_{31}N_5O_8Co$ (%) : C, 44.19; H, 6.05; N, 13.56. Found: C, 44.33; H, 6.10; N, 13.44. IR (KBr pellet, cm^{-1}) : 1630(ν_{CO}); molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$) : 34.6 ($CH_3CN$), 20.0 (MeOH).

2.2.4. [Ni(O-dmap)(H_2O)$_3$](NO_3)$_2$ (4). [Ni(NO_3)$_2 \cdot 6H_2O$, 2.90 g, 10 mmol; dmap, 2.21 g, 10 mmol; CH_3CN, 50 mL, yield, 3.1 g, 69%]. Light green, m.p. 228°C. Anal. Calcd for $C_{11}H_{21}N_5O_{11}Ni$ (%) : C, 28.82; H, 4.62; N, 15.29. Found: C, 28.29; H, 4.30; N, 14.90. IR (KBr pellet, cm^{-1}) : 1615(ν_{CO}); molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$) : 244.0 ($CH_3CN$).

2.2.5. [Ni(O-deap)(H_2O)$_2$(NO_3)](NO_3) (5). [Ni(NO_3)$_2 \cdot 6H_2O$, 2.90 g, 10 mmol; deap, 2.80 g, 10 mmol; CH_3CN, 50 mL, yield, 3.82 g, 77%]. Light green, m.p. 220°C. Anal. Calcd for $C_{15}H_{29}N_5O_{11}Ni$ (%) : C, 36.31; H, 5.45; N, 14.12. Found: C, 36.17; H, 5.12; N, 13.94. IR (KBr pellet, cm^{-1}) : 3430, 3286 (ν_{OH}); 1605(ν_{CO}); molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$) : 110.0 ($CH_3CN$).

2.2.6. [Cu(O-deap)(NO_3)$_2$] (6). [Cu(NO_3)$_2 \cdot 3H_2O$, 2.40 g, 10 mmol; deap, 2.80 g, 10 mmol; CH_3CN, 50 mL, yield, 4.0 g, 86%]. Blue–green, m.p. 234°C. Anal. Calcd for $C_{15}H_{23}N_5O_8Cu$ (%) : C, 38.75; H, 4.99; N, 15.06. Found: C, 38.54; H, 4.84; N, 14.88. IR (KBr pellet, cm^{-1}) : 1615(ν_{CO}); molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$) : 32.0 ($CH_3CN$).

2.2.7. [Cu(O-dpap)(NO_3)$_2$] (7). [Cu(NO_3)$_2 \cdot 3H_2O$, 2.40 g, 10 mmol; dpap, 3.35 g, 10 mmol; CH_3CN, 50 mL, yield, 4.1 g, 79%]. Blue–green, m.p. 232°C. Anal. Calcd for $C_{19}H_{31}N_5O_8Cu$ (%) : C, 43.80; H, 6.00; N, 13.44. Found: C, 43.67; H, 5.99; N, 13.18. IR (KBr pellet, cm^{-1}) : 1605(ν_{CO}); molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$) : 30.7 ($CH_3CN$).

2.3. *Physical methods*

Elemental analyses (C, H, N) were performed on a Perkin-Elmer model 2400 CHN analyzer. IR spectra were recorded as KBr pellets on a Perkin-Elmer RX-1 FT-IR spectrophotometer. Thermal analyses were carried out on a Shimadzu-DTG 60 analyzer under dry N_2. UV-Vis spectra were recorded on a Shimadzu Pharmaspec UV-1700 spectrophotometer. Molar conductance of millimolar solutions were measured on a conductivity bridge Digital conductivity meter CC 601.

2.4. *X-ray crystallography*

Crystallization of **1**, **2**, **4**, **5**, and **7** by very slow evaporation of their saturated solution in acetonitrile at room temperature yielded suitable single crystals for X-ray analysis. The data were collected at 298 K on a Siemens P4 Single crystal X-ray diffractometer using XSCANS [20]. The θ–2θ scan mode was used to measure the intensities, up to a maximum of $2\theta = 60°$ using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). To monitor the stability of the crystal, three standard reflections were measured after every 97 reflections. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods using SIR97 [21] and refined by full-matrix least-squares on F^2 using SHELXS-97 [22] in the Wingx package [23] of programs. All atoms were refined anisotropically. Hydrogens were attached geometrically riding on their respective carrier atoms with U_{iso} being 1.5, 1.2, and 1.2 times the U_{iso} of their carrier methyl, methylene, and aromatic carbons, respectively. Table 1 gives the crystallographic parameters for all the complexes.

N3, C12, and C13 (alkyl chain and amine nitrogen) in **2** and O7 (nitrate group) in **5** show disorder which could be resolved by splitting each of these atoms into two parts with total site occupancy factor of one. Their site occupancy factors and U_{iso} values were refined as free variables. The structure of **7** has two crystallographically independent molecules in the unit cell, both showing disorder in one of the coordinated nitrates, O7 of one and N10 and O16 of the other nitrate. The disorder could be resolved for O7 and O16 but not for N10. All the disordered atoms in **2** and **7** were later refined anisotropically with restraints on their bond lengths. Because of the disorder in **7**, its Crystallographic Information File shows two A level errors which are justified.

3. Results and discussion

3.1. *IR, UV-Vis, and thermal studies*

Reactions between metal nitrates and O-daap ligands in 1 : 1 or 1 : 2 molar ratio yielded **1** to **7**. The Co(II) complexes are light red while Cu(II) and Ni(II) complexes are blue to bluish-green crystalline solids. These complexes were characterized through elemental analyses, IR data, UV-Vis spectroscopy, thermal analyses, conductivity measurements, and X-ray crystallography. The compounds dissolve in polar solvents and their millimolar solutions in CH_3CN show very little dissociation except Ni complexes which exhibit conductance values corresponding to 1 : 2 (**4**) and 1 : 1 (**5**) electrolytes, respectively [24]. IR spectra of **1** to **7** show ν_{CO} at lower wave numbers than the values observed for ν_{CO} in the neat ligand [1–7, 19], indicating coordination through carbonyl oxygen in each case. Generally, IR spectra of complexes containing nitrate ligands provide vital information regarding the coordination mode adopted by nitrate, but in this study, IR spectra of complexes did not provide conclusive information owing to a large number of pyridine ring vibrations below 1500 cm^{-1} [25]. Structure determination of all these complexes by X-ray crystallography provided us with the clear evidence of the varied coordination modes adopted by nitrate.

