Kariuki, B. M. & Jones, W. (1990). *Mol. Cryst. Liq. Cryst.* **186**, 45–52.

Kariuki, B. M. & Jones, W. (1992). *Mol. Cryst. Liq. Cryst.* **211**, 233–255.

Küppers, H. (1990). *Z. Kristallogr.* **192**, 97.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Structures of 2,6-Bis(aminomethyl)pyridine (bamp) Complexes of Fe^{II}, Ni^{II}, Zn^{II}, Mn^{II}, Co^{III} and Cu^{II}

Pierre Bonhôte, Michel Ferigo, Helen Stoeckli-Evans* and Werner Marty†

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

Abstract

The structures of bis[2,6-bis(aminomethyl)pyridine]iron dichloride hydrate [(I), Febamp], bis[2,6-bis(aminomethyl)pyridine]nickel dichloride hydrate [(II), Nibamp], bis-[2,6-bis(aminomethyl)pyridine]zinc dichloride hydrate [(III), Znbamp], bis[2,6-bis(aminomethyl)pyridine]manganese dichloride hydrate [(IV), Mnbamp], bis[2,6-bis(aminomethyl)pyridine]cobalt trichloride hemihydrate [(V), Cobamp] and chloro[2,6-bis(aminomethyl)pyridine]copper perchlorate [(VI), Cubamp] are reported. The bamp ligand complexes in a tridentate manner and except in the case of Cu^{II}, which is mono-tridentate coordinated, the complexes are all bis-tridentate. The Fe^{II}, Ni^{II} and Zn^{II} complexes are isomorphous. In general, the M—N(pyridine) distances are shorter than normal, while the M—N(amino) distances are slightly longer than normal.

Comment

In our search for ligands that will coordinate in a bis-tridentate fashion to 3d metals and Zn, we investigated the structural features of the title compounds. The 2,6-bis(aminomethyl)pyridine (bamp) ligand was originally

---

† Deceased.

synthesized by Lions & Martin (1957) starting from 2,6-dimethylpyridine. They also synthesized the Fe^{II} and Ni^{II} bis-complexes [M(bamp)$_2$]$^{2+}$. Schwarzenbach, Boesch & Egli (1971) synthesized the same ligand starting from 2,6-pyridinedicarbonitrile and prepared compounds of the form [Co(bamp)X_3]$^{3+}$, where X = H$_2$O, Cl, NO$_2$. Tinner & Marty (1977) used bamp to selectively produce meridional coordination in Co^{III} complexes when other ligands were present, however, [Co(bamp)$_2$]$^{3+}$ was a major reaction product. Here, we describe the systematic investigation of the crystal structures of complexes of bamp with Fe^{II}, Ni^{II}, Zn^{II}, Mn^{II}, Co^{III} and Cu^{II} [(I)–(VI), respectively]. With the exception of the bis-complexes of Mn^{II} (IV) and Zn^{II} (III), the syntheses of these complexes have been described previously (Lions & Martin, 1957; Schwarzenbach *et al.*, 1971; Tinner & Marty, 1977; Couturier & Petitfaux, 1975), but their crystal structures have not been reported. bamp behaves as a tridentate ligand in all six complexes and except in the case of Cu^{II} (VI), which is mono-tridentate coordinated, the complexes are all bis-tridentate. The Fe^{II}, Ni^{II} and Zn^{II} complexes [(I), (II) and (III)] are isomorphous, with two molecules per asymmetric unit. The unit cell contains eight molecules with approximate C_2 symmetry and four with crystallographic C_2 symmetry (Fig. 1). The geometry of the metal centres is distorted octahedral in all three complexes. The Mn^{II} complex (IV) crystallizes in the same space group, is also a bis-tridentate complex, but is not isomorphous with the previous three complexes. The cation has crystallographic C_2 symmetry (Fig. 2) and the geometry of the metal centre is distorted octahedral. In the case of the Co^{III} complex (V), the geometry of the metal centre is also distorted octahedral and the complex has only approximate C_2 symmetry (Fig. 3). In the Cu^{II} complex (VI), the coordination is best described as square pyramidal (Fig. 4). The Cu atom is displaced by 0.118 (2) Å from the best plane through atoms N1, N2, N3 and Cl1 [planar to within 0.014 (2) Å]. The apical position is occupied by atom Cl1^i of a molecule related by the twofold screw axis in the c direction. The Cu···Cl1^i distance is 2.936 (1) Å, while Cu···Cl1^{ii} (atom Cl1^{ii} is displaced by one unit cell in the c direction) is 3.695 (1) Å. The Cu···Cu^i distance is 4.079 (1) Å. This situation is illustrated in Fig. 5.

