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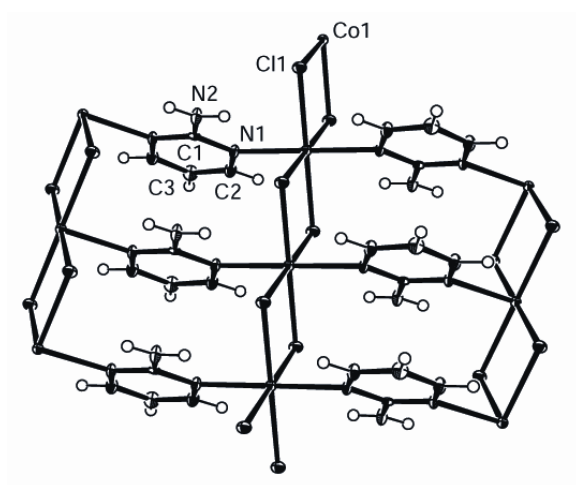
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Index Abstract:

Nickel(II) and cobalt(II) nitrate and chloride networks with 2-aminopyrimidine.

Robert D. Pike,* Mi-Jung Lim, Ellen A. L. Willcox, and Tristan A. Tronic.

The coordination chemistry and network formation of nickel(II) nitrate, cobalt(II) nitrate nickel(II) chloride, and cobalt(II) chloride with 2-aminopyrimidine is presented.



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Abstract

The coordination chemistry of 2-aminopyrimidine (PymNH₂) with nickel(II) and cobalt(II) nitrate and chloride is reported, including seven new X-ray crystal structures. Two [Ni(NO₃)₂(PymNH₂)₂(OH₂)] isomers were found (**A**: *C2/c*, *a* = 13.3006(5), *b* = 7.9727(3), *c* = 28.5453(11), β = 101.758(2), *V* = 2963.48(19), *Z* = 8 and **B**• $\frac{1}{2}$ acetone: *P2₁/c*, *a* = 7.66060(10), *b* = 10.6792(2), *c* = 20.6790(3), β = 100.2970(10), 1664.48(5), *Z* = 4). In both cases one nitrate is monodentate and the other is chelating and the PymNH₂ ligands coordinate through ring nitrogen atoms. Hydrogen bonding results in double sheet structure for isomer **A**, and a three dimensional channeled network for isomer **B**. [Co(NO₃)₂(PymNH₂)₂(OH₂)] (*C2/c*, *a* = 13.3507(2), *b* = 7.99520(10), *c* = 28.6734(3), β = 102.3540(10), *V* = 2989.77(7), *Z* = 8) is isostructural to Ni isomer **A**. [CoCl₂(PymNH₂)] (*Cmcm*, *a* = 3.6139(2), *b* = 14.3170(7), *c* = 12.9986(7), *V* = 672.55(6), *Z* = 4) is a sheet coordination network, consisting of corner-sharing chains of Co₂(μ -Cl)₂ bridged by PymNH₂ through ring nitrogen atoms; [CoCl₂(PymNH₂)₂] (*C2/c*, *a* = 11.2774(6), *b* = 6.5947(4), *c* = 16.5687(9), β = 92.269(3), *V* = 1231.27(12), *Z* = 4) is a tetrahedral molecule knit into a ribbon structures through pairs of hydrogen bonds. Isostructural *trans*-[NiCl₂(PymNH₂)₄] (*C2/c*, *a* = 7.67760(10), *b* = 18.7224(3), *c* = 15.0418(2), β = 99.6740(10), *V* = 2131.41(5), *Z* = 4) and *trans*-[CoCl₂(PymNH₂)₄] (*C2/c*, *a* = 7.69120(10), *b* = 18.5957(2), *c* =

15.1091(2), $\beta = 99.5280(10)$, $V = 2131.14(5)$, $Z = 4$) are simple octahedral molecules, with hydrogen-bonding producing sheet structures.

