Three yttrium crotonate complexes with diimines

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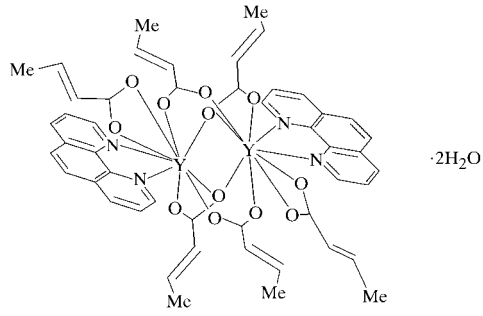
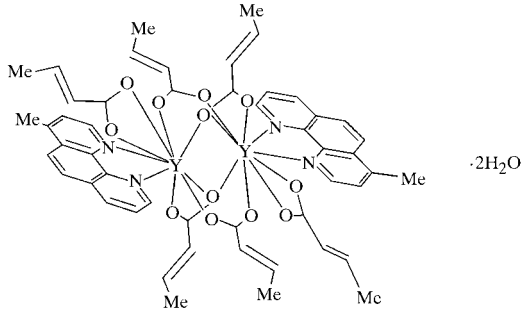
The synthesis and crystal structures of three new yttrium crotonate (crot) compounds, associated with three different nitrogenous bases, namely 1,10-phenanthroline (phen), 4-methyl-1,10-phenanthroline (mphen) and 2,2′-bipyridylamine (bpa), are presented. All three compounds organize as centrosymmetric dimers, to give tetra-μ-crotonato-bis[crotonato(1,10-phenanthroline)yttrium(III)] dihydrate, $[Y_2(C_4H_5O_2)_6(C_{12}H_8N_2)_2]\cdot 2H_2O$ or $[Y(crot)_3(phen)]_2\cdot 2H_2O$, (I), tetra-$\mu$-crotonato-bis[crotonato(4-methyl-1,10-phenanthroline)yttrium(III)] dihydrate, $[Y_2(C_4H_5O_2)_6(C_{13}H_{10}N_2)_2]\cdot 2H_2O$ or $[Y(crot)_3(mphen)]_2\cdot 2H_2O$, (II), and tetra-$\mu$-crotonato-bis[diaqua(crotonato)yttrium(III)] 2,2′-bipyridylamine tetrasolvate, $[Y_2(C_4H_5O_2)_6(H_2O)_4]\cdot 4C_{10}H_9N_3$ or $[Y(crot)_3(aq)_2]_2\cdot 4(bpa)$, (III). Complexes (I) and (II) are isomorphous, with the bases acting as chelating ligands. In complex (III), the coordination sphere is built up of carboxylate and aqua ligands, with the non-coordinated diimine acting as included solvent.

Comment

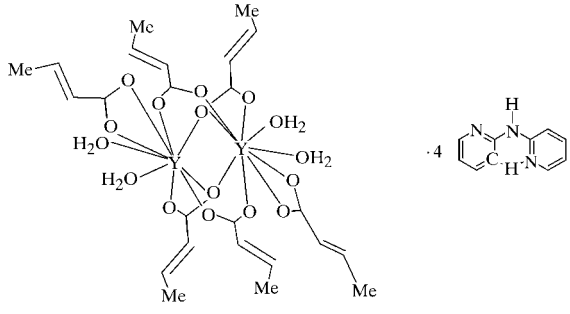
In a long-term project studying magnetic interactions in homo- and heteronuclear systems, we have focused on carboxylate compounds (Atria *et al.*, 1990, 1992, 2002; Baggio *et al.*, 2000), as they usually present a diversity of coordination modes, leading to very interesting structures. In particular, when lanthanide cations are used as metallic centres, the carboxylate group is found to bind in a *syn–syn, syn–anti* or *anti–anti* mode ($\eta^1\eta^1\mu_2$ type; for nomenclature, see *e.g.* Cotton & Wilkinson, 1988). Less common, but not rare, is the chelato-bridging mode ($\eta^2\eta^1\mu_2$ type). At present, we are exploring the complexing capabilities of the crotonate ion in these types of compounds, and report herein the syntheses and full structural characterizations of three new yttrium crotonate complexes, $[Y(crot)_3(phen)]_2\cdot 2H_2O$, (I), $[Y(crot)_3(mphen)]_2\cdot 2H_2O$, (II), and $[Y(crot)_3(aq)_2]_2\cdot 4(bpa)$, (III), where crot is the crotonate anion, phen is 1,10-phenanthroline, mphen is 4-methyl-1,10-phenanthroline and bpa is 2,2′-bipyridylamine. All three compounds are dimeric species.