A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed a number of structures with the ligand 2-aminomethylpyridine. In Table 4 we compare the geometry of the various metal centres in the two series of compounds. While the N—M—N bond angles are similar, it can be seen that in general the M—N(py) distances in the title compounds are shorter than those in the 2-aminomethylpyridine complexes. Likewise, the M—N(amine) distances are generally longer. This could be an indication of a higher degree of delocalization in the M—N(py) bond for the bamp complexes. The conformations of the chelate rings in the bamp complexes
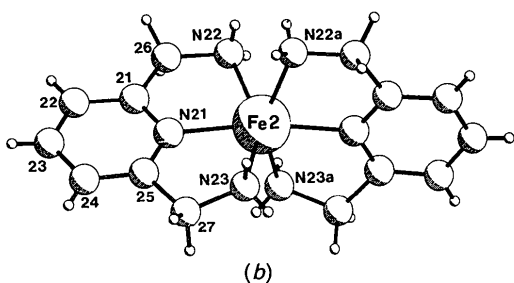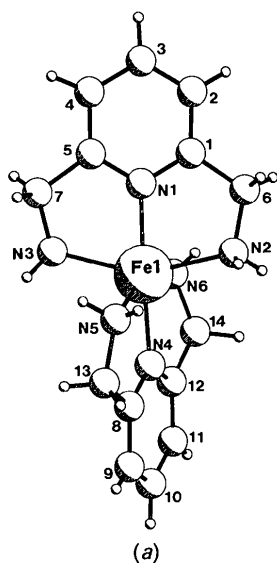
(a)

(b)

Fig. 1. Perspective views of (a) the first [Fe(bamp)]$^{2+}$ cation which has only approximate C_2 symmetry, and (b), the second [Fe(bamp)]$^{2+}$ cation, viewed perpendicular to the twofold axis, which possesses crystallographic C_2 symmetry.

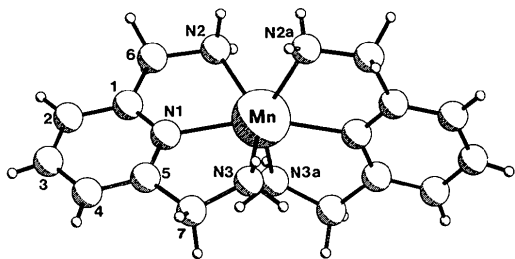

Fig. 2. Perspective view of the [Mn(bamp)]$^{2+}$ cation, which possess crystallographic C_2 symmetry, viewed perpendicular to the crystallographic twofold axis.

Fig. 3. Perspective view of the [Co(bamp)]$^{3+}$ cation.
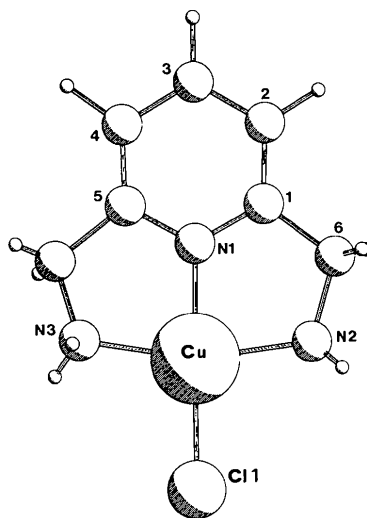
Fig. 4. Perspective view of the [CuCl(bamp)]$^+$ cation.
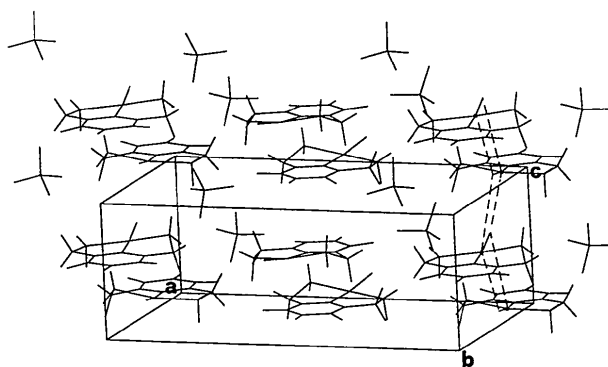
Fig. 5. Packing diagram of the [Cu(bamp)Cl](ClO$_4$) complex.

indicate that one of each pair is generally more puckered than the other. However, the chelate ring of the 2-aminomethylpyridine complexes is even more puckered as indicated by the absolute magnitude of the largest chelate-ring torsion angles. This may be due to hydrogen bonding as in the case of the Cu complex DUJREF (some H$\cdots$O distances of about 2.1 Å). Considering non-bonded