Absorption spectra for **1–7** were observed in methanol. Electronic spectra of **1**, **2**, and **3** show d–d bands around 520 nm (19,230 cm^{-1}) in each case. Nelson *et al.* [26, 27] have described a seven-coordinate Co(II) complex with pentagonal bipyramidal environment. The characteristic feature of such complexes is the low energy absorption in the visible region near 500 nm as observed in **1** [519 nm (19,267 cm^{-1}, $\varepsilon = 27\,\mathrm{l\,mol^{-1}cm^{-1}}$)], **2** [518 nm (19,305 cm^{-1}, $\varepsilon = 75\,\mathrm{l\,mol^{-1}cm^{-1}}$)], and **3** [527 nm (18,975 cm^{-1}, $\varepsilon = 57\,\mathrm{l\,mol^{-1}cm^{-1}}$)]. Electronic spectra of **4** and **5** exhibit three spin-allowed d–d transitions whose positions are typical for octahedral Ni(II) [28]. The d–d transitions appeared at 383 nm (26,109 cm^{-1}, $\varepsilon = 16\,\mathrm{l\,mol^{-1}cm^{-1}}$), 567 nm (17,636 cm^{-1}, $\varepsilon = 17\,\mathrm{l\,mol^{-1}cm^{-1}}$), and 709 nm (14,104 cm^{-1}, $\varepsilon = 32\,\mathrm{l\,mol^{-1}cm^{-1}}$) for **4** and at

Table 1. Crystallographic data for **1**, **2**, **4**, **5**, and **7**.

	1	**2**	**4**	**5**	**7**
Empirical formula	$C_{11}H_{15}CoN_5O_8$	$C_{15}H_{23}CoN_5O_8$	$C_{11}H_{21}N_5NiO_{11}$	$C_{15}H_{27}N_5NiO_{10}$	$C_{19}H_{31}CuN_5O_8$
Formula weight	404.21	460.31	458.02	494.65	521.20
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	*Pbcn*	$P2_1/n$	$P2_1/c$
Unit cell dimensions (Å, °)					
a	7.683(5)	8.813(5)	7.740(3)	8.989(3)	13.665(5)
b	15.456(3)	15.844(4)	12.446(4)	19.321(4)	11.574(4)
c	13.936(4)	14.792(3)	20.324(5)	13.226(5)	32.570(5)
β	96.895(5)	97.390(5)	90	107.870(5)	32.570(5)
Volume (Å^3), Z	1642.9(12), 4	2048.3(13), 4	1957.9(11), 4	2186.2(1), 4	5093(3), 8
Calculated density (Mg m^{-3})	1.634	1.493	1.554	1.507	1.359
Absorption coefficient (mm^{-1})	1.097	0.889	1.055	0.948	0.907
$F(0\ 0\ 0)$	828	956	952	1040	2184
θ range for data collection (°)	1.98–25.50	1.89–25.15	3.10–25.50	1.93–25.50	1.26–25.50
Reflections collected/unique	3303/3065	3917/3668	1828/1828	4334/4066	11,868/9471
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0476$, $wR_2 = 0.1107$	$R_1 = 0.0524$, $wR_2 = 0.1204$	$R_1 = 0.0369$, $wR_2 = 0.0867$	$R_1 = 0.0382$, $wR_2 = 0.1024$	$R_1 = 0.0761$, $wR_2 = 0.1658$
CCDC No.	787313	787314	787315	787316	787317

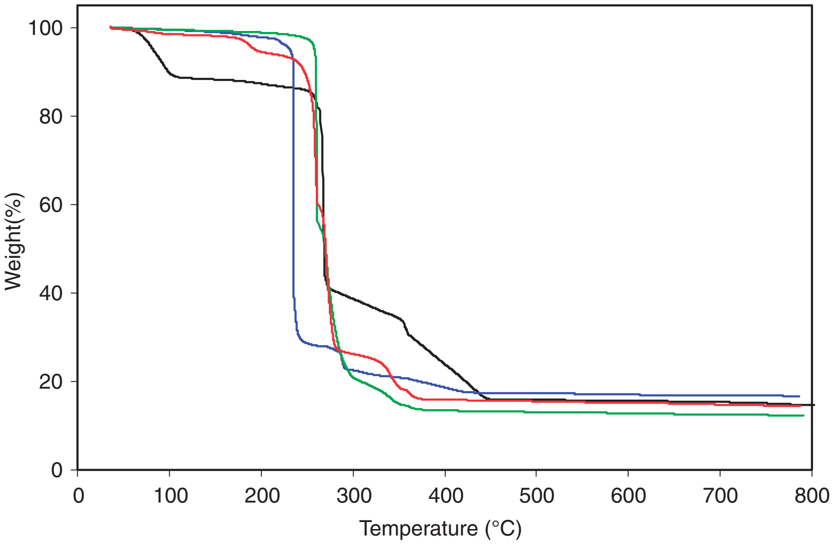


Figure 1. TGA curves for 1 (blue), 3 (red), 4 (black), and 7 (green) up to 800°C.

382 nm (26,178 cm^{-1}, $\varepsilon = 140\,l\,mol^{-1}cm^{-1}$), 576 nm (17,361 cm^{-1}, $\varepsilon = 131\,l\,mol^{-1}cm^{-1}$), and 740 nm (13,513 cm^{-1}, $\varepsilon = 51\,l\,mol^{-1}cm^{-1}$) for **5**. These three bands are assigned in the order of increasing energy to the $^3T_{2g} \leftarrow {}^3A_{2g}(F)$, $^3T_{1g}(F), \leftarrow {}^3A_{2g}(F)$, and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transitions. The absorption spectra of copper(II) complexes, **6** and **7**, show one broad d–d bands around 800 nm in both cases, 797 nm (12,547 cm^{-1}, $\varepsilon = 70\,l\,mol^{-1}cm^{-1}$) for **6** and 808 nm (12,376 cm^{-1}, $\varepsilon = 235\,l\,mol^{-1}cm^{-1}$), characteristic of five-coordinate distorted Cu(II) complexes where the bands arise from the d_{xz} $(d_{yz}) \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions [28].

The thermogravimetric analysis (TGA) curves for **1**, **3**, **4**, and **7** are shown in figure 1. Complex **1** begins to lose weight above 80°C. In the first step, major weight loss corresponding to loss of ligand and nitrate is observed to 250°C (Calcd wt loss, 70%; obs. wt loss, 71.2%). Between 250°C to 450°C, NO_2 is released, leading to the formation of CoO as the residue (Calcd wt loss, 11.4%; obs. wt loss, 11.0%). The pattern of weight loss in **3** is very similar to what was observed in **1**. The initial weight loss between 150°C and 330°C corresponds to the loss of ligand and nitrate (Calcd wt loss, 76.5%; obs. wt loss, 75.2%). Above this temperature, NO_2 is lost (Calcd wt loss, 8.9%; obs. wt loss, 9.1%); the final residue, CoO, is formed at 400°C. Complex **4** begins to lose weight on heating above 80°C, losing three molecules of H_2O (Calcd wt loss, 11.7%; obs. wt loss, 11.6%). On heating above 130°C, the complex loses the ligand (Calcd wt loss, 48.2%; obs. wt loss, 48.0%). Between 280°C and 450°C, $Ni(NO_3)_2$ loses NO_2 and NO_3 to yield NiO as the final product (Calcd wt loss, 83.8%; obs. wt loss, 83.9%). Complex **7** loses weight in two overlapping steps to yield CuO as the final residue. The first step involves a sudden loss in weight between 200°C and 250°C corresponding to loss of dpap and one of the nitrate groups (Calcd wt loss, 75.8%; obs. wt loss, 75.5%). In the next step, NO_2 is lost between 250°C and 400°C (Calcd wt loss, 8.8%; obs. wt loss, 10.5%).