Key Words: nickel, cobalt, 2-aminopyrimidine, hydrogen bonding, metal organic network

Shortened Title: Nickel and Cobalt 2-Aminopyrimidine Networks

Introduction

Metal-organic networks represent an area of intense scrutiny. In addition to network formation mediated through polydentate bridging ligands, hydrogen bonding can play an important role in supramolecular assembly.¹ Ligands that can potentially engage in both of these behaviors are of particular interest in the quest for highly networked materials. One such ligand is 2-aminopyrimidine (PymNH₂) which is known to form hydrogen bonded dimers via Watson-Crick-type pairing.² Numerous metal complexes of PymNH₂ and PymNH₃⁺ are known. Most notable with respect to the current study are *trans*-[M(SCN)₂(PymNH₂)₂(OH₂)₂]•H₂O (M = Ni, Co),³ *cis,mer*-[Co₂(μ -SO₄)₂(PymNH₂)₂(OH₂)₆]•H₂O,⁴ *catena-cis*-[Ni(μ -SO₄)(PymNH₂)₂(OH₂)₂]•PymNH₂,⁴ [Ni(PymNH₂)(OH₂)₅]SO₄•PymNH₂,⁴ and *trans*-[MX₄(PymNH₃)₂] (M = Co, X = Cl; M = Ni, X = Cl, Br).⁵ Although sulfate shows bidentate bridging behavior, PymNH₂ is monodentate and bonds exclusively through a ring nitrogen atom in each of these complexes.⁴ Unit cell data, but no structural coordinates, have been reported for [NiX₂(PymNH₂)₂]•4H₂O (X = Cl, Br).⁶ Several previously reported copper species are closely related to the cobalt and nickel complexes discussed herein: [CuCl₂(PymNH₂)],⁷ *trans*-[CuX₂(PymNH₂)₂] (X = Cl, Br, NO₃),⁷⁻⁹ *catena-trans*-[Cu(μ -SO₄)(PymNH₂)₂(OH₂)]•H₂O,⁴ *trans*-[CuBr₄(PymNH₃)₂],⁸ [CuBr(PymNH₂)],^{8,10} and [(CuBr)₂(PymNH₂)].⁸ Surprisingly, no complete structures for simple nickel or cobalt nitrate or chloride complexes of PymNH₂ appear in the Cambridge Structural Database.

In the current study, we undertook to produce complexes of the type $[M(\text{NO}_3)_2(\text{PymNH}_2)_n]$ and $[\text{MCl}_2(\text{PymNH}_2)_n]$ ($M = \text{Ni}, \text{Co}$). We herein report the synthesis of nine new complexes of PymNH_2 with cobalt and nickel salts and seven X-ray crystal structures.

Experimental

Synthesis.

An acetone solution containing 50 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 100 mM PymNH_2 was layered with diethyl ether in 5 mm i.d. tubes, resulting in growth of X-ray quality crystals of isomer **B** over several days at room temperature. Alternatively, the above solution in acetone was allowed to stand overnight without addition of ether, resulting in growth of X-ray quality crystals of isomer **A**. Crystals of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with PymNH_2 were grown as described for $\text{Ni}(\text{NO}_3)_2$ complex, isomer **B**. Crystals of $[\text{CoCl}_2(\text{PymNH}_2)]$ were grown by layering a 25 mM solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in EtOH with a 100 mM solution of PymNH_2 in EtOH in 5 mm i.d. tubes. Crystals of $[\text{CoCl}_2(\text{PymNH}_2)_2]$ were grown by slow evaporation of a MeOH solution containing 12.5 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 50 mM PymNH_2 . Crystals of *trans*- $[\text{NiCl}_2(\text{PymNH}_2)_4]$ or *trans*- $[\text{CoCl}_2(\text{PymNH}_2)_4]$ were produced by slowly evaporating a 95% EtOH solution containing either 50 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 200 mM PymNH_2 .

Bulk samples of all complexes except *trans*- $[\text{CoCl}_2(\text{PymNH}_2)_4]$ were readily prepared by stirring together in the appropriate ratio acetone solutions of the metal nitrate and PymNH_2 , or EtOH solutions of the metal chloride and PymNH_2 . Products precipitated from solution within a few minutes. Attempts to make bulk samples of *trans*- $[\text{CoCl}_2(\text{PymNH}_2)_4]$ using 4–10 fold excess of PymNH_2 in EtOH or acetone consistently produced blue $[\text{CoCl}_2(\text{PymNH}_2)_2]$ as the major product mixed with only trace amounts of the desired purple product. Microanalyses for C, H, and N were carried out by Atlantic Microlab, Inc., Norcross, GA. Synthetic results are summarized in Table 1. Infrared spectra were collected on a Digilab FTS 7000 FTIR spectrophotometer.

X-ray crystallography.