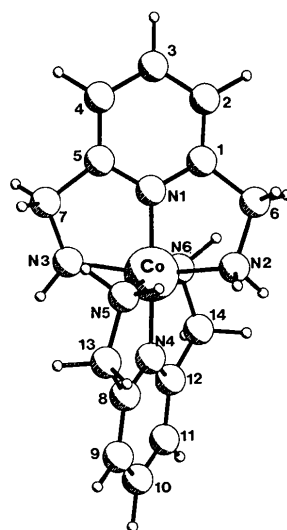distances less than 3.2 Å , hydrogen bonding does not appear to play a significant role in the case of the bamp complexes. In the isomorphous complexes (I)-(III), there are only weak hydrogen bonds involving the water molecules (2.21-2.31 Å) and the amino protons. The stronger hydrogen bonds are those between the Cl anions and the water molecules (2.04-2.44 Å). This pattern is repeated in the Mn complex (IV) with a slightly stronger hydrogen bond between the N2 proton and the water molecule (2.11 Å) and a strong hydrogen bond linking the water molecule and the Cl anion (2.27 Å). In the Co complex (V), the N—H· · ·Cl bonds are strong (2.01-2.15 Å), while atom OW1 is close to Cl2 (3.16 Å), Cl4 (3.04 Å) and a symmetry-related OW1 molecule (2.78 Å). In the Cu complex (VI), there are no short intermolecular contacts less than 3.2 Å between heteroatoms. Full details of both the torsion angles and the hydrogen bonding are given in the supplementary tables.

Experimental

Compound (I)

Crystal data

[Fe(C$_7$H$_{11}$N$_3$)$_2$]Cl$_2$.1.67H$_2$O
M_r = 431.14
Monoclinic
$I2/a$
a = 16.562 (1) Å
b = 9.704 (1) Å
c = 36.591 (2) Å
β = 92.21 (1)°
V = 5876.4 (8) Å^3
Z = 12
D_x = 1.462 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 27 reflections
θ = 9–15°
μ = 1.07 mm^{-1}
T = 294 (1) K
Rods
0.46 × 0.27 × 0.19 mm
Dark brown

Data collection

Stoe AED-2 four-circle diffractometer
ω/θ scans
Absorption correction: none
5741 measured reflections
4993 independent reflections
3548 observed reflections
[I_{net} > 2.5$\sigma(I_{net})$]

R_{int} = 0.015
θ_{max} = 25°
h = −19 → 19
k = 0 → 11
l = 0 → 43
3 standard reflections
frequency: 60 min
intensity variation: 1.0%

Refinement

Refinement on F
R = 0.029
wR = 0.049
S = 0.74
3548 reflections
487 parameters
All H-atom parameters refined
w = 1/[$\sigma^2(F)$ + 0.0034F^2]

$(\Delta/\sigma)_{max}$ = 0.091
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Compound (II)

Crystal data

[Ni(C$_7$H$_{11}$N$_3$)$_2$]Cl$_2$.1.67H$_2$O
M_r = 434.00
Monoclinic
$I2/a$
a = 16.477 (2) Å
b = 9.677 (1) Å
c = 36.534 (5) Å
β = 91.90 (1)°
V = 5822.1 (12) Å^3
Z = 12

D_x = 1.485 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 45 reflections
θ = 12.5– 19.0°
μ = 1.30 mm^{-1}
T = 294 (1) K
Plates
0.34 × 0.30 × 0.19 mm
Violet

Data collection

Stoe AED-2 four-circle diffractometer
ω/θ scans
Absorption correction: none
5106 measured reflections
5024 independent reflections
3761 observed reflections
[I_{net} > 3.5$\sigma(I_{net})$]

R_{int} = 0.017
θ_{max} = 25°
h = −19 → 19
k = 0 → 11
l = 0 → 43
4 standard reflections
frequency: 60 min
intensity variation: 3.0%

Refinement

Refinement on F
R = 0.036
wR = 0.051
S = 0.94
3761 reflections
487 parameters
All H-atom parameters refined
w = 1/[$\sigma^2(F)$ + 0.0025F^2]

$(\Delta/\sigma)_{max}$ = 0.068
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.81 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Compound (III)

Crystal data

[Zn(C$_7$H$_{11}$N$_3$)$_2$]Cl$_2$.1.67H$_2$O
M_r = 440.67
Monoclinic
$I2/a$
a = 16.540 (1) Å
b = 9.709 (1) Å
c = 36.607 (2) Å
β = 92.01 (1)°
V = 5878.2 (8) Å^3
Z = 12
D_x = 1.494 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 10.0–22.5°
μ = 1.58 mm^{-1}
T = 294 (1) K
Blocks
0.65 × 0.61 × 0.53 mm
Transparent pale yellow

