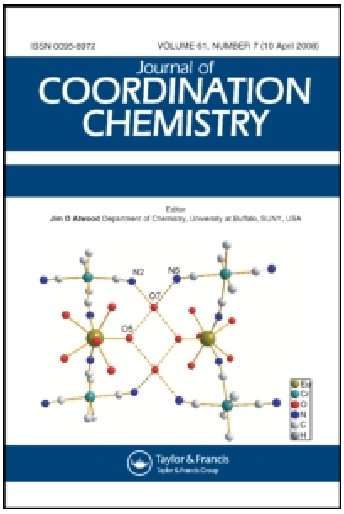

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TRANSITION METAL HALIDE SALTS AND COMPLEXES OF 2-AMINOPYRIMIDINE: COBALT(II) AND NICKEL(II) COMPOUNDS, CRYSTAL STRUCTURES OF BIS(2-AMINOPYRIMIDINIUM)MX_4 [M = Co, Ni; X = Cl, Br] AND 2-AMINOPYRIMIDINIUM(+ 2) $[NiBr_2(H_2O)_4]Br_2$

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The reaction of MX_2 (M = Co(II), Ni(II); X = Cl, Br) with 2-aminopyrimidine in aqueous acid yields compounds $[(2\text{-apmH})_2MX_4]$, $(2\text{-apmH})_2[MX_4]$, or $(2\text{-apmH}_2)\,[MX_2(H_2O)_4]X_2$ (2-apmH = 2-aminopyrimidinium; 2-apmH_2 = 2-aminopyrimidinium(2+)). All compounds have been characterized by single crystal X-ray diffraction. The compounds $[(2\text{-apmH})_2MX_4]$ with M = Co, X = Cl (**1**); M = Ni, X = Cl (**3**); and M = Ni, X = Br (**4**) are isomorphous and crystallize as nearly square planar MX_4 units with the 2-apmH cations coordinated in the axial sites through the unprotonated ring nitrogen. $(2\text{-ApmH})_2[CoBr_4]$ (**2**) crystallizes as the salt with a nearly tetrahedral $CuBr_4^{2-}$ anion. $(2\text{-ApmH}_2)\,[NiBr_2(H_2O)_4]Br_2$ (**5**) forms as a cocrystal of the neutral, six-coordinate nickel complex and $(2\text{-ampH}_2)Br_2$, stabilized by extensive hydrogen bonding. Crystal data (**1**): monoclinic, $P2_1/c$, $a = 7.540(4)$, $b = 12.954(4)$, $c = 7.277(3)$ Å, $\beta = 110.09(6)$, $V = 667.4(5)$ Å^3, $Z = 2$, $D_{calc} = 1.955\,Mg/m^3$, $\mu = 2.079\,mm^{-1}$, $R = 0.0501$ for $[|I| \geq 2\sigma(I)]$. For (**2**): triclinic, P-1, $a = 7.720(2)$, $b = 7.916(2)$, $c = 14.797(3)$ Å, $\alpha = 97.264(3)$, $\beta = 104.788(3)$, $\gamma = 105.171(3)°$, $V = 825.3(3)$ Å^3, $Z = 2$, $D_{calc} = 2.296\,Mg/m^3$, $\mu = 10.715\,mm^{-1}$, $R = 0.0308$ for $[|I| \geq 2\sigma(I)]$. For (**3**): monoclinic, $P2_1/c$, $a = 7.595(3)$, $b = 12.891(4)$, $c = 7.204(3)$ Å, $\beta = 111.07(3)°$, $V = 658.2$ Å^3, $Z = 2$, $D_{calc} = 1.982\,Mg/m^3$, $\mu = 2.279\,mm^{-1}$, $R = 0.0552$ for $[|I| \geq 2\sigma(I)]$. For (**4**): monoclinic, $P2_1/c$, $a = 7.840(2)$, $b = 13.358(4)$, $c = 7.518(2)$ Å, $\beta = 110.923(3)°$, $V = 938.6(3)$ Å^3, $Z = 2$, $D_{calc} = 2.577\,Mg/m^3$, $\mu = 12.18\,mm^{-1}$, $R = 0.0280$ for $[|I| \geq 2\sigma(I)]$. For (**5**): orthorhombic, Pnma, $a = 16.776(6)$, $b = 11.943(4)$, $c = 7.079(3)$ Å, $V = 1418.2(9)$ Å^3, $Z = 4$, $D_{calc} = 2.564\,Mg/m^3$, $\mu = 12.639\,mm^{-1}$, $R = 0.0381$ for $[|I| \geq 2\sigma(I)]$.

Keywords: Metal halides; 2-Aminopyrimidine; Cobalt; Nickel crystal structure

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INTRODUCTION

The packing of transition metal ions in their salts and coordination complexes is strongly affected by the size and shape of the ligands bound to the metal and the counter ions present in the lattice. A wide variety of packing motifs for the metal ions in molecular compounds has been realized as exemplified by copper halides salts which are known to form chains [1], ladders [2], and sheets [3]. We are specifically interested in the packing of molecules of the general formula A_2MX_4, where A is an organic cation, usually a protonated amine, M is a (2+) transition metal ion and X is Cl or Br. In the past, we have worked with 3- [4], and 5-substituted [5] 2-aminopyridines as the organic bases and found a variety of packing patterns. We have observed families of related complexes where the packing motifs were retained, generating isostructural compounds [6], while in others, apparently minor changes in the organic base resulted in major changes in the crystal packing [7]. In most of these compounds, hydrogen bonding between the protonated organic cation and the halides bonded to the metal ion plays a significant role in stabilizing the structure. Thus, we were interested in the effect of changing the base to 2-aminopyrimidine with its additional protonation/coordination site. We present here our initial studies with 2-aminopyrimidine and Co(II) and Ni(II) chloride and bromide.