Crystals were mounted on glass fibers. All measurements were made using graphite-monochromated Cu K α radiation on a Bruker-AXS three-circle diffractometer, equipped with a SMART APEX II CCD detector. Initial space group determination was based on a matrix of 120 frames. The data were reduced using SAINT+,¹¹ and empirical absorption correction applied using SADABS.¹²

Structures were solved using direct methods, except for *trans*-[NiCl₂(PymNH₂)₄], which was solved by the Patterson method. Least-squares refinement for all structures was carried out on F^2 . The non-hydrogen atoms were refined anisotropically. All hydrogen atoms in each structure, except for CoCl₂(PymNH₂), were located by standard difference Fourier techniques and were refined with isotropic thermal parameters. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL package of computer programs.¹³ Packing diagrams were produced using Mercury.¹⁴ Details of the X-ray experiments and crystal data are summarized in Table 2. Selected bond lengths and bond angles for the nitrate structures are given in Table 3 and those for the chloride structures are found in Table 4.

Results and Discussion

[Co(NO₃)₂(PymNH₂)₂(OH₂)] and [Ni(NO₃)₂(PymNH₂)₂(OH₂)] Isomers

Nickel(II) and cobalt(II) nitrate complexes coordinating PymNH₂ were readily synthesized. Two geometric isomers of the nickel complex were crystallized from acetone under only slightly different conditions. Molecular diagrams for isomers **A** and **B** are shown in Figures 1 and 2, respectively. The unit cell for isomer **B** contains a disordered acetone molecule, which is not shown. The two nickel isomers show identical coordination spheres consisting of two ring-coordinated PymNH₂ ligands, a monodentate (η^1) and a bidentate (η^2) nitrate ion, and an aqua

ligand. The overall geometry around the metal center is best regarded as that of a distorted octahedron with η^2 -NO₃ occupying two coordination sites. In both isomers the PymNH₂ ligands are mutually *cis*, as are the nitrates. However, in isomer **A**, the water ligand is *trans* to the η^1 -NO₃ and in isomer **B**, the water is *trans* to a PymNH₂ ligand. The observed *cis* relationships of the PymNH₂ ligand pairs has previously been observed in catena-*cis*-[Ni(μ -SO₄)(PymNH₂)₂(OH₂)₂] \cdot PymNH₂.⁴ In this case the bridging sulfate ligands are mutually *trans*. However, an all *trans* arrangement is more common, being found in *trans*-[M(SCN)₂(PymNH₂)₂(OH₂)₂] (M = Ni, Co),⁹ *trans*-[CuX₂(PymNH₂)₂] (X = Cl, Br, NO₃),⁷⁻⁹ and in the new complexes [CoCl₂(PymNH₂)] and *trans*-[MCl₂(PymNH₂)₄] (M = Ni, Co) described herein (see below).

Both nickel nitrate isomers form networks through hydrogen bonding, as illustrated in Figures 3 and 4. The isomer **A** network, shown in Figure 3, comprises a double sheet propagating along the (001) direction. The sheets result from intermolecular O1–H \cdots O6 (H₂O \cdots η^1 -NO₃, 2.803(3) Å), O1–H \cdots N6 (H₂O \cdots ring N, 2.753(3) Å), and N5–H \cdots O3 (NH₂ \cdots η^2 -NO₃, 3.064(3) Å) hydrogen bonds. These layers are linked together by N3–H \cdots N5 (NH₂ \cdots ring N, 3.080(3) Å) Watson-Crick hydrogen bonds. In addition, in this complex, as well as the other two nitrate complexes, there are several intramolecular hydrogen bonds.

The isomer **B** network, shown in Figure 4, forms a three-dimensional channeled network. The superstructure results from O1–H \cdots O3 (H₂O \cdots η^2 -NO₃, 2.845(2) Å), O1–H \cdots N6 (H₂O \cdots ring N, 2.738(2) Å) and N5–H \cdots N3 (NH₂ \cdots ring N, 3.075(3) Å) intermolecular H-bonds. Viewed along the crystallographic *a*-axis (Figure 4), the hydrogen bonded macrocycles that comprise the channels are formed from groups of six molecules per helical turn. Viewed along the crystallographic *b*-axis, a second set of roughly square hydrogen bonded macrocycles formed from groups of four molecules per helical turn channels can be seen. The acetone molecules are found within the channels.

The single cobalt nitrate complex identified in the current study, $[\text{Co}(\text{NO}_3)_2(\text{PymNH}_2)_2(\text{OH}_2)]$, is isostructural and isomorphous to $[\text{Ni}(\text{NO}_3)_2(\text{PymNH}_2)_2(\text{OH}_2)]$ isomer **A** (see Figure 5): $\text{O1-H}\cdots\text{O6}$ ($\text{H}_2\text{O}\cdots\eta^1\text{-NO}_3$, 2.793(3) Å), $\text{O1-H}\cdots\text{N6}$ ($\text{H}_2\text{O}\cdots\text{ring N}$, 2.731(3) Å), $\text{N5-H}\cdots\text{O3}$ ($\text{NH}_2\cdots\eta^2\text{-NO}_3$, 3.133(3) Å), and $\text{N3-H}\cdots\text{N5}$ ($\text{NH}_2\cdots\text{ring N}$, 3.111(3) Å). The only significant difference in the unit cell is that the *b*-axis is reversed between the two structures.