Data collection

Stoe AED-2 four-circle diffractometer
ω/θ scans
Absorption correction: empirical (*EMPIR*; Stoe & Cie, 1985)
T_{min} = 0.358, T_{max} = 0.475
9991 measured reflections
5104 independent reflections

5066 observed reflections
[I_{net} > 3.5$\sigma(I_{net})$]
R_{int} = 0.021
θ_{max} = 25°
h = −19 → 19
k = −11 → 11
l = 0 → 43
4 standard reflections
frequency: 60 min
intensity variation: 1.0%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.091$
$S = 1.73$
5066 reflections
487 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0025F^2]$

$(\Delta/\sigma)_{max} = 0.014$
$\Delta\rho_{max} = 0.46$ e $\mathring{A}^{-3}$
$\Delta\rho_{min} = -0.37$ e $\mathring{A}^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Compound (IV)

Crystal data

$[Mn(C_7H_{11}N_3)_2]Cl_2.H_2O$
$M_r = 418.22$
Monoclinic
$I2/a$
$a = 13.010$ (1) $\mathring{A}$
$b = 9.162$ (1) $\mathring{A}$
$c = 15.669$ (2) $\mathring{A}$
$\beta = 93.25$ (1)$°$
$V = 1864.7$ (3) $\mathring{A}^3$
$Z = 4$
$D_x = 1.490$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ $\mathring{A}$
Cell parameters from 49 reflections
$\theta = 7.5-20.0°$
$\mu = 0.98$ mm^{-1}
$T = 294$ (1) K
Rods
$0.46 \times 0.42 \times 0.34$ mm
Pale yellow

Data collection

Stoe AED-2 four-circle diffractometer
ω/θ scans
Absorption correction: none
3231 measured reflections
1638 independent reflections
1489 observed reflections
$[I_{net} > 3.0\sigma(I_{net})]$

$R_{int} = 0.022$
$\theta_{max} = 25°$
$h = -15 \rightarrow 15$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 18$
4 standard reflections frequency: 60 min intensity variation: 2.0%

Refinement

Refinement on F
$R = 0.034$
$wR = 0.064$
$S = 0.60$
1489 reflections
158 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0020F^2]$

$(\Delta/\sigma)_{max} = 0.053$
$\Delta\rho_{max} = 0.26$ e $\mathring{A}^{-3}$
$\Delta\rho_{min} = -0.36$ e $\mathring{A}^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Compound (V)

Crystal data

$[Co(C_7H_{11}N_3)_2]Cl_3.0.5H_2O$
$M_r = 447.66$
Orthorhombic
$Pccn$
$a = 8.758$ (2) $\mathring{A}$
$b = 26.749$ (5) $\mathring{A}$
$c = 17.320$ (3) $\mathring{A}$
$V = 4057.5$ (14) $\mathring{A}^3$
$Z = 8$
$D_x = 1.466$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ $\mathring{A}$
Cell parameters from 20 reflections
$\theta = 9-14°$
$\mu = 1.26$ mm^{-1}
$T = 294$ (1) K
Blocks
$0.46 \times 0.23 \times 0.15$ mm
Orange

Data collection

Stoe AED-2 four-circle diffractometer
ω/θ scans
Absorption correction: none
4835 measured reflections
4667 independent reflections
2679 observed reflections
$[I_{net} > 4.0\sigma(I_{net})]$

$R_{int} = 0.05$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 34$
$l = 0 \rightarrow 22$
3 standard reflections frequency: 60 min intensity variation: 6.0%

Refinement

Refinement on F
$R = 0.072$
$wR = 0.117$
$S = 1.83$
2679 reflections
231 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0030F^2]$

$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 1.23$ e $\mathring{A}^{-3}$
$\Delta\rho_{min} = -0.80$ e $\mathring{A}^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

The H atoms were included in calculated positions [C—H = 1.08 $\mathring{A}$, $U_{iso} = U_{eq}(C, N + 0.01)$ $\mathring{A}^2$] and renormalized after every second refinement cycle. In this complex, the third Cl anion is divided between two sites. One is in a special position and the other in a general position, which must have an occupancy of 0.5 to satisfy the charges in the complex. The region of high residual density in the final difference map is found near this second site, Cl4.