(I)



(II)



(III)

Compounds (I) and (II) are isomorphous, which is not unexpected given their ligand similarities; both dimers are almost identical in their molecular structure (Figs. 1 and 2). Each cation is coordinated *via* the O atoms to three crotonate groups binding in dissimilar coordination modes (the atoms are labelled accordingly), namely unit *A*, which is purely chelating, unit *B*, a pure *syn–syn* bridge, and unit *C*, which is tridentate, with one O atom chelating to one of the Y centres while the other bridges both Y atoms. The first difference between these closely related structures is that the crotonate unit *A* in compound (I) is disordered over two sites of similar occupancies [0.53 (2)/0.47 (2)], while it is ordered in (II). A bidentate dinitrogenated base [phen in (I) and mphen in (II)] completes the coordination sphere around the cation through both N atoms. Here, the second difference between the

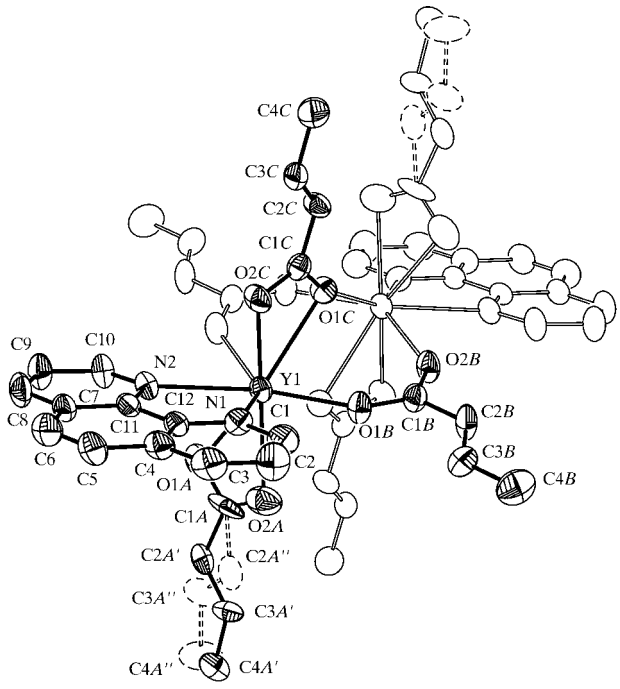


Figure 1
Molecular diagram of the centrosymmetric dimeric unit in (I). Displacement ellipsoids are drawn at the 30% probability level. Dashed ellipsoids and bonds indicate the observed crotonate ligand disorder.

structures arises: while the phen group in structure (I) is ordered, the mphen ligand in (II) is disordered over two positions, which are rotated by 180° relative to one another, as shown in Fig. 2. The fact that this rotation takes place around the symmetry axis of the molecular core allowed refinement of the group as if it were ordered and had full occupancy, except for the terminal methyl groups, which then appear at different sites in the molecule with populations of 0.600 (5) and 0.400 (5).