[CoCl₂(PymNH₂)] and [NiCl₂(PymNH₂)]

A 1:1 complex between CoCl_2 and PymNH_2 is formed (see Figure 6). Unlike the other structures reported herein, this species comprises a true coordination network. The geometry at cobalt, which lies on the crystallographic special position $(\frac{1}{2}, 0, 0)$, is octahedral with *trans*-axial PymNH_2 ligands and equatorial bridging chlorides. Similar *trans*-axial arrangements have been noted in *trans*- $[\text{MX}_4(\text{PymNH}_3)_2]$ ($\text{M} = \text{Co}$, $\text{X} = \text{Cl}$; $\text{M} = \text{Ni}$, $\text{X} = \text{Cl}$, Br ; $\text{M} = \text{Cu}$, $\text{X} = \text{Br}$).^{5,8} The angles around the cobalt center are only slightly distorted from 90°. Infinite corner-sharing chains of $\dots\text{Co}(\mu\text{-Cl})_2\text{Co}(\mu\text{-Cl})_2\dots$ propagate along the *a*-axis. These chains are knit together into rippled layers through bridging of the PymNH_2 ligands using ring nitrogen atoms propagating along the *c*-axis. This pyrimidine-type network formation is recognized in the Cu(I) complexes $[\text{CuBr}(\text{PymNH}_2)]$,^{8,10} and $[(\text{CuBr})_2(\text{PymNH}_2)]$.⁸ The layers are separated by a distance of roughly 3.7 Å (distance between Cl and PymNH_2). A packing diagram, shown in Figure 7 illustrates the efficient packing of the layers. The only hydrogen bonding contact is intramolecular between Cl1 and H-N2. An analogous nickel chloride complex was synthesized; its identity was confirmed on the basis of elemental analysis (see Table 1). Although the nickel complex was not successfully crystallized, the X-ray powder diffraction patterns of $[\text{MCl}_2(\text{PymNH}_2)]$ ($\text{M} = \text{Co}$, Ni) were found to be very similar, suggesting that these materials possess isomorphous structures.

[CoCl₂(PymNH₂)₂] and [NiCl₂(PymNH₂)₂]•½H₂O

A 1:2 complex of CoCl₂ and PymNH₂ can also be produced (see Figure 8). In contrast to the 1:1 complex, here the metal center is four-coordinate and exhibits nearly perfect tetrahedral geometry. Half of the molecule is crystallographically independent. Hydrogen bonding involves the familiar reciprocal Watson-Crick pairs of amine-ring nitrogen linkages. This variety of hydrogen bonding produces dimers in the crystal structure of PymNH₂ itself,² and is widely encountered in metal complexes of PymNH₂.^{4,7-9,15,16} In the present case, since two PymNH₂ ligands are present on each molecule, intermolecular N2–H··N3 hydrogen bonding (3.056(3) Å) produces one-dimensional chains that propagate perpendicular to the crystallographic *b*-axis (see Figure 9). An intermolecular N2–H··Cl1 hydrogen bond is also present. As was the case with the 1:1 MCl₂:PymNH₂ complex, a nickel analog of the 1:2 MCl₂:PymNH₂ complex was synthesized as a bulk powder, but could not be induced to crystallize. In contrast to the cobalt species, elemental analysis results suggest a partially hydrated formula. Therefore, it is not surprising that [NiCl₂(PymNH₂)₂]•½H₂O and [CoCl₂(PymNH₂)₂] exhibited significantly different X-ray powder patterns.

trans-[NiCl₂(PymNH₂)₄] and trans-[CoCl₂(PymNH₂)₄]

The reaction of NiCl₂•6H₂O with four equivalents of PymNH₂ in ethanol produces a 1:4 complex *trans*-[NiCl₂(PymNH₂)₄] (see Figure 10). Analogous synthesis using CoCl₂•6H₂O produced traces of the purple 1:4 cobalt analog amongst the major CoCl₂(PymNH₂)₂ product only when low concentrations were used and the resulting ethanol or acetone solution was allowed to slowly evaporate. At higher concentrations the royal blue [CoCl₂(PymNH₂)₂] crystallized exclusively. The structure of *trans*-[NiCl₂(PymNH₂)₄], only half of which is crystallographically independent, reveals a nearly perfect octahedron. The two-dimensional network formed by this complex is illustrated in Figure 11. A pair of internal N2–H··Cl1 and N5–H··Cl1 hydrogen bonds is present. Each octahedron is linked to four others via intramolecular N5–H··N3 hydrogen bonds

(3.0145(19) Å) to form a planar sheet superstructure. The cobalt analog is isostructural (see Figure 12).