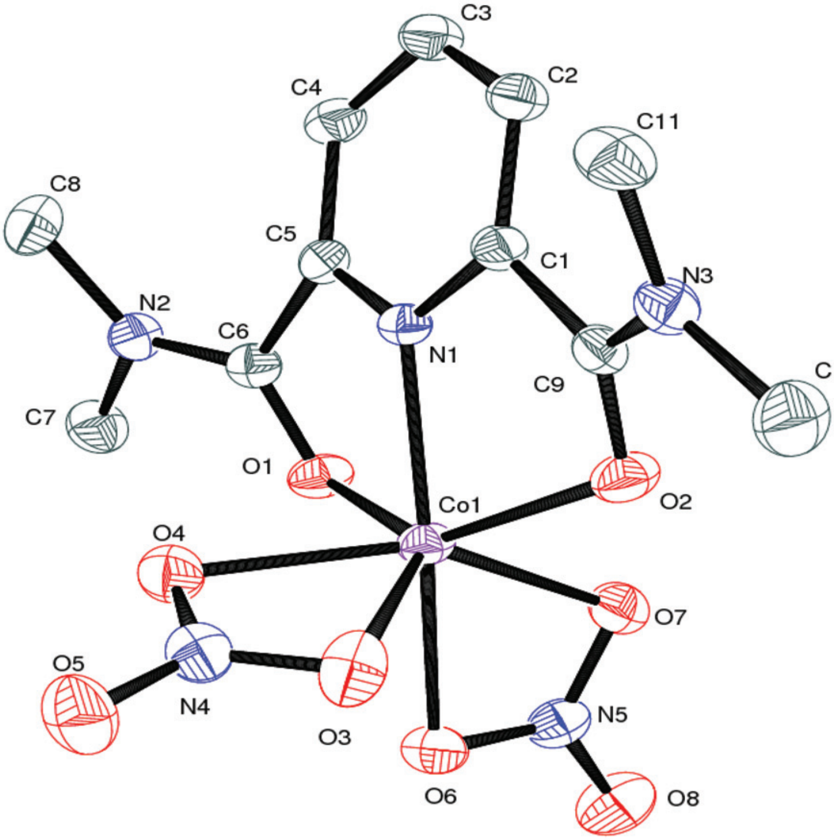


Figure 2. ORTEP diagram and atom numbering scheme of **1**. Hydrogens are omitted for clarity.

3.2. *X-ray molecular and crystal structure analysis*

3.2.1. Molecular and crystal structures of 1 and 2. Being very similar in structure, cobalt(II) complexes **1** and **2** can be discussed together. Figure 2 shows the molecular structure and atom numbering scheme used for **1**, while figure 3 shows the final structure, disorder in one ethyl group, and the labeling scheme used for **2**. The Co(II) is unexpectedly seven-coordinate with distorted pentagonal bipyramidal geometry in both the complexes. In each case, one ligand (O-dmap in **1** and O-deap in **2**) coordinates to metal center in a tridentate fashion using its pyridine nitrogen and both the carboxamide oxygens. Each nitrate coordinates bidentate to metal using two oxygens bringing the coordination number to seven. Table 2 lists the important bond angles and bond distances for **1** and **2**. In both complexes, the carboxamide moieties are twisted with respect to the plane of the pyridine ring so as to facilitate maximum coordination *via* carboxamide oxygens. This twisting is indicated by the torsion angles with respect to C5–C6 and C1–C9 bonds for **1** [27.7(5)° (N1–C5–C6–O1) and 26.3(5)° (N1–C1–C9–O2), respectively] and C5–C6 and C1–C11 bonds for **2** [−27.3(7)° (N1–C5–C6–O1), −28.2(7)° (N1–C1–C11–O2), respectively].

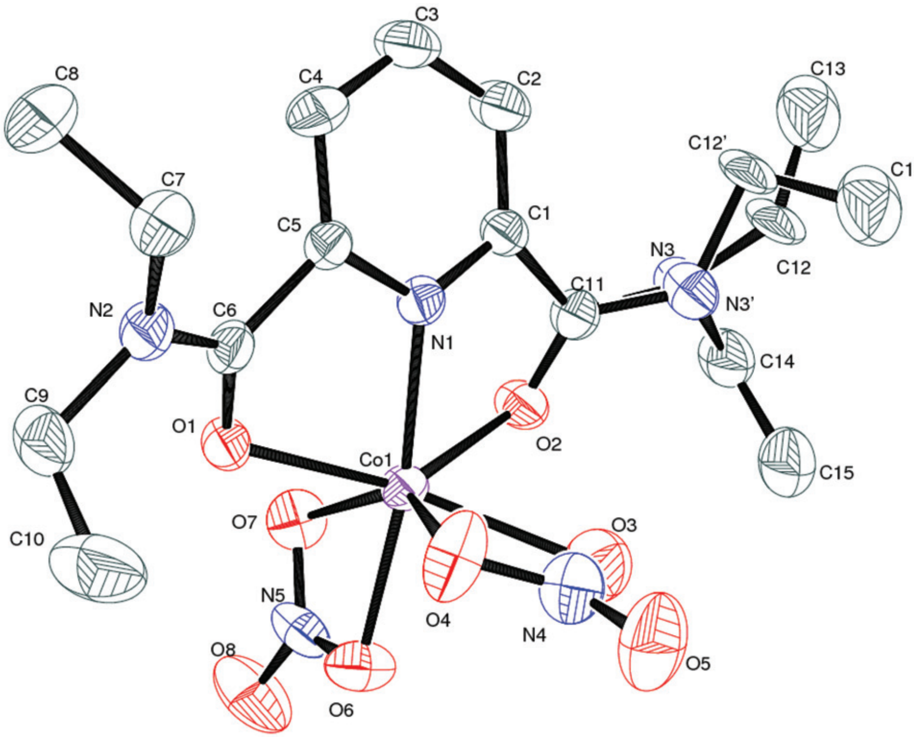


Figure 3. ORTEP with atom numbering scheme of **2**. Disorder is observed on one of the ethyls. Hydrogens have been removed for clarity.

In **1**, the terminal alkyl carbons C7, C8, C10, and C11 are almost in the carboxamide plane with torsion angle values of −8.1(6)° (O1–C6–N2–C7), 166.1(4)° (O1–C6–N2–C8), 4.2(6)° (O2–C9–N3–C10), and −168.4(4)° (O2–C9–N3–C11). As the alkyl bulk on the nitrogens of the carboxamide side arms increases in **2**, the terminal carbons (of ethyl groups) adopt an orientation so as to minimize strain in the structure. In this complex, the terminal ethyl carbon atoms C8 and C13 are above the carboxamide plane, while the atoms C10 and C15 are below this plane.