Compound (VI)

Crystal data

$[CuCl(C_7H_{11}N_3)].ClO_4$
$M_r = 335.63$
Orthorhombic
$Pna2_1$
$a = 17.628$ (4) $\mathring{A}$
$b = 10.168$ (1) $\mathring{A}$
$c = 6.496$ (1) $\mathring{A}$
$V = 1164.4$ (3) $\mathring{A}^3$
$Z = 4$
$D_x = 1.915$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ $\mathring{A}$
Cell parameters from 46 reflections
$\theta = 10.5-19.5°$
$\mu = 2.35$ mm^{-1}
$T = 294$ (1) K
Plates
$0.38 \times 0.30 \times 0.19$ mm
Blue

Data collection

Stoe AED-2 four-circle diffractometer
ω/θ scans
Absorption correction: by integration from crystal shape (*SHELX76*; Sheldrick, 1976)
$T_{min} = 0.455$, $T_{max} = 0.689$
2779 measured reflections
2674 independent reflections

2493 observed reflections (1033 Friedel pairs)
$[I_{net} > 2.5\sigma(I_{net})]$
$R_{int} = 0.02$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 13$
$l = -8 \rightarrow 8$
4 standard reflections frequency: 60 min intensity variation: 1.0%

Refinement

Refinement on F
$R = 0.032$
$wR = 0.049$

$(\Delta/\sigma)_{max} = 0.115$
$\Delta\rho_{max} = 0.32$ e $\mathring{A}^{-3}$
$\Delta\rho_{min} = -0.72$ e $\mathring{A}^{-3}$

$S = 0.84$
1354 reflections
198 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0030F^2]$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

The E statistics indicated a non-centrosymmetric space group and this was confirmed by the successful refinement. When treated in space group *Pnma* (with the appropriate matrix transformation), where both the cation and the anion must have C_s symmetry, the lowest R factor achieved was 0.147, with poor distances and angles and high thermal parameters for atoms Cl1, N3, O1, O2 and O3.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for compounds* (I), (IV), (V) *and* (VI)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$. Atomic parameters for compounds (II) and (III) are available as supplementary material.

	x	y	z	B_{eq}
(I)				
Fe2	0.75000	0.85584 (6)	0.50000	2.89 (2)
N21	0.8773 (1)	0.8383 (3)	0.5109 (1)	3.12 (10)
N22	0.7793 (2)	1.0219 (3)	0.5413 (1)	3.57 (12)
N23	0.7913 (2)	0.7133 (3)	0.4575 (1)	3.80 (12)
C21	0.9151 (2)	0.9186 (3)	0.5358 (1)	3.30 (12)
C22	0.9979 (2)	0.9115 (4)	0.5424 (1)	4.39 (16)
C23	1.0409 (2)	0.8186 (5)	0.5227 (1)	4.89 (18)
C24	1.0021 (2)	0.7336 (4)	0.4978 (1)	4.66 (16)
C25	0.9199 (2)	0.7461 (3)	0.4921 (1)	3.63 (12)
C26	0.8616 (2)	1.0142 (5)	0.5569 (1)	4.57 (17)
C27	0.8713 (2)	0.6549 (4)	0.4665 (1)	4.63 (16)
Fe1	1.08020 (2)	0.55595 (4)	0.3253 (1)	2.53 (2)
N1	0.9695 (1)	0.5018 (2)	0.3470 (1)	2.79 (9)
N2	0.9926 (2)	0.6992 (3)	0.2976 (1)	3.41 (11)
N3	1.1132 (2)	0.3856 (3)	0.3631 (1)	3.37 (11)
N4	1.1911 (1)	0.6235 (2)	0.3057 (1)	2.90 (9)
N5	1.0981 (2)	0.4250 (3)	0.2762 (1)	3.71 (12)
N6	1.1174 (2)	0.7164 (3)	0.3647 (1)	3.29 (11)
C1	0.9052 (2)	0.5825 (3)	0.3412 (1)	3.13 (12)
C2	0.8357 (2)	0.5635 (4)	0.3601 (1)	4.20 (15)
C3	0.8327 (2)	0.4583 (4)	0.3849 (1)	4.77 (17)
C4	0.8983 (2)	0.3725 (4)	0.3905 (1)	4.45 (15)
C5	0.9669 (2)	0.3976 (3)	0.3712 (1)	3.34 (12)
C6	0.9133 (2)	0.6965 (4)	0.3136 (1)	4.19 (15)
C7	1.0418 (2)	0.3101 (4)	0.3740 (1)	4.76 (18)
C8	1.2262 (2)	0.5552 (3)	0.2790 (1)	3.35 (12)
C9	1.3021 (2)	0.5934 (4)	0.2677 (1)	4.40 (15)
C10	1.3409 (2)	0.7020 (4)	0.2846 (1)	4.73 (16)
C11	1.3042 (2)	0.7728 (4)	0.3121 (1)	4.46 (15)
C12	1.2289 (3)	0.7304 (3)	0.3222 (1)	3.30 (12)
C13	1.1804 (3)	0.4342 (4)	0.2632 (1)	4.57 (16)
C14	1.1823 (2)	0.8023 (4)	0.3512 (1)	4.41 (15)
Cl1	0.96375 (5)	0.93418 (9)	0.71281 (2)	4.34 (4)
Cl2	0.15262 (6)	0.54013 (10)	0.44236 (2)	4.79 (4)
Cl3	1.17632 (6)	0.06169 (10)	0.61285 (3)	5.34 (4)
OW1	0.9950 (2)	0.0463 (3)	0.63257 (10)	5.48 (14)
OW2	0.7883 (2)	0.8316 (3)	0.67895 (10)	6.04 (16)
OW3	0.75000	0.2103 (5)	0.00000	10.5 (4)
(IV)				
Mn	0.25000	0.66041 (6)	0.00000	2.84 (3)
N1	0.2896 (2)	0.6209 (3)	−0.1338 (1)	3.05 (8)
N2	0.3704 (2)	0.8332 (3)	−0.0299 (2)	3.78 (11)
N3	0.1280 (2)	0.5058 (3)	−0.0595 (1)	3.59 (10)
C1	0.3669 (2)	0.6953 (3)	−0.1656 (2)	3.16 (9)
C2	0.3993 (3)	0.6647 (4)	−0.2470 (2)	4.34 (12)
C3	0.3500 (3)	0.5565 (4)	−0.2938 (2)	5.17 (15)
C4	0.2709 (3)	0.4794 (4)	−0.2604 (2)	4.37 (13)
C5	0.2424 (2)	0.5152 (3)	−0.1799 (1)	3.35 (9)
C6	0.4184 (2)	0.8123 (4)	−0.1111 (2)	4.13 (12)