Infrared Spectra

Infrared data are summarized in Table 5. The IR spectrum of PymNH₂ has previously been interpreted.¹⁷ Most prominent in its spectrum are N–H stretching modes (3167, 3242, 3341 cm⁻¹), NH₂ scissoring mode (1654 cm⁻¹), and ring stretching modes (1575, 1562, 1479, 1445 cm⁻¹). These bands are all affected by coordination of PymNH₂ to metal centers; the N–H bands in particular show major changes on coordination. This effect has previously been interpreted as indicating coordination through the amine, rather than the ring, nitrogen.¹⁷ However, similar IR effects are seen in the current work coupled with confirmation of coordination exclusively through ring nitrogen atoms. In general, coordination of PymNH₂ to the metal salts reported herein results in increased complexity in the N–H stretching region, with several sharp non-hydrogen-bonded IR peaks >3200 cm⁻¹ and an indeterminate number of broad hydrogen-bonded IR features <3200 cm⁻¹. The NH₂ scissoring mode is also strongly influenced by metal coordination. This sharp peak moves from 1654 cm⁻¹ in PymNH₂ to 1560–1590 in the metal complexes. The two higher frequency ring breathing modes in the complexes exhibited increases in frequency over those of PymNH₂, while the two lower frequency ring bands were essentially unchanged.

Conclusions

A wide range of stoichiometries and structural types has been identified for the complexes of M(NO₃)₂ and MCl₂ (M = Co, Ni) with PymNH₂. Extensive hydrogen bonding in the nitrate complexes involves nitrate, aqua, and PymNH₂ ligands, and produces two- and three-dimensional supramolecular networks. The chloride complexes show less extensive hydrogen bonding networks with variations on simple Watson-Crick pairing to produce one- and two-

dimensional networks. In contrast, $[\text{CoCl}_2(\text{PymNH}_2)]$ forms a fully covalent two-dimensional network through pyrimidine-type bridging.

Supplementary Material: Tables of atomic coordinates for each structure are available as supplementary material. CCDC 608624–608629 and 610478 contain the crystallographic data for this paper. These data can be obtained free of charge by e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ UK; Fax +44(0)1223-336033; www.ccdc.cam.ac.uk/data_request/cif.

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Table 1. Yield and Analytical Data^a

Complex	% Yield	Color	%C (calcd)	%H (calcd)	%N (calcd)
[Ni(NO ₃) ₂ (PymNH ₂) ₂ (OH ₂)]	68.3	green	24.38 (24.58)	3.16 (3.09)	28.43 (28.66)
[Co(NO ₃) ₂ (PymNH ₂) ₂ (OH ₂)]	72.1	rose	24.30 (24.56)	3.18 (3.09)	28.15 (28.65)
[CoCl ₂ (PymNH ₂) ₂]	89.4	lavender	21.86 (21.36)	2.53 (2.24)	18.78 (18.68)
[NiCl ₂ (PymNH ₂) ₂]	93.2	yellow	22.54 (21.38)	2.63 (2.24)	18.95 (18.70)
[CoCl ₂ (PymNH ₂) ₂]	70.6	blue	30.18 (30.02)	3.17 (3.15)	26.00 (26.26)
[NiCl ₂ (PymNH ₂) ₂] $\cdot\frac{1}{2}$ H ₂ O	97.1	pale green	29.55 (29.22)	3.37 (3.37)	25.05 (25.56)
<i>trans</i> -[NiCl ₂ (PymNH ₂) ₄]	68.6	lime	38.35 (37.68)	4.23 (3.95)	31.16 (32.96)

^aPurple *trans*-[CoCl₂(PymNH₂)₄] is formed only in trace amounts in [CoCl₂(PymNH₂)₂] products, see text.