The nitrate coordinating bidentate to metal using two oxygens and resulting in high coordination number is observed in other seven-coordinate cobalt complexes, such as [Co(NO$_3$)$_2$(CH$_3$CN)(dcdpq)], where (dcdpq) = dicyanodipyridoquinoxaline [8]. The Co(II) center has the distorted pentagonal-bipyramid coordination geometry, consisting of two nitrogens of the pyridine rings, four oxygens of two nitrates, and a N of CH$_3$CN. The Co–O distances involving coordinated nitrates are 2.183(2)–2.310(3) Å, in agreement with the corresponding distances in **1** and **2** (2.087(4)–2.284(5) Å) (table 2). Bidentate coordination of nitrate in **1** and **2** is slightly unsymmetrical with Co1–O3 = 2.258(4) Å, Co1–O4 = 2.188(3) Å, Co1–O6 = 2.148(3) Å, and Co1–O7 = 2.177(3) Å for **1** while Co1–O3 = 2.284(5) Å, Co1–O4 = 2.208(5) Å, Co1–O6 = 2.087(4) Å, and Co1–O7 = 2.162(4) Å for **2**. Another seven-coordinate complex, [Cd(NTB)(NO$_3$)$_2$] [NTB is *tris*(2-benzimidazolylmethyl)amine, C$_{24}$H$_{21}$N$_7$], contains a neutral monomeric cadmium(II) [9]. The Cd(II) is coordinated by four

Table 2. Selected bond distances (Å) and angles (°) for **1**, **2**, **4**, **5**, and **7**.

	1	**2**	
O1–Co1	2.175(3)	2.152(3)	
O2–Co1	2.179(3)	2.185(4)	
O3–Co1	2.258(4)	2.284(5)	
O4–Co1	2.188(3)	2.208(5)	
O6–Co1	2.148(3)	2.087(4)	
O7–Co1	2.177(3)	2.162(4)	
N4–O3–Co1	91.9(3)	94.3(4)	
N4–O4–Co1	94.8(3)	97.2(4)	
N5–O6–Co1	93.2(2)	94.6(3)	
N5–O7–Co1	91.9(2)	91.0(3)	
O6–Co1–O7	59.19(2)	59.88(16)	
O4–Co1–O3	57.16(3)	55.14(18)	
	4	**5**	
O(1)–Ni1	2.109(2)	O(1)–Ni1	2.067(2)
O(2W)–Ni1	2.047(2)	O(2)–Ni1	2.078(2)
O(3W)–Ni1	2.008(3)	O(3)–Ni1	2.071(2)
		O(4)–Ni1	2.043(2)
		O(5)–Ni1	2.052(2)
O(3W)–Ni1–O(2W)	87.38(6)	N(1)–Ni1–O(4)	92.64(10)
Ni1–O(3W)–H(13W)	121.0	O(4)–Ni1–O(5)	93.12(9)
N(1)–Ni1–O(3W)	180.0	O(4)–Ni1–O(1)	90.33(10)
N(1)–Ni1–O(2W)	92.62(6)	O(5)–Ni1–O(1)	105.69(9)
N(1)–Ni1–O(1)	77.79(6)	O(4)–Ni1–O(3)	174.23(9)
O(3W)–Ni1–O(1)	102.21(6)	O(5)–Ni1–O(3)	83.04(9)
O(2W)–Ni1–O(1)	91.43(11)	O(1)–Ni1–O(3)	86.58(10)
		O(4)–Ni1–O(2)	94.13(10)
		O(5)–Ni1–O(2)	96.94(9)
	7		
N(1)–Cu(1)	1.934(5)		
O(1)–Cu(1)	2.061(5)		
O(2)–Cu(1)	2.063(5)		
O(3)–Cu(1)	1.927(5)		
O(6)–Cu(1)	2.122(6)		
N(4)–O(3)–Cu(1)	108.1(5)	(1)–Cu(1)–O(2)	79.5(2)
O(1)–Cu(1)–O(2)	153.5(2)	O(3)–Cu(1)–O(6)	85.3(2)
N(5)–O(6)–Cu(1)	121.9(5)	O(3)–Cu(1)–N(1)	166.9(3)
O(3)–Cu(1)–O(1)	98.1(2)	N(1)–Cu(1)–O(1)	79.3(2)
O(3)–Cu(1)–O(2)	98.9(2)		

nitrogens from NTB and three oxygens from two nitrates, one bidentate nitrate while the other is unidentate. The coordination polyhedron for each Cd is a distorted pentagonal bipyramid. Nitrato 1-allylimidazole coordination compounds of the general formula $[ML_3(NO_3)_2]$, where M is cobalt(II) or nickel(II) and L is 1-allylimidazole, also contain two nitrate groups coordinating bidentate [10]. With M = Co, the Co–O distances involving coordinated nitrates are 2.196(3) Å and 2.411(3) Å, while these distances are 2.093(2) Å and 2.529(2) Å in Ni(II) analogs.

In **1**, the carbonyl oxygen O2 is donor to C3–H3 $\cdots$ O2^{i} (2.636(3) Å, $^{i} = x-1/2, -y+1/2, +z-1/2$) while nitrate oxygen O3 is involved in C4–H4 $\cdots$ O3^{i} (2.699(2) Å, $^{i} = x-1/2, -y+1/2, +z-1/2$) intermolecular hydrogen bonding giving 1-D chains. These parallel chains are held together by C2–H2 $\cdots$ O4^{ii} (2.642(2) Å, $^{ii} = x+1/2, -y+1/2, +z-1/2$) and C10–H10B $\cdots$ O4^{iii} (2.698(2) Å, $^{iii} = x+1, +y, +z$)

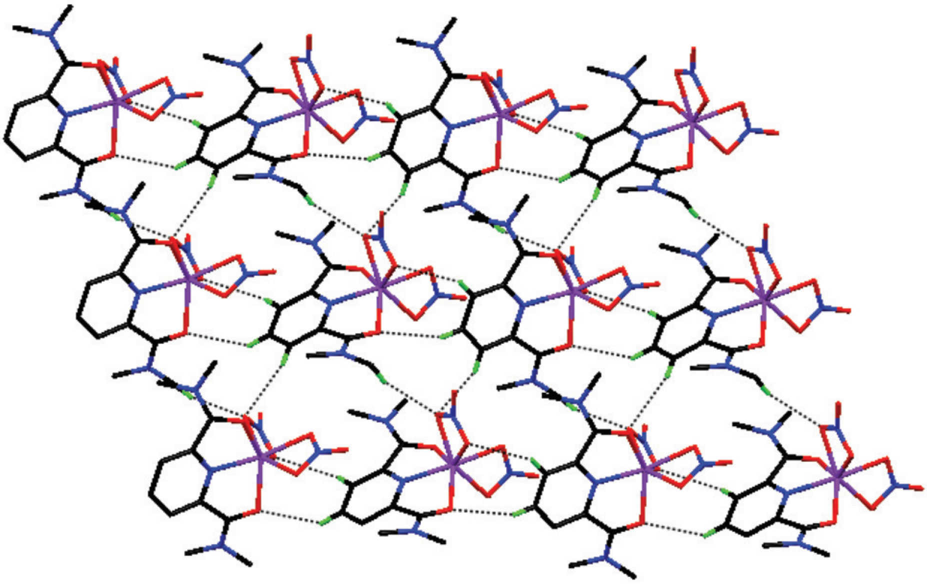


Figure 4. 2-D sheet structure formed by intermolecular H-bonding in **1**. The hydrogens other than those involved in H-bonding are omitted for a clear view.