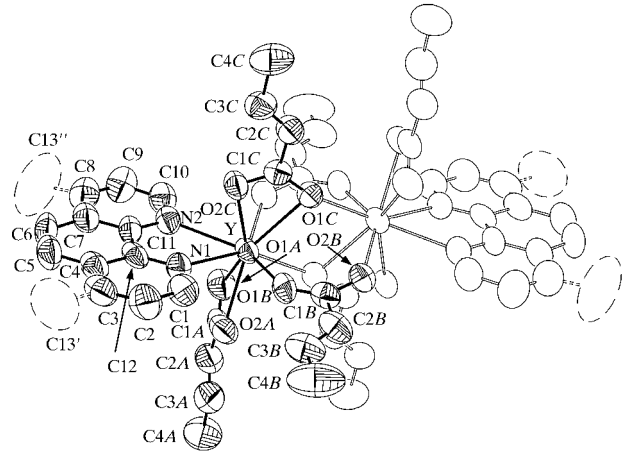


Figure 2
Molecular diagram of the centrosymmetric dimeric unit in (II). Displacement ellipsoids are drawn at the 30% probability level. Disordered methyl groups are drawn with dashed lines and labelled with primes (see text).

This binding scheme results in a ninefold coordination for the Y^{III} cations, which are linked to each other through quadruple bridges. Two of these are through a single O atom (Y—O—Y′) and two through a complete carboxylate, in a Y—O—C—O—Y′ sequence. The resulting Y···Y′ distance is 3.8948 (16) Å in (I) and 3.9009 (10) Å in (II). The main interaction between the rather isolated dimeric entities is achieved through the aromatic groups related by the centre of symmetry at ($\frac{1}{2}$,1,0), which show a significant π–π interaction. Being parallel by symmetry requirements, they lie at graphitic distances from each other [3.40 (1) Å for (I) and 3.49 (1) Å for (II)]. The central rings show roughly the same 'slippage' (deviation from exact superposition viewed normal to the rings) of the rings in both structures [approximately 0.85 (2) Å], leading to an overlap of *ca* 60% of the complete ring area.

The structures are completed by one hydrate water molecule disordered over two sites. It was not possible to find its H atoms, thus preventing a detailed study of the hydrogen-bonding scheme. However, the short $OW\cdots O_{crot}$ distances present in both structures strongly suggest these hydrogen-bonding interactions are a stabilizing factor for the packing. Short O···O distances for (I)/(II) are O1*WA*···O2*A* = 2.819 (9)/2.895 (7) Å, O1*WB*···O1*A* = 2.631 (11)/2.689 (11) Å and O1*WB*···O1*A*^{iv} = 2.858 (17)/2.918 (11) Å [symmetry code: (iv) $1-x, 1-y, -z$].

The major difference between structure (III) and structures (I) and (II) resides with the nitrogenous bases, which are not coordinated in (III), acting instead as solvates. The crotonate units are attached to the cations in an analogous way to (I) and

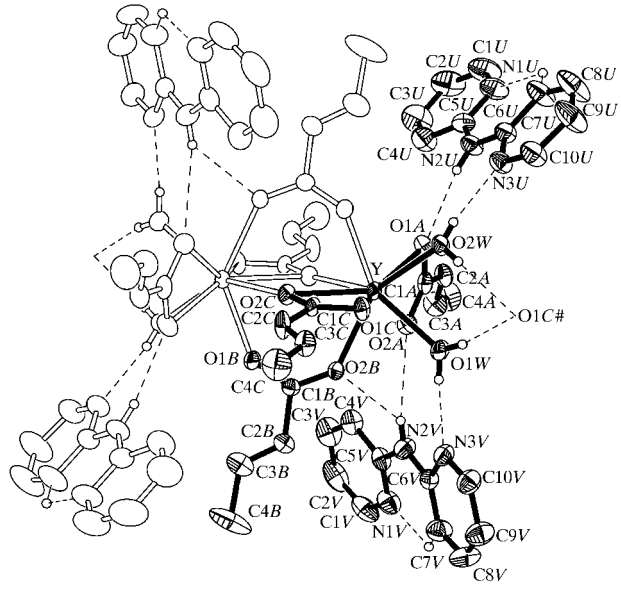


Figure 3
Molecular diagram of the centrosymmetric dimeric unit in (III). Independent atoms are drawn as full shaded ellipsoids. Only those H atoms relevant to the hydrogen-bonding description have been included. Hydrogen bonds are shown by broken lines and displacement ellipsoids are drawn at the 30% probability level. Atom O1*C*# is at symmetry position ($\frac{1}{2}-x, \frac{3}{2}-y, 1-z$).