C7	0.1585 (2)	0.4337 (4)	−0.1377 (2)	4.15 (11)
Cl	0.57586 (5)	0.74351 (9)	0.09174 (4)	4.43 (3)
OW	1.0000	0.8926 (5)	0.0000	9.9 (4)
(V)				
Co	0.70161 (10)	0.39578 (3)	0.15779 (6)	2.00 (4)
N1	0.7626 (7)	0.3656 (2)	0.2505 (3)	2.1 (2)
N2	0.5479 (7)	0.4288 (2)	0.2228 (4)	2.9 (3)
N3	0.8712 (7)	0.3568 (2)	0.1135 (4)	2.3 (2)
N4	0.6424 (7)	0.4237 (2)	0.0625 (4)	2.2 (2)
N5	0.8374 (7)	0.4544 (2)	0.1635 (4)	2.4 (3)
N6	0.5537 (7)	0.3429 (3)	0.1321 (4)	2.8 (3)
C1	0.6731 (9)	0.3688 (3)	0.3121 (5)	2.6 (3)
C2	0.7009 (10)	0.3420 (3)	0.3777 (5)	3.4 (4)
C3	0.8257 (12)	0.3106 (4)	0.3785 (5)	4.1 (4)
C4	0.9203 (11)	0.3072 (3)	0.3142 (5)	3.5 (4)
C5	0.8862 (9)	0.3360 (3)	0.2499 (5)	2.7 (3)
C6	0.5397 (11)	0.4039 (4)	0.3022 (5)	3.6 (4)
C7	0.9760 (10)	0.3385 (3)	0.1749 (5)	3.1 (3)
C8	0.7228 (8)	0.4625 (3)	0.0340 (5)	2.5 (3)
C9	0.6911 (10)	0.4799 (3)	−0.0396 (5)	3.1 (3)
C10	0.5785 (12)	0.4578 (4)	−0.0818 (5)	4.0 (4)
C11	0.4950 (10)	0.4172 (3)	−0.0500 (5)	3.3 (4)
C12	0.5291 (9)	0.4013 (3)	0.0219 (5)	2.7 (3)
C13	0.8429 (10)	0.4814 (3)	0.0880 (5)	3.1 (3)
C14	0.4529 (10)	0.3593 (3)	0.0675 (6)	3.7 (4)
Cl1	0.6843 (2)	0.53909 (8)	0.27205 (14)	3.57 (9)
Cl2	0.1022 (3)	0.40091 (9)	0.99556 (13)	3.70 (9)
Cl3	0.75000	0.25000	0.0608 (2)	4.11 (15)
Cl4	0.3283 (5)	0.2958 (2)	0.2419 (3)	4.5 (2)
OW1	0.710 (2)	0.8003 (7)	0.0835 (9)	7.4 (9)
(VI)				
Cu	0.99403 (2)	0.37910 (3)	1.00000	2.509 (16)
Cl1	0.97211 (6)	0.59259 (8)	0.6536 (2)	3.58 (3)
N1	1.0115 (1)	0.1920 (2)	0.5737 (5)	2.08 (8)
N2	0.8850 (2)	0.3204 (3)	0.5703 (7)	3.28(11)
N3	1.1064 (2)	0.3797 (2)	0.6487 (6)	3.09 (11)
C1	0.9524 (2)	0.1090 (3)	0.5742 (5)	2.18 (9)
C2	0.9640 (2)	−0.0252 (3)	0.5718 (5)	2.66 (10)
C3	1.0376 (2)	−0.0714 (3)	0.5719 (6)	2.78 (11)
C4	1.0991 (2)	0.0159 (3)	0.5710 (6)	2.76 (10)
C5	1.0836 (2)	0.1490 (3)	0.5724 (5)	2.33 (10)
C6	0.8758 (2)	0.1757 (3)	0.5779 (7)	2.96 (11)
C7	1.1412 (2)	0.2578 (3)	0.5640 (6)	2.81 (11)
Cl2	0.73967 (4)	0.84714 (7)	0.56688 (17)	2.93 (3)
O1	0.7364 (3)	0.9346 (5)	0.3944 (7)	6.9 (2)
O2	0.6679 (3)	0.7921 (7)	0.5796 (11)	10.7 (3)
O3	0.7969 (3)	0.7551 (7)	0.5397 (9)	10.6 (3)
O4	0.7535 (3)	0.9196 (4)	0.7510 (7)	6.5 (2)