H–bonds, leading to a 2-D sheet structure parallel to the *ac* plane (figure 4). In **2**, very similar to **1**, a similar sheet structure is formed by C12–H12B $\cdots$ O6^{i} (2.463(2) Å, $^{i} = x + 1/2, -y + 1/2, +z + 1/2$), C13A–H13A $\cdots$ N4^{i} (2.448(3) Å, $^{i} = x + 1/2, -y + 1/2, +z + 1/2$), C13–H13A $\cdots$ O5^{i} (2.353(2) Å, $^{i} = x + 1/2, -y + 1/2, +z + 1/2$), and C8–H8 $\cdots$ O6^{ii} (2.705(4) Å, $^{ii} = x + 1/2, -y + 1/2, +z + 1/2$) intermolecular H-bonding interactions (figure 5).

3.2.2. Molecular and crystal structure of 4.

Ni(II) lies on a twofold axis of rotation (1/2 x, y, 1/4 z) and is octahedral in **4**. Figure 6 shows the ORTEP representation of **4** with atom labeling scheme. One O-dmap coordinates tridentate to nickel using its carboxamide oxygen and pyridine nitrogen. The other three positions in the octahedra are occupied by coordinating water. The pyridine nitrogen N1, coordinated water oxygen O3W, carbonyl oxygen O1 along with its symmetry equivalent form the basal plane, while the *trans* positions are occupied by O2W and its symmetry equivalent in the octahedron. Important bond lengths and angles are summarized in table 2. Nitrates are not coordinated to nickel but are present in the crystal lattice. Both carboxamide moieties are twisted in opposite directions with respect to the pyridine ring to facilitate maximum coordination of the ligand with N1–C1–C4–O1 torsion angle of −13.61(4)°.

The presence of coordinated water and nitrates in the lattice gives interesting intermolecular H-bonding interactions in the crystal lattice. The H-bonding interactions O12W–H12W $\cdots$ O6^{i} (2.007(3) Å, $^{i} = -x + 1/2, +y - 1/2, +z$) and O12W–H22W $\cdots$ O5 (1.760(2) Å) involving coordinated water and nitrate lead to chains "zipping" the complex molecules from two sides in the crystal lattice (figure 7).

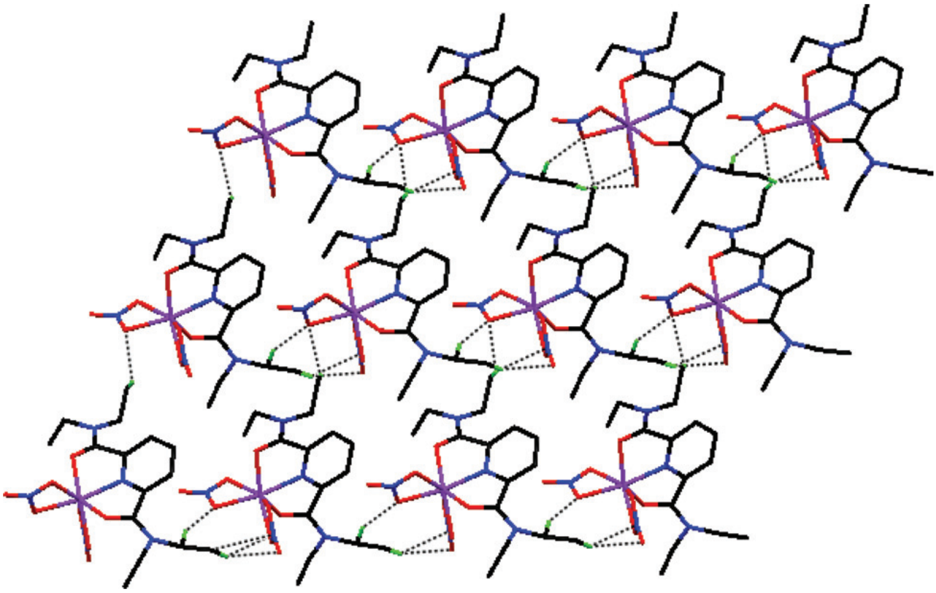


Figure 5. 2-D sheet structure formed by intermolecular hydrogen-bonding interactions in **2**. Hydrogens other than those involved in H-bonding are omitted for clarity.

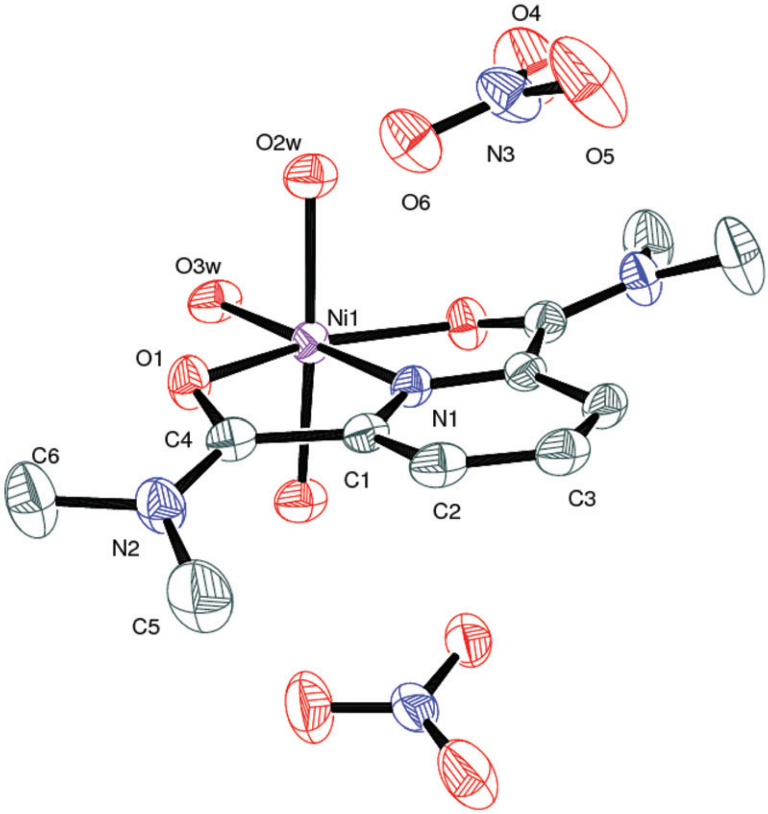


Figure 6. ORTEP diagram and atom numbering scheme for **4**. Hydrogens are omitted for clarity.