EXPERIMENTAL

Metal salts and acids were purchased from Alfa-Aesar and VWR respectively. 2-Aminopyrimidine was purchased from Aldrich Chemical. All materials were used as received. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR. Combustion analyses were performed at the Department of Chemistry, University of Otago, Dunedin, NZ or University Instrumentation Center, University of New Hampshire, Durham, NH.

General Synthesis

Compounds **1–4** were prepared by reaction of 10 mmol of the appropriate metal halide salt dissolved in 5 mL of water with 20 mmol of 2-aminopyrimidine dissolved in 5 mL of water and 40 mmol of 1.0 M aqueous HX. The use of equimolar amounts of acid occasionally resulted in crystallization of the pyrimidine·HX salt alone. Compounds **5** and **6** were prepared by reaction of 10 mmol of 2-aminopyrimidine with 5 mmol of $NiBr_2$ or $CoBr_2$ in 15 mL of 15% aqueous HBr. The resulting solutions were allowed to evaporate slowly at room temperature over the course of two weeks to two months. The crystals were isolated by vacuum filtration and air dried to give the various salts in 25–76% yield (no effort was made to maximize yields). All compounds gave satisfactory combustion analyses. Yields and IR data are given below.

Bis(2-aminopyrimidinium)tetrachlorocobalt(II) (**1**) Purple, 42%. IR (KBr): ν 3360 m, 3082 m/br, 1674 s, 1616 s, 1541 m, 1344 s, 1211 s, 1074 w, 773 m cm^{-1}. *Bis(2-aminopyrimidinium) tetrabromocobaltate(II)* (**2**) Light blue, 54%. IR (KBr): ν 3375 m, 3346 m, 3095 m/br, 1672 s, 1624 s, 1539 w, 1340 m, 1205 w, 777 m cm^{-1}. A small amount of dark blue crystals of a second compound, (2-aminopyrimidinium)(2+)

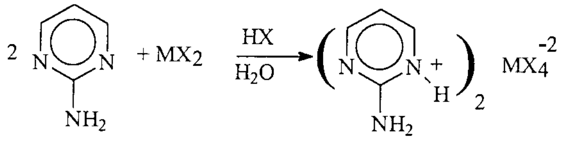
tetrabromocobaltate(II) (**6**) was isolated by separation from **2** under a stereomicroscope. *Bis(2-aminopyrimidinium)tetrachloronickel(II)* (**3**) Yellow, 32%. IR (KBr): ν 3346 m/br, 3072 w, 1672 s, 1618 s, 1539 m, 1344 s, 794 m cm^{-1}. *Bis(2-aminopyrimidinium)tetrabromonickel(II)* (**4**) Orange, 25%. IR (KBr): ν 3384 s/br, 3220 m, 3105 w, 1676 s, 1610 s, 1340 m, 1205 m, 767 m, 748 m cm^{-1}. *(2-Aminopyrimidinium)(2+)tetraaquadi bromonickel(II) dibromide* (**5**) Yellow–green, 76%. IR (KBr): ν 3374 s, 3230 m, 3076 m, 1667 s, 1619 s, 1278 m, 1205 m, 772 m cm^{-1}. *(2-Aminopyrimidinium)(2+) tetrabromocobaltate(II)monohydrate* (**6**) Dark blue–green, 47%. IR (KBr): ν 3384 m, 3346 m, 3124 m/br, 1667 s, 1619 s, 1278 m, 1205 m, 772 m cm^{-1}.

X-ray Structure Determination

All data collections were carried out on a Siemens P4 diffractometer employing MoKα radiation (λ = 0.71073) and a graphite monochromator. Data collection via ω-scans, cell refinement and data reduction for **1** and **3** were performed using SHELXTL (VMS) software [8]. Absorption corrections were made via ψ-scans. Data collection via φ and ω-scans, cell refinement and data reduction for **2**, **4** and **5** were performed by using a Bruker SMART system [9]. Absorption corrections were performed using SADABS [10]. The structures were solved using the heavy atom Patterson method (SHELXS-97) and full-matrix least-squares refinement was done via SHELXL-97 [11]. The aromatic hydrogen atoms were refined via a riding model with fixed isotropic U's while the coordinates of the NH hydrogens were allowed to refine with fixed isotropic U's. Neutral scattering factors and anomalous dispersion corrections for nonhydrogen atoms were taken from Ibers and Hamilton [12]. Crystallographic data may be found in Table I. Selected bond lengths and angles are given in Table II. Significant hydrogen bonds are listed in Table III. Full crystallographic details, atomic coordinates and isotropic thermal parameters, full tables of bond lengths and angles, observed and calculated structure factors and anisotropic thermal parameters are available [13].

RESULTS

Reaction of two equivalents of 2-aminopyrimidine (2-apm) with MX_2 in an excess of aqueous acid (HCl or HBr) gave complexes of the general formula $(2\text{-apmH})_2\ MX_4$ (2-apmH = 2-aminopyrimidinium).



1-M=Co, X=Cl; **2**-M=Co, X=Br; **3**-M=Ni, X=Cl; **4**-M=Ni, X=Br

Crystallization from solutions with equimolar amounts of acid (2-aminopyrimidine to HX) resulted in cocrystallization of the corresponding 2-aminopyrimidinium halide. Reaction of 2-aminopyrimidine with $NiBr_2$ and a 10-fold excess of acid gave compound **5**, containing the diprotonated complex $(2\text{-apmH}_2)_2\ [NiBr_2(H_2O)_4]Br_2$. Crystals suitable for X-ray diffraction were isolated directly from the solution.