Table 2. Crystal and Structure Refinement Data.^a

	[Ni(NO ₃) ₂ (PymNH ₂) ₂ (OH ₂)], A	[Ni(NO ₃) ₂ (PymNH ₂) ₂ (OH ₂) •1/2 acetone, B
CCDC deposit no.	608624	608626
color and habit	green block	green prism
size, mm	0.11 × 0.10 × 0.10	0.29 × 0.08 × 0.08
formula	C ₈ H ₁₂ N ₈ NiO ₇	C ₈ H ₁₂ N ₈ NiO ₇
formula weight	390.92	390.92
space group	<i>C</i> 2/ <i>c</i> (#15)	<i>P</i> 2 ₁ / <i>c</i> (#14)
<i>a</i> , Å	13.3006(5)	7.66060(10)
<i>b</i> , Å	7.9727(3)	10.6792(2)
<i>c</i> , Å	28.5453(11)	20.6790(3)
β, deg	101.758(2)	100.2970(10)
volume, Å ³	2963.48(19)	1664.48(5)
<i>Z</i>	8	4
ρ _{calc} , g cm ⁻³	1.753	1.732
<i>F</i> ₀₀₀	1600	892
μ(Cu Kα), mm ⁻¹	2.429	2.279
radiation	CuKα (λ = 1.54178 Å)	CuKα (λ = 1.54178 Å)
temperature, K	296	296
residuals: ^a <i>R</i> ; <i>R</i> _w	0.0318; 0.0729	0.0380; 0.1144
goodness of fit	1.080	1.432

^a $R = R_I = \sum ||F_o| - |F_c|| / \sum |F_o|$ for observed data only. $R_w = wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ for all data.

	[Co(NO ₃) ₂ (PymNH ₂) ₂ (OH ₂)]	[CoCl ₂ (PymNH ₂)]
CCDC deposit no.	608625	608629
color and habit	purple prism	purple block
size, mm	0.36 × 0.26 × 0.23	0.15 × 0.10 × 0.10
formula	C ₈ H ₁₂ CoN ₈ O ₇	C ₄ H ₅ Cl ₂ CoN ₃
formula weight	391.17	224.94
space group	<i>C2/c</i> (#15)	<i>Cmcm</i> (#63)
<i>a</i> , Å	13.3507(2)	3.6139(2)
<i>b</i> , Å	7.99520(10)	14.3170(7)
<i>c</i> , Å	28.6734(3)	12.9986(7)
β, deg	102.3540(10)	90
volume, Å ³	2989.77(7)	672.55(6)
<i>Z</i>	8	4
ρ _{calc} , g cm ⁻³	1.738	2.222
<i>F</i> ₀₀₀	1592	444
μ(Cu Kα), mm ⁻¹	9.536	26.622
radiation	CuKα (λ = 1.54178 Å)	CuKα (λ = 1.54178 Å)
temperature, K	296	100
residuals: ^a <i>R</i> ; <i>R</i> _w	0.0300; 0.0749	0.0296; 0.0772
goodness of fit	1.048	1.051

Table 2. (cont'd)

	[CoCl ₂ (PymNH ₂) ₂]	<i>trans</i> -[NiCl ₂ (PymNH ₂) ₄]
CCDC deposit no.	608628	608627
color and habit	blue block	green block
size, mm	0.13 × 0.10 × 0.07	0.24 × 0.19 × 0.10
formula	C ₈ H ₁₀ Cl ₂ CoN ₆	C ₁₆ H ₂₀ Cl ₂ NiN ₁₂
formula weight	320.05	510.05
space group	<i>C2/c</i> (#15)	<i>C2/c</i> (#15)
<i>a</i> , Å	11.2774(6)	7.69120(10)
<i>b</i> , Å	6.5947(4)	18.5957(2)
<i>c</i> , Å	16.5687(9)	15.1091(2)
β, deg	92.269(3)	99.5280(10)
volume, Å ³	1231.27(12)	2131.14(5)
<i>Z</i>	4	4
ρ _{calc} , g cm ⁻³	1.727	1.590
<i>F</i> ₀₀₀	644	1048
μ(Cu Kα), mm ⁻¹	14.828	3.898
radiation	CuKα	CuKα
	(λ = 1.54178 Å)	(λ = 1.54178 Å)
temperature, K	200	100
residuals: ^a <i>R</i> ; <i>R</i> _w	0.0285; 0.0704	0.0237; 0.0705
goodness of fit	1.085	1.043

Table 2. (cont'd)

<i>trans</i> -[CoCl ₂ (PymNH ₂) ₄]	
CCDC deposit no.	610478
color and habit	purple block
size, mm	0.26 × 0.23 × 0.12
formula	C ₁₆ H ₂₀ Cl ₂ CoN ₁₂
formula weight	510.27
space group	C2/c (#15)
<i>a</i> , Å	7.67760(10)
<i>b</i> , Å	18.7224(3)
<i>c</i> , Å	15.0418(2)
β, deg	99.6740(10)
volume, Å ³	2131.41(5)
<i>Z</i>	4
ρ _{calc} , g cm ⁻³	1.590
F ₀₀₀	1044
μ(Cu Kα), mm ⁻¹	8.897
radiation	CuKα (λ = 1.54178 Å)
temperature, K	200
residuals: ^a R; R _w	0.0264; 0.0679
goodness of fit	1.064

Table 3. Selected Bond Distances (Å) and Angles (°) for Nitrate Complexes.