Table 2. *Corresponding distances* (Å) *and angles* (°) *about the metal centres in the three isomorphous* bamp *complexes* (I)–(III)

	(I)		(II)		(III)	
	Fe2	Fe1	Ni2	Ni1	Zn2	Zn1
M—N1	2.137	2.092	2.025	2.001	2.106	2.081
M—N4		2.103		2.004		2.085
M—N2	2.249	2.226	2.168	2.161	2.235	2.237
M—N5		2.230		2.157		2.232
M—N3	2.210	2.210	2.147	2.151	2.203	2.208
M—N6		2.193		2.128		2.192
Average e.s.d.	0.003	0.003	0.003	0.003	0.003	0.003
N1—M—N1A/N4	170.84	175.94	173.37	177.20	171.40	176.69
N1—M—N2	75.30	76.34	79.00	79.51	76.33	76.66
N4—M—N5		75.94		79.11		77.07
N1—M—N3	75.60	76.97	79.16	79.25	76.39	77.76
N4—M—N6		77.05		80.02		77.90
N1—M—N2A/N5	111.61	107.95	105.87	103.69	110.05	105.85
N4—M—N2		102.25		100.61		101.73
N1—M—N3A/N6	98.55	99.07	96.45	97.18	98.05	99.19
N4—M—N3		104.41		100.61		103.89
N2—M—N3	148.94	153.30	157.14	158.76	151.26	154.38
N5—M—N6		152.98		159.13		154.98
N2—M—N2A/N5	88.44	95.38	88.70	93.32	89.47	93.90

N2—*M*—N3*A*/N6	92.31	91.00	90.80	90.76	91.46	91.61
N5—*M*—N3		92.28			91.36	91.77
N3—*M*—N3*A*/N6	102.52	93.69	98.31	92.20	101.15	93.74
Average e.s.d.	0.11	0.10	0.12	0.11	0.11	0.11

Table 3. *Corresponding distances (Å) and angles (°) about the metal centres in the* bamp *complexes (IV), (V) and (VI)*

	(IV)	(V)	(VI)
M—N1,N4	2.218	1.875,1.883	1.932
M—N2,N5	2.294	1.965,1.969	2.019
M—N3,N6	2.286	1.970,1.971	2.012
Cu—Cl1			2.239
Cu—Cl1^i			2.936
Cu—Cl1^{ii}			3.695
Average e.s.d.	0.002	0.006	0.002
N1—*M*—N1*A*,N4	161.21	177.68	
N1—*M*—N2	73.84	84.1	81.69
N4—*M*—N5		84.6	
N1—*M*—N3	72.94	83.7	81.84
N4—*M*—N6		84.0	
N1—*M*—N2*A*,N5	120.25	94.1	
N4—*M*—N2		97.8	
N1—*M*—N3*A*,N6	95.23	97.4	
N4—*M*—N3		94.4	
N2—*M*—N3	144.16	167.8	162.10
N5—*M*—N6		168.5	
N2—*M*—N2*A*,N5	92.7	90.1	
N2—*M*—N3*A*,N6	92.56	91.6	
N5—*M*—N3		91.6	
N3—*M*—N3*A*,N6	103.43	89.2	
N1—Cu—Cl1			173.88
N2—Cu—Cl1			97.77
N3—Cu—Cl1			97.85
Average e.s.d.	0.09	0.3	0.10

Symmetry codes: (i) $2 - x, 1 - y, z - \frac{1}{2}$; (ii) $2 - x, 1 - y, z + \frac{1}{2}$.