TABLE I Crystal data and structure refinement for **1**–**5**

	1	**2**	**3**	**4**	**5**
Empirical formula:	$C_8H_{12}N_6Cl_4Co$	$C_8H_{12}N_6Br_4Co$	$C_8H_{12}N_6Cl_4Ni$	$C_8H_{12}N_6Br_4Ni$	$C_4H_{15}N_3O_4Br_4Ni$
Formula weight	392.97	570.81	392.75	570.53	547.54
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Crystal habit	Purple plate	Blue chip	Pale yellow rod	Orange plate	Pale yellow plate
Space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1/c$	Pnma
Unit cell dimensions:					
a (Å)	7.540(4)	7.720(2)	7.595(3)	7.840(2)	16.776(6)
b (Å)	12.954(4)	7.916(2)	12.891(4)	13.358(4)	11.943(4)
c (Å)	7.277(3)	14.797(3)	7.204(3)	7.518(2)	7.079(3)
α (°)	90	97.264(3)	90	90	90
β (°)	110.09(6)	104.788(3)	111.07(3)	110.923(3)	90
γ (°)	90	105.171(3)	90	90	90
Volume	667.4(5)	825.3(3)	658.2	735.4	1418.2(9)
Z	2	2	2	2	4
Density (calc) (g/cm^3)	1.955	2.296	1.982	2.577	2.564
Size	0.8 × 0.12 × 0.04	0.7 × 0.41 × 0.36	0.7 × 0.04 × 0.02	0.70 × 0.15 × 0.09	0.56 × 0.30 × 0.02
F(000)	394	538	396	540	1040
μ (mm^{-1})	2.079	10.715	2.279	12.180	12.639
Data collection:					
Temperature (K)	158(2)	163(2)	158(2)	163(2)	163(2)
Max., min. transmission	0.3458, 0.2935	1.0000, 0.7431	0.9558–0.2984	1.0000–0.8159	1.0000–0.5045
Reflections collected	1715	10 808	1473	9146	16 789
Independent reflections	863	3519	1151	1585	1514
θ range (°)	2.88–22.49	2.73–27.55	2.87–24.98	2.78–27.54	2.43–26.42
Range h, k, l	$-8 \le h \le 7$	$-9 \le h \le 7$	$-8 \le h \le 8$	$-10 \le h \le 9$	$-20 \le h \le 20$
	$-13 \le k \le 0$	$-10 \le k \le 10$	$-15 \le k \le 1$	$-17 \le k \le 16$	$-14 \le k \le 7$
	$-7 \le l \le 7$	$-18 \le l \le 18$	$-8 \le l \le 1$	$-4 \le l \le 9$	$-8 \le l \le 8$
Refinement:					
Data/restraints/parameters	863/0/97	3519/0/191	1151/0/106	1585/0/98	1514/0/101
Goodness-of-fit on F^2	1.027	1.044	0.875	1.126	1.013
Final R indices [$I > 2\sigma(I)$]					
R_1	0.0420	0.0308	0.0552	0.0280	0.0381
wR_2	0.1088	0.0813	0.1165	0.0706	0.0921
R indices (all data)					
R_1	0.0501	0.0355	0.0861	0.0292	0.0422
wR_2	0.1114	0.0831	0.1251	0.0712	0.0931
Largest difference peak (e/Å^3)	0.570	0.857	1.037 (near Ni)	1.877 (near Br2)	2.100 (both
Largest difference hole (e/Å^3)	−0.448	−1.139 (near Br3)	−0.685	−0.942	−1.247 near Br2)

TABLE II Selected bond lengths (Å) and angles (°) for **1–5**

	1		**2**		**3**		**4**		**5**	
M–X1	Co–Cl1	2.371(2)	Co–Br1	2.4467(7)	Ni–Cl1	2.360(2)	Ni–Br1	2.5077(6)	Ni–Br1	2.5483(9)
M–X2	Co–Cl2	2.519(2)	Co–Br2	2.4058(7)	Ni–Cl2	2.465(2)	Ni–Br2	2.6312(7)		
M–X3			Co–Br3	2.3922(8)						
M–X4			Co–Br4	2.4115(7)						
M–N or O	Co–N1	2.300(4)			Ni–N1	2.242(5)	Ni–N1	2.290(2)	Ni–O1	2.065(4)
									Ni–O2	2.082(4)
									Ni–O3	2.077(3)
X1–M–X2	Cl1–Co–Cl2	89.16(7)	Br2–Co–Br1	106.44(2)	Cl1–Ni–Cl2	88.80(7)	Br1–Ni–Br2	89.28(2)	Br1–Ni–Br1#2	91.69(4)
X1–M–X3			Br3–Co–Br1	109.69(2)						
X1–M–X4			Br4–Co–Br1	109.15(3)						
X1–M–N1	N1–Co–Cl1	93.2(1)			N1–Ni–Cl1	93.33(15)	N1–Ni–Br1	86.83(6)	O1–Ni–Br1	92.89(9)
									O2–Ni–Br1	92.73(8)
									O3–Ni–Br1	90.9(1)
X2–M–X3			Br3–Co–Br2	112.42(2)						
X2–M–X4			Br2–Co–Br4	109.67(2)						
X2–M–N or O	N1–Co–Cl2	85.6(1)			N1–Ni–Cl2	85.60(15)	N1–Ni–Br2	94.54(6)	O3–Ni–Br1#2	177.4(1)
X3–M–X4			Br3–Co–Br4	109.39(2)						
O1–M–O2									O1–Ni–O2	171.9(2)
O1–M–O3									O1–Ni–O3	86.8(1)
O2–M–O3									O3–Ni–O2	87.3(1)
O3–M–O3									O3–Ni–O3#2	86.5(2)

Symmetry transforms #1: −x, −y, −z; #2: x, −y − 0.5, z.