	[Ni(NO ₃) ₂ (PymNH ₂) ₂ (OH ₂)], A	[Ni(NO ₃) ₂ (PymNH ₂) ₂ (OH ₂)] •1/2 acetone, B	[Co(NO ₃) ₂ (PymNH ₂) ₂ (OH ₂)]
M–O1	2.0469(17)	2.0399(16)	2.0547(18)
M–O2	2.1005(17)	2.1868(15)	2.1769(18)
M–O3	2.1715(17)	2.1279(15)	2.1804(18)
M–O5	2.0851(15)	2.0365(15)	2.1301(16)
M–N1	2.0623(18)	2.0883(18)	2.1037(18)
M–N4	2.0658(18)	2.0791(17)	2.1190(19)
O1–M–O2	86.67(8)	86.74(6)	84.31(8)
O1–M–O3	87.51(7)	86.56(7)	89.22(8)
O1–M–O5	167.77(7)	89.22(7)	165.51(7)
O1–M–N1	90.08(8)	174.75(7)	95.77(8)
O1–M–N4	92.58(7)	88.43(7)	89.59(8)
O2–M–O3	60.23(7)	59.70(6)	58.90(7)
O2–M–O5	95.15(7)	110.59(6)	99.76(7)
O2–M–N1	166.28(7)	88.54(6)	92.13(7)
O2–M–N4	92.78(7)	155.12(6)	166.35(7)
O3–M–O5	82.95(7)	169.60(5)	81.19(7)
O3–M–N1	106.34(7)	89.07(6)	150.03(7)
O3–M–N4	152.98(7)	95.67(6)	108.94(7)
O5–M–N1	85.30(7)	94.60(7)	97.96(7)
O5–M–N4	99.40(7)	93.71(6)	83.34(7)
N1–M–N4	100.69(7)	94.91(6)	100.65(7)

Table 4. Selected Bond Distances (Å) and Angles (°) for Chloride Complexes.

	[CoCl ₂ (PymNH ₂)]	[CoCl ₂ (PymNH ₂) ₂]	<i>trans</i> - [NiCl ₂ (PymNH ₂) ₄]	<i>trans</i> - [CoCl ₂ (PymNH ₂) ₄]]
M–Cl1	2.4668(6)	2.2371(7)	2.4456(3)	2.4451(4)
M–N1	2.228(3)	2.0369(18)	2.1890(12)	2.2324(14)
M–N4	–	–	2.1796(12)	2.2213(14)
Cl1–M–Cl1	94.19(3), 180, 85.81(3)	116.54(5)	179.14(2)	179.19(2)
N1–M–N1	180	110.73(11)	92.31(6)	91.95(7)
N1–M–Cl1	88.05(6), 91.95(6)	111.00(6), 103.85(5)	88.22(3), 91.19(3)	88.55(4), 90.89(4)
Cl1–M–N4	–	–	91.90(3), 88.69(3)	91.65(4), 88.91(4)
N1–M–N4			87.89(5), 176.91(4)	88.11(5), 177.46(5)
N4–M–N4	–	–	92.07(6)	91.95(7)