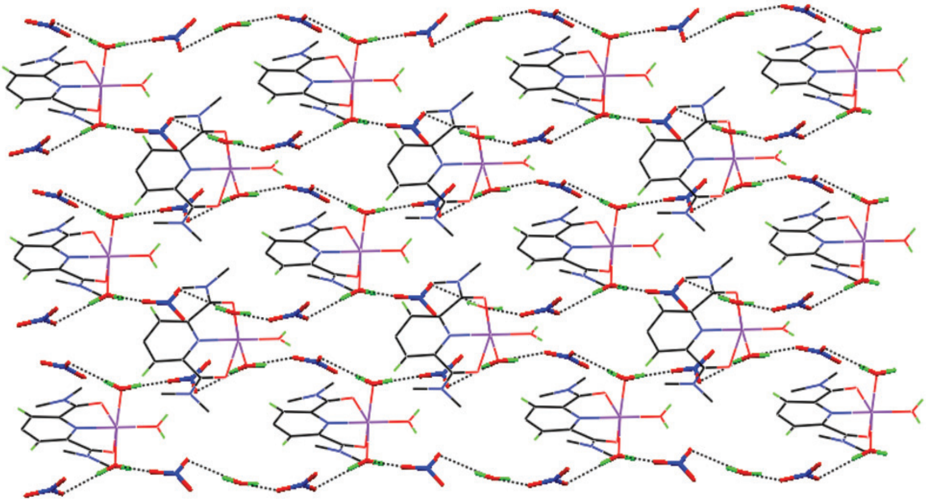


Figure 7. Intermolecular hydrogen-bonding interactions between nitrates and coordinated water molecules zip the complex molecules from two sides in **4**.

3.2.3. Molecular and crystal structure of 5. In **5**, O-deap coordinates tridentate to Ni(II) as observed for **4** (with O-dmap). An ORTEP view of **5** with atom numbering scheme is shown in figure 8. The Ni(II) in **5** is similar to **4** except that in this case a nitrate is coordinated unidentate instead of a third water molecule. Important bond lengths and angles are listed in table 2. The Ni1–O5 short distance of 2.052(2) Å indicates that nitrate is strongly coordinated to nickel. A mean plane can be passed through O1, O2, N1, and O5 with +0.007 Å, +0.008 Å, −0.011 Å, and −0.006 Å being the deviations for these atoms from this plane, respectively. The Ni(II) lies 0.090 Å above this plane. The coordinated water molecules, O3 and O4, occupy the *trans* positions in the octahedron. Carboxamides are twisted with respect to the pyridine ring plane to ensure maximum coordination as indicated by the torsional angles of −19.9(4)° (N1–C1–C11–O2) and −15.8(4)° (N1–C5–C6–O1). The orientation of the terminal alkyl carbons on the carboxamide side arms in the complex is such that C10 and C15 are above the amide plane while C8 and C13 are below this plane.

The presence of coordinated and ionic nitrates in the crystal lattice leads to extensive intermolecular H-bonding. The coordinated nitrates are involved in C4–H4 ⋯ O6^{i} (2.633(3) Å), C3–H3 ⋯ O6^{i} (2.560(3) Å) and C8–H8A ⋯ O2^{i} (2.715(3) Å, $^{i} = -x + 1/2, +y - 1/2, -z + 1/2 + 1$) hydrogen-bonding interactions forming 1-D chains running along the *a*-axis. These parallel chains are held together by nitrates in the crystal lattice *via* O3–H32 ⋯ O8^{ii} (2.664(5) Å), O3–H32 ⋯ O9^{ii} (2.031(4) Å), and O3–H32 ⋯ N5^{ii} (2.676(4) Å (where $^{ii} = x,\ y,\ z$), O4–H42 ⋯ O8^{iii} (2.052(5) Å, O4–H42 ⋯ O10^{iii} (2.618(4) Å), O4–H42 ⋯ N5^{iii} (2.712(4) Å (where $^{iii} = x - 1,\ +y,\ +z$) H-bonding interactions, thus forming 2-D sheets parallel to the *ab* plane (figure 9).

Comparing **4** and **5**, changing the ligand from O-dmap (in **4**) to O-deap (in **5**) (i.e., increasing alkyl bulk on the side arms of the ligand) while keeping the other conditions the same affects the molecular and hence crystal structure of the complexes. Although both are octahedral, the coordination sphere of **4** is devoid of nitrate while **5** has a unidentate nitrate. Ionic nitrates are present in lattice structures of

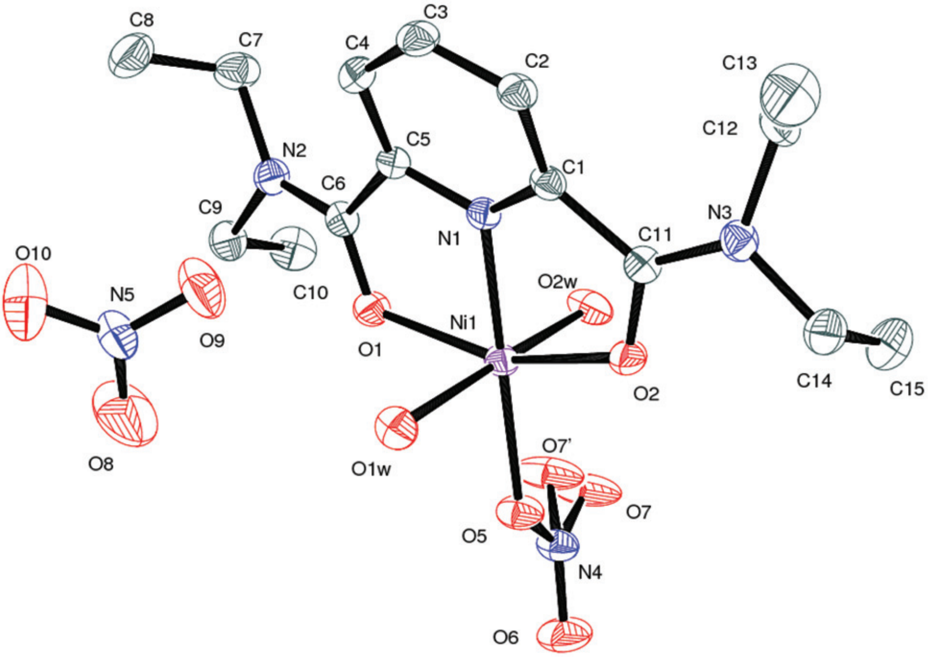


Figure 8. ORTEP diagram and atom numbering scheme used for **5**. Disorder is applied in nitrate oxygen O7. Hydrogens are omitted for clarity.