TABLE III Hydrogen bonds for **1**–**5** (Å and °)

For **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N2–H2A···Cl2#1	0.91(7)	2.26(7)	3.153(6)	167(5)
N2–H2B···Cl1#2	1.01(7)	2.13(7)	3.115(5)	163(5)
N3–H3···Cl2#2	0.83(7)	2.50(7)	3.241(5)	149(5)

Symmetry transformations used to generate equivalent atoms:
#1: −x, −y, −z; #2: x, −y + 1/2, z − 1/2

For **2**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N11–H11···Br1#1	0.86(5)	2.43(5)	3.271(3)	165(4)
N12–H12B···N13#2	0.81(5)	2.16(6)	2.948(5)	165(5)
N21–H21···Br4	0.87(5)	2.57(5)	3.397(3)	159(4)
N22–H22A···N23#3	0.83(5)	2.23(5)	3.059(5)	175(5)

Symmetry transformations used to generate equivalent atoms:
#1: −x + 2, −y + 2, −z + 2; #2: −x + 3, −y + 2, −z + 2; #3: −x, −y + 1, −z + 1

For **3**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N2–H2A···Cl2#1	0.77(8)	2.36(9)	3.123(7)	171(7)
N2–H2B···Cl1#2	0.94(8)	2.17(8)	3.104(7)	170(7)
N3–H3···Cl2#2	0.99(8)	2.39(8)	3.229(6)	142(6)

Symmetry transformations used to generate equivalent atoms:
#1: −x, −y + 1, −z; #2: x, −y + 3/2, z–1/2

For **4**

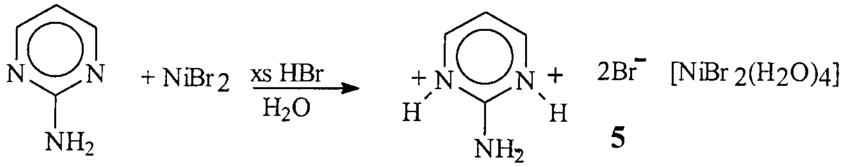
D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N2–H2A···Br1#1	0.97(4)	2.38(4)	3.271(3)	153(3)
N2–H2B···Br2	0.66(4)	2.67(4)	3.274(3)	152(5)
N3–H3···Br2#1	0.86(4)	2.76(4)	3.408(3)	134(3)

Symmetry transformations used to generate equivalent atoms:
#1: −x + 1, y − 1/2, −z − 1/2

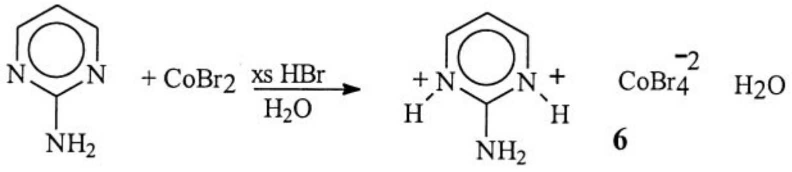
For **5**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O1–H1A···Br2#1	0.77(5)	2.58(5)	3.307(3)	157(5)
O2–H2A···Br2	0.81(5)	2.53(5)	3.333(3)	172(5)
O3–H3A···Br1#2	0.94(6)	2.44(6)	3.364(4)	166(4)
N1–H1···Br2	0.87(7)	2.38(7)	3.181(4)	152(6)
N2–H2···Br1#3	0.81(6)	2.70(5)	3.379(5)	142(5)
O3–H3B···Br2#4	0.97(7)	2.49(7)	3.423(4)	161(5)

Symmetry transformations used to generate equivalent atoms:
#1: x–1/2, y, −z + 1/2; #2: −x + 1/2, −y, z + 1/2; #3: −x + 1, −y, −z; #4: −x + 1, −y, −z + 1



In the preparation of **2**, a small amount of much darker, blue–green crystals were observed in the product and separated manually. A check of the crystallographic cell constants revealed the product to be distinct from **2** and data collection and refinement revealed the second compound to be (2-apmH$_2$)CoBr$_4$···H$_2$O (**6**). Compound **6** was subsequently prepared by direct synthesis in excess HBr.



The complexes were analyzed by single crystal X-ray diffraction. Crystallographic data for **1–5** are given in Table I and selected bond lengths and angles in Table II. Repeated efforts with **6** failed to yield high quality crystals and so full structure refinement and analysis was not possible, but the general structure and coordination geometry are clear. Data were collected and refined with only the Co and Br atoms refined anisotropically [14].

Compound **1** crystallizes in the monoclinic space group $P2_1/c$. The molecular unit is shown in Fig. 1. The Co-atom sits on an inversion center and is coordinated to the four chloride ions and the two 2-aminopyrimidinium ions through their unprotonated ring nitrogens.

Bond angles about the cobalt are nearly octahedral with the largest deviation being $\angle_{N1-Co-Cl2} = 85.6(1)^\circ$. The complex packs in puckered sheets parallel to the *bc*-plane (see Fig. 2). The 2-aminopyrimidinium ligands are stacked parallel to the *c*-axis with adjacent, inversion-related stacks having opposite orientations.

The sheets are held together by a network of hydrogen bonds (see Table III) between the pyrimidinium and amino hydrogens and the chlorine atoms (see Fig. 3).

Each Cl2 atom is involved in hydrogen bonds to two pyrimidinium hydrogen atoms, the stronger of which shows $d_{N3\text{–}H3\cdots Cl2} = 3.24$ Å, $\angle = 149^\circ$, while Cl1 atoms are hydrogen bonded to an amino hydrogen ($d_{N2\text{–}H2B\cdots Cl1} = 3.115$ Å, $\angle = 163^\circ$. The other amino hydrogen from each pyrimidinium ligand forms an intramolecular hydrogen bond to Cl2 (not shown in Fig. 3 for clarity). Complexes **3** and **4** are isostructural to **1**.