(II), with the ligand displaying the three different coordination modes and building up quadruple bridges, to join Y^{III} cations together at a distance of 3.9664 (5) Å (Fig. 3). The coordination sphere around each Y centre is, in this case, completed by two water molecules, located in similar positions to those occupied in (I) and (II) by the imine N atoms.

The two independent bpa groups in structure (III) (four units per dimer) present a *trans* disposition of their bpy groups, with pyridine atom N3 pointing outwards and being involved in hydrogen-bonding interactions. The other pyridine N atom (N1) points inwards and is shielded from intermolecular contacts by a weak C7—H7···N1 intramolecular hydrogen bond, with average parameters H···N ∼ 2.20 Å and C—H···N ∼ 120° (Fig. 3). Both moieties are distorted from planarity, through opposite rotations of the lateral pyridine groups around the corresponding N2—C5 and N2—C6 bonds. The combined effect leads to a dihedral angle between rings of 6.0 (1)° in unit *U* and 11.3 (1)° in unit *V*.

All the active H atoms in the structure of (III) (four aqua and two amino) take part in hydrogen bonding, in a complex scheme presented in Table 4 and shown in Fig. 3. The main effects of these interactions are, firstly, the attachment of the bpa molecules to the dimeric units to create a kind of a 'cluster', and, secondly, to join the resulting entities into one-dimensional chains running along the crystallographic *b* axis (entries 4 and 5 in Table 4). The columnar structures interact weakly with each other, mainly through van der Waals interactions. There are no π–π interactions between the planar groups of neighbouring bpa groups.

In summary, we have synthesized and solved the structures of three yttrium crotonate complexes characterized by a similar bridging mode between the cations, *i.e.* two 'short' (Y—O—Y) and two 'long' (Y—O—C—O—Y) bridges. A search in the Cambridge Structural Database (CSD, version 5.24; Allen, 2002) of dimeric carboxylate-bridged Y^{III} centres showed only four fully reported structures, one of which presented a simpler bridging scheme with just two Y—O—Y links, namely bis(μ_2-acetato)tetrakis(acetato)tetraaquadiyttrium tetrahydrate (CSD refcode TACETZ01; Ribot *et al.*, 1991). The remaining three, bis([μ_2-(trimethylsilyl)acetato-*O*,*O*,*O*′][μ_2-(trimethylsilyl)acetato-*O*,*O*′]{μ_2-1-[dimethyl(prop-2-enyl)silyl]-2,3,4,5-tetramethylcyclopentadienyl}yttrium) (AFINIM; Evans *et al.*, 2001), bis[(μ_2-κO:κO′-acetato)(μ_2-κO:$\kappa^2 O$′-acetato)(η^5-cyclopentadienyl)tris(μ_2-dimethylphosphito-*O*,*P*)cobaltyttrium(III)] (WEQKEI; Han *et al.*, 1999) and bis(μ_2-salicylato-*O*,*O*,*O*′)bis(μ_2-salicylato-*O*,*O*′)bis(salicylato-*O*,*O*′)diyttrium tetrahydrate (LESMUR; Ma *et al.*, 1994), present very similar yttrium environments to the ones reported herein, in spite of the diversity of their carboxylate ligands. It can thus be concluded that this type of dimeric bridging is common for the yttrium–carboxylate system, leading to a rather constrained geometry with a narrow spread (3.347–4.028 Å) in the Y···Y distances. The distances found here for (I), (II) and (III) lie within the extreme values found in the literature. The existence of these structures supports the feasibility of generating heteronuclear complexes containing magnetic lanthanide cations combined with Y as a non-magnetic centre. We are at present engaged in the synthesis and characterization of compounds of this type, which ought to be useful tools for studying 4*f*–4*f* magnetic interactions.