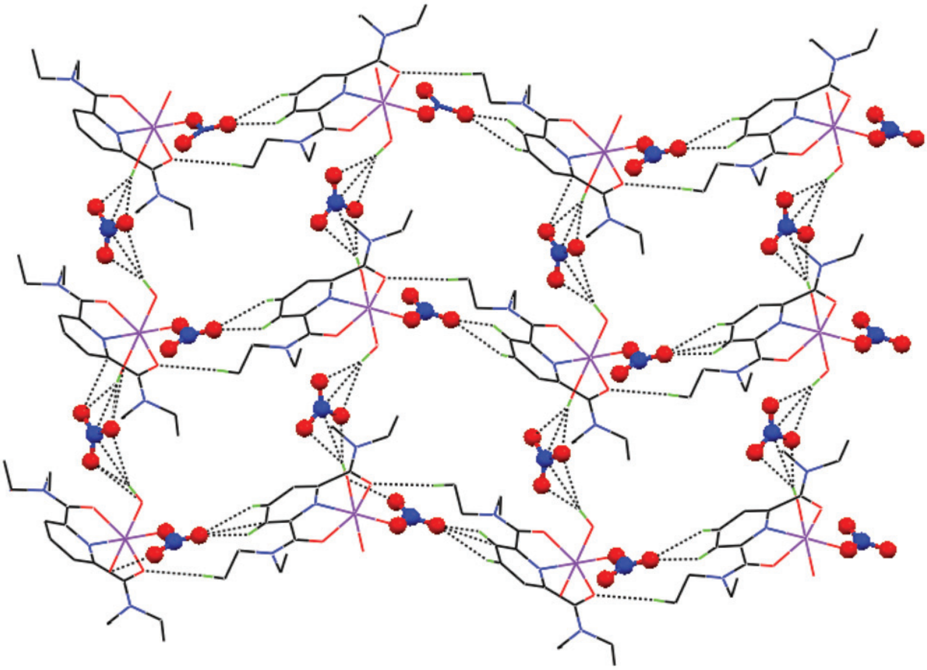


Figure 9. Ionic and coordinated nitrates involved in intermolecular hydrogen bonds forming a sheet structure in **5**. Nitrates are shown in ball-and-stick mode. The hydrogens other than those involved in hydrogen bonding are omitted for a clear view.

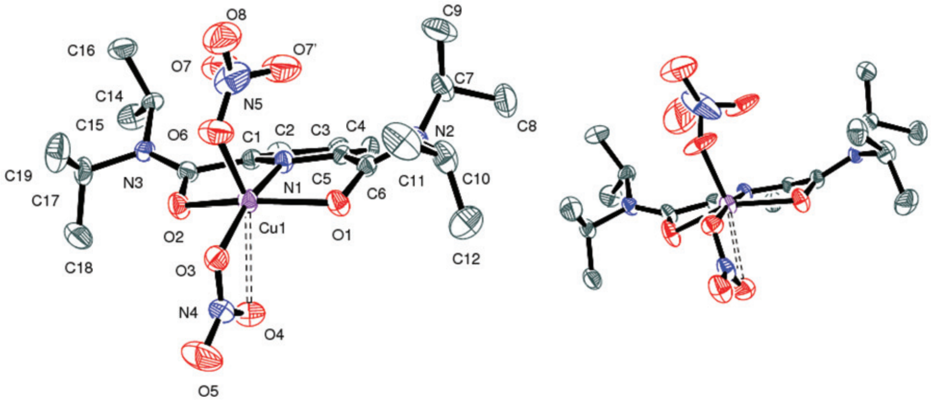


Figure 10. ORTEP diagram and atom numbering scheme for 7. Hydrogens are omitted for clarity.

both the complexes. As in **4**, octahedral $[Ni\{(NH_2)_2CO\}_4(H_2O)_2](NO_3)_2$ and $[Co\{(NH_2)_2CO\}_4(H_2O)_2](NO_3)_2$ [11] are devoid of nitrate in their coordination spheres but have coordinated water molecules as well as ionic nitrates. The Ni–O distance involving coordinated water is 2.082 Å, in agreement with the corresponding Ni–O distances involving coordinated water in **4** and **5** (2.008(4)–2.071(2) Å). The complexes $Cu(urea)_2(H_2O)_3(NO_3).(urea)(NO_3)$ and $Zn(urea)_4(H_2O)_22(NO_3)$ have both coordinated (monodentate) as well as ionic nitrates along with coordinated water [12]. Extensive intermolecular H-bonding involving nitrates (coordinated as well as ionic) and water (coordinated as well as lattice) is reported for all the above-mentioned urea complexes [11, 12], in agreement with the lattice structure of **4** and **5** (figures 7 and 9). A few more Ni(II) complexes containing ionic, monodentate, or bidentate nitrates are $[Ni(en)_3](NO_3)_2$, $[Ni(dien)_2](NO_3)_2$, $[Ni(en)_2(H_2O)_2](NO_3)_2$, and $[Ni(tmd)_2(H_2O)_2](NO_3)_2$ with ionic nitrate as observed in **4**, while $Ni(en)_2(NO_3)$ has unidentate nitrate as observed in **5** [where the abbreviations are ethylenediamine (en), diethylenetriamine (dien), and trimethylenediamine (tmd)]. $[Ni(tmd)_2NO_3]C1O_4$ has IR spectra similar to those of other chelate nitrate compounds indicating bidentate coordination [13].

3.2.4. Molecular structure of 7. The structure of $[Cu(dpap)(NO_3)_2]$ **7** has two crystallographically independent entities shown in figure 10. Cu(II) is coordinated by O-dpap and two nitrates in a distorted square pyramidal geometry with τ [14] equal to 0.22. O-dpap coordinates tridentate to copper using the O–N–O donors. One of the two nitrates coordinates unidentate to Cu(II) using O3, Cu1–O3 = 1.927(5) Å and also involves a weak interaction through O4, Cu–O4 distance being 2.565(2) Å. The other nitrate is unidentate using O6 with Cu1–O6 distance being 2.122(6) Å.

The bulky isopropyls on the carboxamide nitrogens orient to minimize strain in the structure. The terminal carbons C16 and C19 are above the carboxamide plane while C15 and C18 are below this plane on one amide side arm, while C9 and C11 are above and C8 and C12 are below their carboxamide plane on the other side arm. A mean plane can be passed through O1, O2, O3, and N1 with +0.04, +0.04, −0.04, and −0.06 Å being deviations of these atoms from the plane. The Cu(II) lies −0.27 Å below this plane.

Important bond lengths and angles for **7** are listed in table 2. The copper–oxygen distances involving unidentate nitrate are 2.42(3) Å and 2.46(3) Å for $[(NO_3)(L')Cu(4,4'\text{-Bipy})Cu(L')(NO_3)]$ where $L' =$ 1-[(2-hydroxyethylimino)methyl]-naphthalene-2-ol and 2.278(2) Å in $[Cu_3(H_2O)_2(4,4'\text{-Bipy})_3(L''_2)_2(NO_3)_2](NO_3)_2$ where L'' is 2-[2-(hydroxyethylimino)methyl] phenol ligand [15]; $[Cu_3(H_2O)_2(4,4'\text{-Bipy})_3(L''_2)_2(NO_3)_2](NO_3)_2$ contains both monodentate and ionic nitrates. The structure of another copper(II) complex $[Cu(pdz)_3(NO_3)_3]_2Cu$ [16] has three distinct types of nitrates distinguished by the mode or strength of coordination to copper, monodentate bridging (Cu1–O1 2.242(2) Å, Cu2–O1 2.255(2) Å), strongly coordinated monodentate terminal (Cu2–O4 1.947(3) Å), and weakly coordinated monodentate terminal (Cu2–O7 2.516(3) Å).