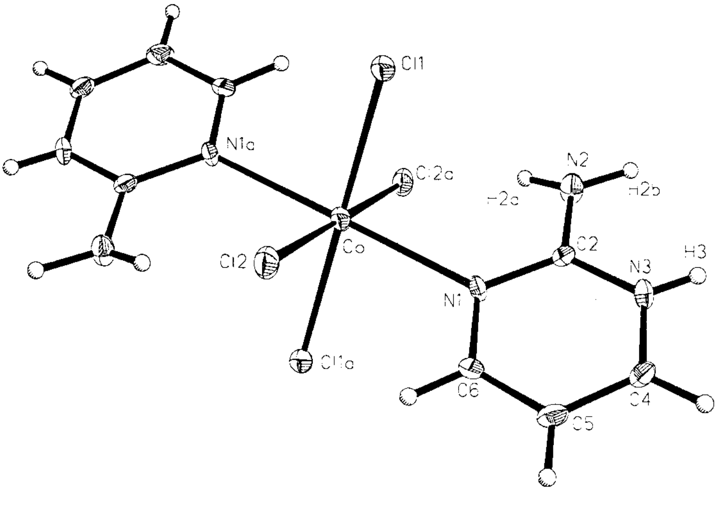


FIGURE 1 ORTEP drawing of the molecular unit of **1**. Only the asymmetric unit and the coordination sphere about the cobalt atom are labeled.

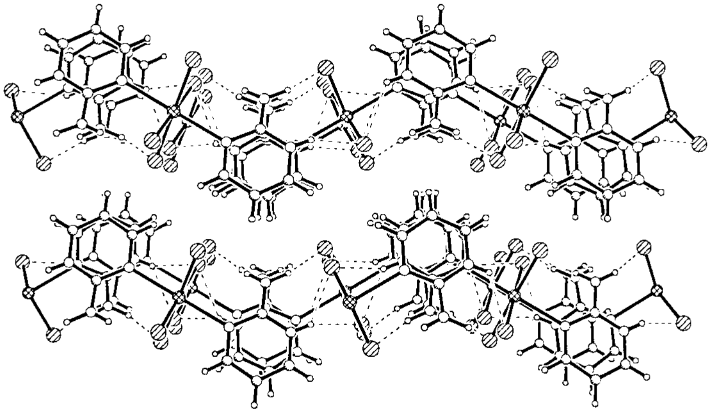


FIGURE 2 Diagram showing packing of layers in **1** viewed parallel to the *c*-axis. Dotted lines represent H-bonds.

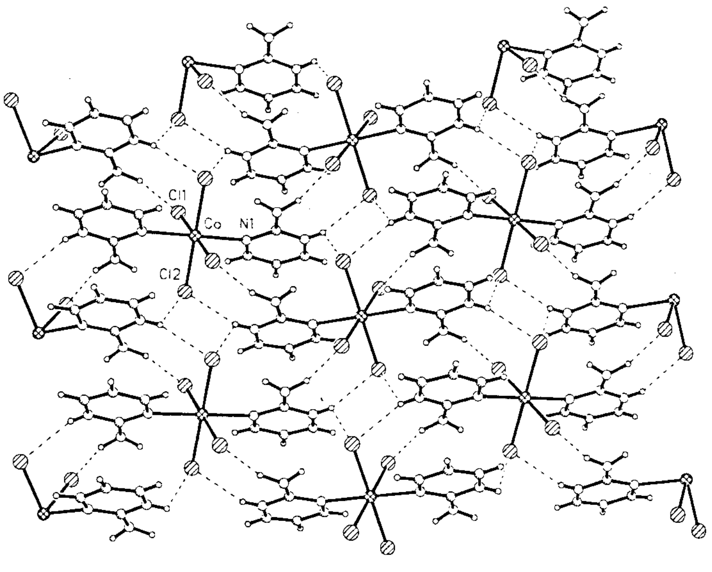


FIGURE 3 Diagram of the packing of **1** within a single sheet. Dotted lines represent H-bonds.

Although compound **2** has the same formula as **1**, **3** and **4**, its structure is distinctly different as the 2-aminopyrimidinium ions are no longer coordinated to the cobalt(II) center (see Fig. 4).

Compound **2** crystallizes in the triclinic space group P-1 with nearly tetrahedral coordination about the Co(II), the largest deviation being $\angle_{\mathrm{Br1-Co-Br2}} = 106.44(2)^\circ$. The two pyrimidinium rings are crystallographically independent and although bond lengths and angles within the rings are similar, they are not all identical within experimental error.

In the crystal lattice, each of the individual pyrimidinium rings form a dimer with its inversion-related counterpart via one of the amino hydrogens and the unprotonated

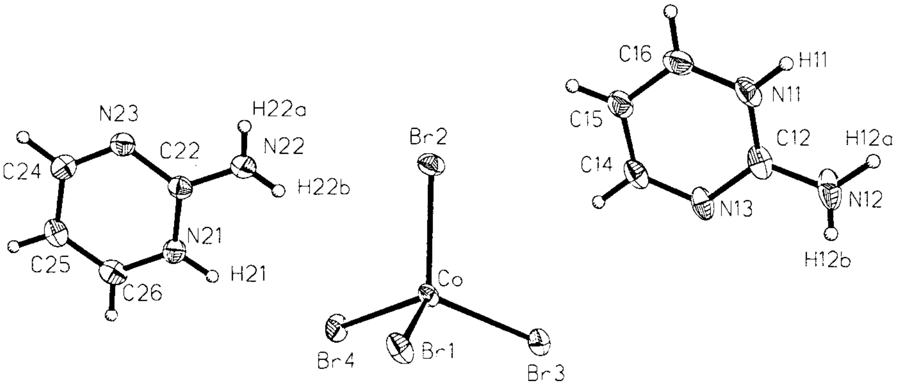


FIGURE 4 ORTEP diagram of **2**. Only those hydrogens whose positions were refined are labeled.