Experimental

The three complexes, (I), (II) and (III), were synthesized by similar methods. A mixture of Y_2O_3 (1 mmol) and crotonic acid (6 mmol) was dissolved in water (100 ml), followed by the addition of the appropriate diimine ligand (1 mmol) dissolved in methanol (10 ml). The resultant mixture was refluxed for 24 h, filtered while hot and then concentrated to 25 ml. The filtrate was left to stand at room temperature and colourless crystals appeared after four weeks. Crystals of compounds (I) and (II) were very poorly diffracting, and the reported data correspond to the best of many data collections obtained from different specimens. All starting materials were used as purchased without further purification. Elemental analyses (C, H) were performed on a Carlo–Erba EA 1108 instrument; the results obtained (% calculated/% found) are as follows: for (I), $C_{48}H_{50}N_4O_{14}Y_2$: C 53.15/52.9 and H 4.65/4.5; for (II), $C_{50}H_{54}N_4O_{14}Y_2$: C 53.97/54.1 and H 4.89/4.8; for (III), $C_{64}H_{74}N_{12}O_{16}Y_2$: C 53.19/53.4 and H 5.16/5.3.

Compound (I)

Crystal data

$[Y_2(C_4H_5O_2)_6(C_{12}H_8N_2)_2]\cdot 2H_2O$
M_r = 1084.74
Triclinic, $P\overline{1}$
a = 10.5565 (14) Å
b = 10.9994 (15) Å
c = 11.4194 (15) Å
α = 78.966 (2)°
β = 71.685 (2)°
γ = 77.256 (3)°
V = 1217.1 (3) Å^3
Z = 1
D_x = 1.480 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 98 reflections
θ = 4.3–24.1°
μ = 2.44 mm^{-1}
T = 293 (2) K
Prisms, colourless
0.32 × 0.24 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-NT*; Bruker, 2000)
T_{min} = 0.50, T_{max} = 0.64
6943 measured reflections
5136 independent reflections
1717 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 28.1°
$h = -12 \rightarrow 13$
$k = -13 \rightarrow 14$
$l = 0 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.115
S = 0.86
5136 reflections
348 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.008P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.012
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}

Table 1
Selected interatomic distances (Å) for (I).

Y1—O2*B*^{i}	2.302 (5)	Y1—N2	2.582 (6)
Y1—O1*C*^{i}	2.320 (5)	Y1—O1*C*	2.585 (4)
Y1—O1*B*	2.323 (5)	Y1—N1	2.586 (6)
Y1—O2*C*	2.390 (5)	Y1—C1*A*	2.757 (8)
Y1—O2*A*	2.442 (5)	Y1—C1*C*	2.907 (7)
Y1—O1*A*	2.474 (6)	Y1···Y1^{i}	3.8948 (16)

Symmetry code: (i) $1-x, 1-y, 1-z$.

Compound (II)

Crystal data

$[Y_2(C_4H_5O_2)_6(C_{13}H_{10}N_2)_2]\cdot 2H_2O$
M_r = 1112.79
Triclinic, $P\overline{1}$
a = 10.6924 (14) Å
b = 10.9060 (15) Å
c = 11.8528 (16) Å
α = 77.832 (2)°
β = 72.329 (2)°
γ = 77.810 (2)°
V = 1271.2 (3) Å^3
Z = 1
D_x = 1.454 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 102 reflections
θ = 3.8–22.9°
μ = 2.34 mm^{-1}
T = 293 (2) K
Prism, colourless
0.22 × 0.20 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-NT*; Bruker, 2000)
T_{min} = 0.61, T_{max} = 0.72
7557 measured reflections
5329 independent reflections
2011 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 28°
$h = -13 \rightarrow 9$
$k = -13 \rightarrow 11$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.084
S = 0.83
5329 reflections
329 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.026P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.008
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 2
Selected interatomic distances (Å) for (II).