The nitrates in $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}M(\eta^1\text{-ONO}_2)$ (M = Zn, Cu, Ni), HB = *tris*(pyrazoly1)hydroborato ligand and $3\text{-Bu}^t\text{pz} = 3\text{-Bu}^tC_3N_3H_2$) [17] coordinate unidentate with M = Zn, Zn–O = 1.978(3) Å, indicating strong coordination along with a weak secondary interaction with the other oxygen [Zn–O = 2.581 (3) Å]. Similarly, in **7**, where a nitrate coordinates unidentate to copper along with a weak interaction with the metal ion involving its other oxygen. With M = Cu and Ni, the complexes exhibit symmetric bidentate nitrate with short M–O bond lengths [Cu–O = 2.042(3) Å; Ni–O = 2.095(2) Å]. In contrast, the cobalt derivative exhibits a noticeably asymmetric coordination mode [Co–O = 2.001(3) Å and 2.339(3) Å], intermediate between unidentate and symmetric bidentate. Similarly, the present cobalt complexes **1** and **2** involve slightly unsymmetrical bidentate coordination with the nitrates (table 2).

4. Conclusions

Seven new transition metal complexes were prepared involving tridentate *N*,*N*,*N′*,*N′*-tetraalkylpyridine-2,6-dicarboxamides and nitrate as the counter ion. Single crystal X-ray crystallographic study of **1**, **2**, **4**, **5**, and **7** shows that nitrate uses diverse coordination modes [monodentate (**5** and **7**), bidentate chelating (**1** and **2**), and ionic (**4** and **5**)], playing a significant role in the molecular and crystal structures of these complexes. Complexes **4** and **5** show the influence of varying the alkyl groups bonded to amide nitrogens in the ligand on the structure of the complexes formed.

Complexation of Co(II), Ni(II), and Cu(II) with the same type of ligands in the presence of nitrate counter ion shows the geometrical preference adopted for each metal ion. Co(II) opts for seven-coordinate complexes, while Ni(II) shows its preference for octahedral and Cu(II) distorted square pyramidal.

Thermal analysis (DT–TGA) of the complexes shows that they are stable with breakdown of the complex moieties starting above 100°C. These complexes contain interesting 2-D architectures (like “zipping” of complex molecules in **4**) involving nitrate (coordinated or ionic) as well as water (coordinated as well as lattice) in intermolecular H-bonding.

Acknowledgments

Ajay Pal Singh Pannu thanks UGC-SAP New Delhi for research fellowship. Dr. Pratibha Kapoor thanks Council of Scientific and Industrial research, New Delhi for the financial support.

References

[1] P. Kapoor, A. Kumar, J. Nistandra, P. Venugopalan. *Transition Met. Chem.*, **25**, 465 (2000).
[2] P. Kapoor, A. Pathak, R. Kapoor, P. Venugopalan, M. Corbella, M. Rodriguez, J. Robles, A. Llobet. *Inorg. Chem.*, **41**, 6153 (2002).
[3] P. Kapoor, A. Kataria, P. Venugopalan, R. Kapoor, M. Corbella, M. Rodriguez, M. Romero, A. Llobet. *Inorg. Chem.*, **43**, 6699 (2004).
[4] R. Kapoor, A. Kataria, P. Kapoor, P. Venugopalan. *Transition Met. Chem.*, **29**, 425 (2004).
[5] R. Kapoor, A. Kataria, A. Pathak, P. Venugopalan, G. Hundal, P. Kapoor. *Polyhedron*, **24**, 1221 (2005).
[6] R. Kapoor, A. Kataria, P. Kapoor, A.P.S. Pannu, M.S. Hundal, M. Corbella. *Polyhedron*, **26**, 5131 (2007).
[7] P. Kapoor, A.P.S. Pannu, M. Sharma, M.S. Hundal, R. Kapoor. *J. Coord. Chem.*, **63**, 3635 (2010).
[8] M. Du, H. Liu, X.-J. Ge, X.-H. Bu, M. Yang. *Acta Crystallogr.*, **E57**, m100 (2001).
[9] J.-L. Tian, M.-J. Xie, S.-P. Yan, D.-Z. Liao, Z.-H. Jiang, P. Cheng. *Acta Crystallogr.*, **E60**, m1689 (2004).
[10] T. Glowiak, K. Kurdziel. *J. Mol. Struct.*, **516**, 1 (2000).
[11] A. Krawczuk, K. Stadnicka. *Acta Crystallogr.*, **C63**, m448 (2007).
[12] T.J. Prior, R.L. Kift. *J. Chem. Crystallogr.*, **39**, 558 (2009).
[13] N.F. Curtis, Y.M. Curtis. *Inorg. Chem.*, **4**, 804 (1965).
[14] A.W. Addison, T.N. Rao, J. Reedijk, J. van Riju, G.C. Verschoor. *J. Chem. Soc., Dalton Trans.*, 1349 (1984).
[15] Y.M. Chumakov, V.L. Tsapkov, P.A. Petrenko, L.G. Popovski, Yu.A. Simonov, G. Bocelli, B.Ya. Antosyak, A.O. Paraschivescu, A.P. Gulea. *Russ. J. Coord. Chem.*, **35**, 504 (2009).
[16] T. Otieno, S.J. Rettig, R.C. Thompson, J. Trotter. *Inorg. Chem.*, **34**, 1718 (1995).
[17] R. Han, G. Parkin. *J. Am. Chem. Soc.*, **113**, 9708 (1991).
[18] W.L.F. Armarego, D.D. Perrin. *Purification of Laboratory Chemicals*, 4th Edn, Butterworth-Heinemann, Oxford (1996).
[19] T. Le Borgne, J.M. Bénech, S. Floquet, G. Bernardinelli, C. Aliprandini, P. Bettens, C. Piguet. *Dalton Trans.* 3856 (2003).
[20] *XSCANS. X-ray Single Crystal System* (Version 2.1), Siemens Analytical Instruments Inc., Madison, WI, USA (1994).
[21] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Crystallogr.*, **32**, 115 (1999).
[22] G.M. Sheldrick. *SHELXS-97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1997).
[23] L.J. Farrugia. *J. Appl. Crystallogr.*, **32**, 837 (1999).
[24] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[25] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edn, Wiley, New York (1997).
[26] M.G.B. Drew, A.H. bin Othman, S.G. McFall, P.D.A. McIlroy, S.M. Nelson. *J. Chem. Soc., Dalton Trans.*, 1173 (1977).
[27] S.M. Nelson, M. McCann, C. Stevenson, M.G.B. Drew. *J. Chem. Soc., Dalton Trans.*, 1477 (1979).
[28] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, p. 568, Elsevier, Amsterdam (1984).