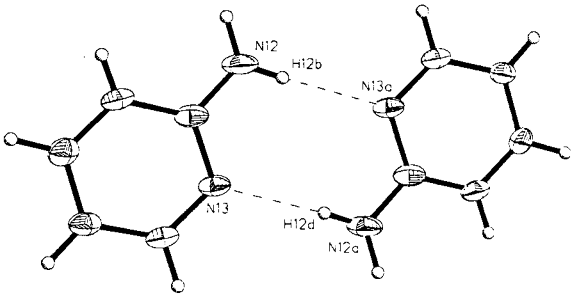


FIGURE 5 ORTEP diagram showing the dimerization of one of the 2-aminopyrimidinium rings via hydrogen bonds (dashed lines).

pyrimidine nitrogen (see Fig. 5). As is true of the bonds within the rings, the hydrogen bonds between the two distinct pyrimidine rings are similar, but not identical.

These dimers pack into layers with the CoBr_4^{2-} ions such that each *pseudo*-tetrahedron has a tripod of three bromine atoms (Br2, Br3, Br4) in the layer and the fourth (Br1) oriented perpendicular to the average plane of the layer (Fig. 6).

Hydrogen bonds between the organic cations and Br2, Br3 and Br4 stabilize the layers. The layers are then linked together through the Br1 atom's incorporation into adjacent layers and by hydrogen bonding to the Br1 atoms from CoBr_4^{2-} ions which protrude in from adjacent layers. The distinction between the two independent pyrimidine rings is clear in this hydrogen bonding pattern as N21–H21 forms a H-bond to Br4, one of the tripodal bromine atoms while N11–H1 provides the strongest H-bond donor to the protruding Br1 atoms.

Compound **5** is effectively a cocrystal of diprotonated 2-aminopyrimidinium(2+) dibromide and $\text{Ni(H}_2\text{O)}_4\text{Br}_2$. The material crystallizes in the orthorhombic space group Pnma with both the $\text{Ni(H}_2\text{O)}_4\text{Br}_2$ unit and the 2-aminopyrimidinium(2+) ring sitting athwart mirror planes (Fig. 7). Three of the four water molecules coordinated to the nickel atom are independent with two of them sitting on the same mirror as the Ni.

The organic cation, nickel complex and bromide ions are linked into a 3-dimensional lattice by an extensive hydrogen bonding network (see Fig. 8). Each Br2 atom forms

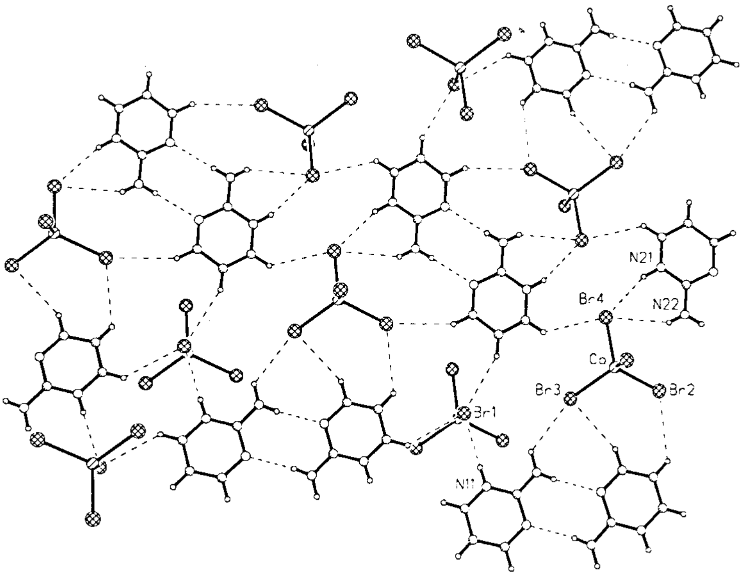


FIGURE 6 Packing diagram of a single layer within the crystal. Hydrogen bonds and close contacts between C–H hydrogens and Br atoms are represented by dashed lines. Representative atoms are labeled to show the positions of the Br atoms within the layer and the N–H···Br bonds.

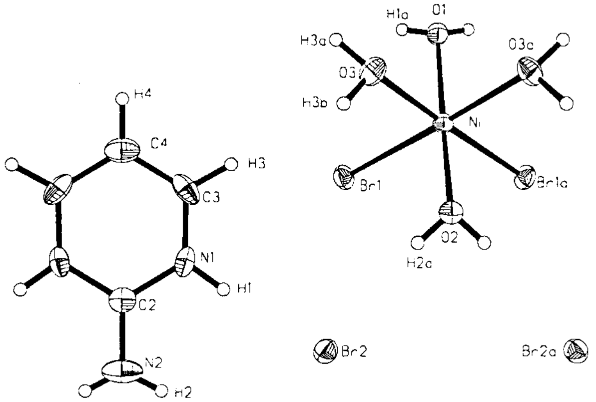


FIGURE 7 ORTEP diagram of the molecular unit of **5**. The asymmetric unit, Ni coordination sphere and ionic bromides are labeled.

hydrogen bonds to three crystallographically distinct water molecules, one each of O1, O2 and O3 from three different $Ni(H_2O)_4Br_2$ units, and completes a highly distorted tetrahedral coordination geometry with a fourth hydrogen bond to a pyrimidinium ion. The Br1 atoms accept two hydrogen bonds, one from an O3 water molecule in an adjacent $Ni(H_2O)_4Br_2$ unit and one from an amino hydrogen.

Full anisotropic refinement of **6** was not possible due to poor crystal quality, but the general structure and packing geometry are clear. The compound crystallizes in the monoclinic space group $P2_1/c$ with two independent formula units in the asymmetric unit (see Fig. 9).