Y—O1C^{i}	2.296 (3)	Y—O1A	2.446 (3)
Y—O2B^{i}	2.307 (3)	Y—N2	2.561 (4)
Y—O1B	2.309 (3)	Y—N1	2.572 (4)
Y—O2C	2.390 (3)	Y—O1C	2.602 (3)
Y—O2A	2.423 (3)	Y···Y^{i}	3.9009 (10)

Symmetry code: (i) $1-x, 1-y, 1-z$.

Compound (III)

Crystal data

$[Y_2(C_4H_5O_2)_6(H_2O)_4]\cdot 4C_{10}H_9N_3$
M_r = 1445.18
Monoclinic, $C2/c$
a = 38.108 (4) Å
b = 8.851 (1) Å
c = 25.539 (3) Å
β = 126.26 (1)°
V = 6945.4 (14) Å^3
Z = 4
D_x = 1.382 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 112 reflections
θ = 4.7–23.4°
μ = 1.74 mm^{-1}
T = 293 (2) K
Prism, colourless
0.38 × 0.20 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-NT*; Bruker, 2000)
T_{min} = 0.62, T_{max} = 0.75
23 271 measured reflections
7877 independent reflections
4815 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 28.2°
$h = -50 \rightarrow 50$
$k = -11 \rightarrow 11$
$l = -30 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.094
S = 0.88
7877 reflections
459 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.014
$\Delta\rho_{max}$ = 1.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 3
Selected interatomic distances (Å) for (III).

Y—O1A	2.4065 (18)	Y^{ii}—O2C	2.3220 (17)
Y—O2A	2.4378 (19)	Y—O2C	2.6426 (18)
Y^{ii}—O1B	2.2893 (18)	Y—O1W	2.374 (2)
Y—O2B	2.3238 (17)	Y—O2W	2.394 (2)
Y—O1C	2.4349 (17)	Y···Y^{ii}	3.9664 (5)

Symmetry code: (ii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
C7V—H7V···N1V	0.95 (4)	2.23 (3)	2.913 (6)	129 (4)
C7U—H7U···N1U	0.94 (2)	2.25 (4)	2.873 (5)	123 (3)
O1W—H1WB···N3V	0.77 (4)	1.99 (4)	2.759 (3)	174 (2)
O1W—H1WA···O1C^{iii}	0.78 (3)	2.01 (3)	2.782 (3)	170 (4)
O2W—H2WB···O1C^{iii}	0.75 (3)	2.15 (3)	2.882 (3)	167 (4)
O2W—H2WA···N3U	0.75 (3)	2.06 (3)	2.797 (4)	168 (3)
N2V—H2NV···O2B	0.79 (3)	2.57 (2)	3.196 (3)	137 (2)
N2V—H2NV···O2A	0.79 (3)	2.61 (2)	3.318 (4)	150 (3)
N2U—H2NU···O1A	0.78 (3)	2.20 (2)	2.970 (3)	168 (3)

Symmetry code: (iii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$.

H atoms unambiguously defined by the stereochemistry (*i.e.* those on C atoms) were placed at their calculated positions and allowed to ride on their parent C atoms, with U_{iso}(H) = 1.2U_{eq}(C). Terminal methyl groups were allowed to rotate as well. H atoms corresponding to the (disordered) hydrate water molecules in structures (I) and (II) were not included in the model. In structure (III), the bound water H atoms were found in the final difference Fourier map and, together with the amino H atoms, were refined with similarity restraints on O—H, H···H and N—H distances, so as to ensure a reasonable geometry.

For all compounds, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*/*PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

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