Table 4. *A comparison of average M—N bond distances (Å) and N—M—N bond angles (°) in complexes of 2,6-bis(aminomethyl)pyridine (first row) and 2-amino-methylpyridine (second row), with the standard average bond distances (third row)*

	M—N(py)	*M*—N(amine)	N(py)—*M*—N(amine)
Fe(II)*	2.112	2.222	76.01
	2.195	2.192	75.84
	2.224	2.035	
Ni(II)	2.014	2.153	79.28
	2.140	2.065	78.44
	2.122	2.097	
Zn(II)	2.095	2.218	76.85
	2.143	2.215	76.39
	2.111	2.152	
Mn(II)	2.218	2.290	73.39
	2.266	2.266	74.74
		2.192	
Co(III)	1.879	1.969	84.10
	1.955	1.960	84.14
	2.034	1.965	
Cu(II)	1.932	2.016	81.77
	2.005	2.024	81.87
	2.024	2.011	

* The list of CCSD codes and references has been added to the supplementary material. It includes four entries (high-spin room-temperature analyses only, APAFEM, FEPICA, FEPICC02, FEPICC20) for Fe^{II}, one entry each for Ni^{II} (APNIFB), Zn^{II} (BAZBEJ), Mn^{II} (JIJKAO) and Co^{III} (ENPCCO10), and four entries for Cu^{II} (BAMPCU, DUJREF, GEVMOJ, SITBUS). The standard average bond distances are from Orpen *et al.* (1989).

The ligand bamp was prepared according the the method of Schwarzenbach *et al.* (1971). For the complexes of Fe^{II}, Ni^{II}, Zn^{II} and Mn^{II}, two equivalents of (bamp).3HCl dissolved in water were first neutralized on a DOWEX-1 resin column and then added to an aqueous solution of one equivalent of the metal chloride. The solutions were heated to 333-353 K and filtered; crystals formed on slow cooling and evaporation. In the case of Fe^{II} and Mn^{II} the reactions were carried out under nitrogen to avoid oxidation. Co^{III} complexes are generally obtained by oxidation of a solution containing a Co^{II} salt and the free ligand. As the ligand is sensitive to oxidation, a Co^{III} complex carrying easily substituted ligands was used from the start, that is Na$_3$[Co(CO$_3$)$_3$].3H$_2$O (Bauer & Drinkard, 1960). In the case of the Cu^{II} complex, a solution of Cu(ClO$_4$)$_2$ was treated with (bamp).3HCl then neutralized with 3 equivalents of base to produce the crystalline complex of [Cu(bamp)Cl](ClO$_4$). The crystal of the Zn^{II} complex was sealed in a Lindemann glass capillary.

The structures were solved by direct methods using *SHELX76* (Sheldrick, 1976). The program system *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) was used for all further calculations. The H atoms were located from difference maps and refined isotropically, except for the Co^{III} complex (V). The numbering schemes used are illustrated in the *PLUTO* plots (Motherwell & Clegg, 1978) of the cations (Figs. 1-4).

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* 16, 146-153.

Bauer, H. F. & Drinkard, W. C. (1960). *J. Am. Chem. Soc.* 82, 5031-5032.

Couturier, Y. & Petitfaux, C. (1975). *Bull. Soc. Chim. Fr.* pp. 1043-1048.

Gabe, E. J., Le Page, Y., Charland,. J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* 22, 384-387.

Lions, F. & Martin, K. V. (1957). *J. Am. Chem. Soc.* 79, 2733-2738.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Orpen, G. A., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* p. S1.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Schwarzenbach, G., Boesch, J. & Egli, H. (1971). *J. Inorg. Nucl. Chem.* 33, 2141-2156.

Stoe & Cie (1985). *EMPIR. Empirical Absorption Correction Program.* Stoe & Cie, Darmstadt, Germany.

Tinner, U. & Marty, W. (1977). *Helv. Chim. Acta,* 60, 1629-1643.