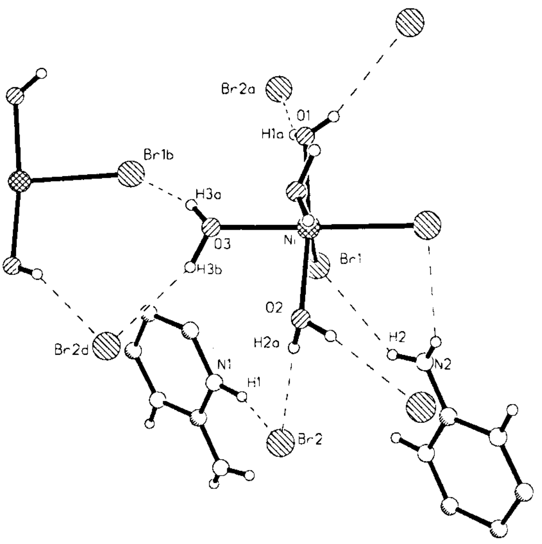


FIGURE 8 Representative hydrogen bonds in the lattice structure of **5**. Labels are provided to show one of each symmetry unique linkage. See Table III for individual bond lengths and angles.

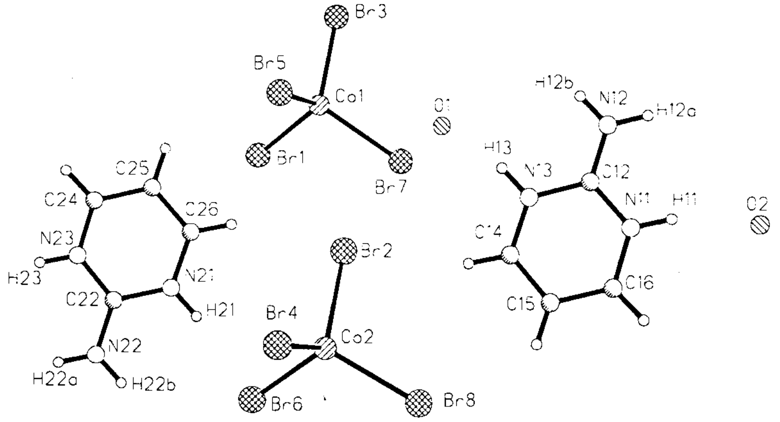


FIGURE 9 Figure showing the asymmetric unit of **6** with spheres of arbitrary size. All hydrogens are in calculated positions and only those potentially involved in hydrogen bonds are labeled.

The $CoBr_4^{2-}$ ions are nearly tetrahedral with the largest deviation being 115° (Br4–Co2–Br8). Bond lengths and angles between the two independent $CoBr_4^{2-}$ ions are similar, as are the two organic dications. The hydrogen atoms on the water molecules could not be located in the difference map. Each oxygen atom had more than two possible locations for hydrogens based upon potential hydrogen-bonds with bromine atoms and so the water hydrogen atoms were not included in the final refinement.

The principle packing motif is one of loose layers which lie parallel to the *b*-axis and the B-face diagonal (Fig. 10). As was the case with complex **2**, the $CoBr_4^{2-}$ ions are oriented such that three of the bromines from each tetrahedron form a tripod within

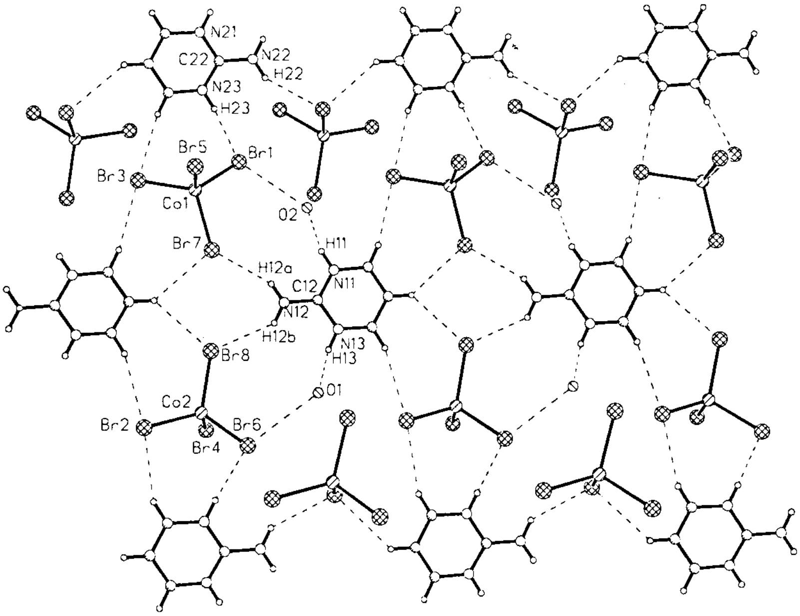


FIGURE 10 Packing of **6**. Dashed lines show hydrogen bonds from N–H hydrogens and close contacts between C–H hydrogens and bromine atoms. Only representative atoms from one asymmetric unit are labeled.

the layer. The layer structure clearly shows the different roles of the two molecules in the asymmetric unit.

The N11 pyrimidinium rings show hydrogen bonding to the water oxygen atoms through H11 and H13 while the pyrimidinium nitrogens of the N21 rings are hydrogen bonded to bromine atoms. The layer comprises rows of N21 rings (A), $CoBr_4^{2-}$ ions/water molecules (B) and N11 rings (C) in an ···ABCBABCB··· pattern. Again, as in complex **2**, the fourth bromine from each tetrahedron is inserted into the adjoining layer and stabilized there by hydrogen bonds, thus linking the layers.