Table 5. Infrared Data

Complex	Infrared bands, cm ⁻¹ (intensity) ^a
PymNH ₂	3341(m), 3242(w), 3167(m), 1654(s), 1575(m), 1562(m), 1479(m), 1445(w), 1358(w), 1225(w), 1180(w), 804(m), 644(w)
[Ni(NO ₃) ₂ (PymNH ₂) ₂ (OH ₂)]	3412(m), 3309(m), 3207(m,sh), 2993(m,sh), 1635/1622(m), 1591(m), 1572(m), 1489(m), 1385(s), 1360(m), 1200(w), 795(w), 662(w)
[Co(NO ₃) ₂ (PymNH ₂) ₂ (OH ₂)]	3408(m), 3358(m), 3313(m), 3177(m,br), 2959(m,sh), 1651(m), 1620(m), 1591(m), 1487(m), 1385(m), 1360(m), 1196(w), 826(w), 795(w), 660(w)
[CoCl ₂ (PymNH ₂) ₂]	3456(s), 3412(s), 3368(s), 3310(s), 3233(m,sh), 2984(m,sh), 1643(m), 1620(m), 1576(s), 1501(m), 1489(m), 1360(m), 1325(w), 1204(w), 791(w), 662(w)
[NiCl ₂ (PymNH ₂) ₂]	3464(m), 3408(m), 3368(m), 3238(w,br,sh), 3102(w), 1642(m), 1570(s), 1501(m), 1361(m), 1325(w), 1206(w), 787(w), 664(w)
[CoCl ₂ (PymNH ₂) ₂]	3412(s), 3310(s), 3204(m,br), 2972(m,br,sh), 1715(w), 1618(s), 1574(s), 1489(s), 1360(m), 1231(w), 1200(w), 797(w), 662(w)
[NiCl ₂ (PymNH ₂) ₂]•½H ₂ O	3447(m), 3368(m), 3283(m), 3177(m,br), 1634(m), 1620(s), 1589(m), 1562(s), 1479(m), 1364/1354(m), 1310(w), 1227(w), 1198(w), 795(w), 783(w), 654(w)
<i>trans</i> -[NiCl ₂ (PymNH ₂) ₄]	3447(m), 3368(m), 3283(m), 3194(m,br,sh), 1634(m), 1620(m), 1589(m), 1562(m), 1479(m), 1362/1354(w), 1310(w), 1227(w), 1198(w), 795(w), 783(w), 654(w)
<i>trans</i> -[CoCl ₂ (PymNH ₂) ₄]	3449(m), 3372(m), 3289(m), 3163(m,br), 1634(m), 1620(s), 1589(m), 1559(s), 1479(s), 1362/1354(m), 1314(s), 1227(w),

1195(m), 871(w), 799(m), 790(m), 783(m), 654(m)

^as = strong, m = medium, w = weak, br = broad, sh = shoulder.

Captions for Figures.

Figure 1. Molecular structure of $[\text{Ni}(\text{NO}_3)_2(\text{PymNH}_2)_2(\text{OH}_2)]$, isomer **A**. Thermal ellipsoids shown at 50%.

Figure 2. Molecular structure of $[\text{Ni}(\text{NO}_3)_2(\text{PymNH}_2)_2(\text{OH}_2)]$, isomer **B**. Half acetone molecule omitted for clarity. Thermal ellipsoids shown at 50%.

Figure 3. Hydrogen bonding network and packing diagram for $[\text{Ni}(\text{NO}_3)_2(\text{PymNH}_2)_2(\text{OH}_2)]$, isomer **A**. Hydrogen atoms and intramolecular hydrogen bonds omitted for clarity.

Figure 4. Hydrogen bonding network and packing diagram for $[\text{Ni}(\text{NO}_3)_2(\text{PymNH}_2)_2(\text{OH}_2)]$, isomer **B**. Half acetone molecule, hydrogen atoms, and intramolecular hydrogen bonds omitted for clarity.

Figure 5. Molecular structure of $[\text{Co}(\text{NO}_3)_2(\text{PymNH}_2)_2(\text{OH}_2)]$. Thermal ellipsoids shown at 50%. Hydrogen atoms omitted for clarity.

Figure 6. Network structure $[\text{CoCl}_2(\text{PymNH}_2)]$. Thermal ellipsoids shown at 50%.

Figure 7. Packing diagram for $[\text{CoCl}_2(\text{PymNH}_2)]$. Hydrogen atoms omitted for clarity.

Figure 8. Molecular structure of $[\text{CoCl}_2(\text{PymNH}_2)_2]$. Thermal ellipsoids shown at 50%.

Figure 9. Hydrogen bonding network and packing diagram for $[\text{CoCl}_2(\text{PymNH}_2)_2]$. Hydrogen atoms and intramolecular hydrogen bonds omitted for clarity.

Figure 10. Molecular structure of *trans*- $[\text{NiCl}_2(\text{PymNH}_2)_4]$. Thermal ellipsoids shown at 50%.

Figure 11. Hydrogen bonding network and packing diagram for *trans*- $[\text{NiCl}_2(\text{PymNH}_2)_4]$. Hydrogen atoms and intramolecular hydrogen bonds omitted for clarity.

Figure 12. Molecular structure of *trans*- $[\text{CoCl}_2(\text{PymNH}_2)_4]$. Thermal ellipsoids shown at 50%.