DISCUSSION

Although the literature contains a number of structures of complexes of 2-aminopyrimidine, the vast majority are copper compounds with only a handful of cobalt and nickel complexes for comparison to the present compounds. The structural type exhibited by the isomorphous compounds **1**, **3** and **4** has not been reported in the literature previously, although the corresponding copper(II) chloride [15] and copper(II) bromide [16] compounds differ only due to the presence of a strong Jahn–Teller distortion which makes the 2-aminopyrimidinium ions semicoordinate. The distances between the Cu atom and the ring nitrogen are 2.675 and 2.787 Å respectively. The reduction in distance for the chloride compound results from the decrease in steric crowding at the metal center due to the smaller radius of the chlorine atoms, even though the chlorine–Cu bonds are shorter (2.295 and 2.353 Å) than the bromine–Cu bonds (2.427 and 2.498 Å). The M–N bonds in the current complexes (**1**, 2.300(4) Å; **3**, 2.242(5) Å; **4** 2.290(2) Å) are significantly shorter than observed in the copper(II) complexes, with those for the Ni(II) complexes shorter than for the Co(II) complex as expected for the smaller radius of the Ni(II) ion. These bond lengths are close to those observed for neutral 2-aminopyrimidine Co(II) and Ni(II) complexes of dicyanamide (Co–N, 2.159 Å; Ni–N, 2.127 Å) [17] where the same relative M–N bond lengths are observed. This small reduction in M–N bond length from Co(II) to Ni(II) is more pronounced in their sulfate complexes where the Co–N bond is 2.200 Å compared to Ni–N bond lengths of 2.130 and 2.116 Å in two different compounds [18]. All of these complexes show roughly tetragonal symmetry with variations in bond angles of only a few degrees from 90.

Complex **2** shows a distinctly different structure, although it has the same stoichiometry as **1**, **3** and **4**. The 2-aminopyrimidinium ions have dissociated from the Co atom, generating a salt. The pyrimidinium ions form homodimers in the lattice via hydrogen bonding between amino hydrogens and the unprotonated ring nitrogens. This type of hydrogen-bonded dimer is a common motif and has been observed in the structure of the free base [19] as well as in the cyanamide compounds [17] and in the free 2-aminopyrimidine solvate molecules of the sulfate complexes [18]. The dimer structure is not general in all instances of 2-aminopyrimidine or 2-aminopyrimidinium as the formation of hydrogen bonds to water [20] or bridging by the pyrimidine [21] may prevent dimer formation.

Cobalt(II) is well known for its propensity to form tetrahedral complexes due to the minimal change in ligand field stabilization energy upon coordination of two additional ligands in d^7 complexes [22] and Silber and Murguia have demonstrated the equilibrium between the tetrahedral and octahedral forms in solution [23]. Thus, the question may be why **1** is six-coordinate rather than why **2** is four-coordinate. However, it is likely that a combination of the steric bulk of the bromines, compared with **1**, and a weak Jahn–Teller distortion, compared with **4** combine to destabilize the Co–N bond sufficiently to prevent its formation. The resulting tetrahedral $CoBr_4^{2-}$ ion has a ^4A ground state and is thus not expected to show the Jahn–Teller effect, accounting for its nearly tetrahedral geometry. The intramolecular hydrogen bond (see Table III) between one of the amino hydrogens and one of the halide ions in **1** (N2–H2A···Cl2a, Fig. 1), **3** (N2–H2A···Cl2′) and **4** (N2–H2B···Br2′) which is lost in **2** is replaced by the hydrogen bonds forming the 2-aminopyrimidinium dimers (the difference in the M–X bond lengths observed in **1**, **3** and **4** likely results from the intramolecular hydrogen bond). Conversely, the greater polarization of the Co–Cl bonds in **1**, reduces the electron density at the cobalt and favors the six-coordinate species.

Nickel complex **5** and cobalt complex **6** both contain the 1,3-diprotonated 2-aminopyrimidinium dication, although the metal ions in these two compounds have very different coordination spheres. We have seen formation of the dication in concentrated aqueous acid before in the formation of the copper(II) bromide complex [16a]. Protonation of both pyrimidine nitrogens prevents formation of the aminopyrimidine dimer structure as well as coordination of those atoms to a metal center. In addition, the amino substituent is not normally a viable ligand due to its strong electron donation to the pyrimidine ring. This electron donation becomes even larger upon protonation of the ring as can be seen in the change in the C–N bond length from 1.355 Å in the free base [19] to 1.298–1.316 Å in **1–6**. As was seen with **2** and **4**, the Co(II) of **6** adopts a tetrahedral geometry as the $CoBr_4^{2-}$ anion while the Ni(II) of **5** prefers a six-coordinate geometry, although in this case with only two coordinated bromines and the remainder of the sphere filled by water molecules. This results in two free bromide ions in the lattice of **5**.

CONCLUSIONS

The use of 2-aminopyrimidine in place of substituted 2-aminopyridines causes significant changes in packing of complexes of the general formula A_2MX_4 as a result of the change in hydrogen bonding characteristics and the availability of an additional coordination site on the pyrimidine ring. While with the pyridine complexes, the organic cation was always dissociated from the metal center, the monoprotonated pyrimidine ring shows both coordinated and free structural contributions. In its uncoordinated form, there is a tendency to form hydrogen bonded dimers between aminopyrimidinium ions leading to a layer structure while the coordinated ring tends to link the metal complexes together via hydrogen bonds to coordinated halide ions. The ring also provides versatility in its ability to function as a dibasic unit and generate related complexes of the formula AMX_4 in varying hydration states. We are currently preparing complexes of additional first-row transition metals to determine if these trends hold for the related metals.

Acknowledgments

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[14] Crystal data for **6**. Monoclinic, $P2_1/c$, $C_4H_9N_3OCoBr_4$; $a = 14.494(5)$, $b = 9.966(4)$, $c = 17.711(6)$, $\beta = 107.285(5)$, $V = 2442.7(15$, $Z = 8$. 5000 ind. rflns (3104 obs.) Final R(obs) = 0.0769 (0.1327 all data), R_w(obs) = 19.56 (22.10 all data), GooF = 1.085. The data has been deposited with the CCDC; Ref. No. 172986.

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