Two isomorphous ZnII/CoII complexes with tri-*tert*-butoxysilanethiol and histamine, and (4-hydroxymethyl-1*H*-imidazole-*κN*)bis(tri-*tert*-butoxy-silanethiolato-*κ²O,S*)zinc(II)

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The complexes [2-(1*H*-imidazol-4-yl-*κN³*)ethylamine-*κN*]-bis(tri-*tert*-butoxysilanethiolato-*κS*)cobalt(II), [Co(C$_{12}$H$_{27}$O$_3$SSi)$_2$(C$_5$H$_9$N$_3$)], and [2-(1*H*-imidazol-4-yl-*κN³*)ethylamine-*κN*]bis(tri-*tert*-butoxysilanethiolato-*κS*)zinc(II), [Zn(C$_{12}$H$_{27}$O$_3$SSi)$_2$(C$_5$H$_9$N$_3$)], are isomorphous. The central ZnII/CoII ions are surrounded by two S atoms from the tri-*tert*-butoxysilanethiolate ligand and by two N atoms from the chelating histamine ligand in a distorted tetrahedral geometry, with two intramolecular N—H···O hydrogen-bonding interactions between the histamine NH$_2$ groups and *tert*-butoxy O atoms. Molecules of the complexes are joined into dimers *via* two intermolecular bifurcated N—H···(S,O) hydrogen bonds. The ZnII atom in [(1*H*-imidazol-4-yl-*κN³*)methanol]bis(tri-*tert*-butoxysilanethiolato-*κ²O,S*)zinc(II), [Zn(C$_{12}$H$_{27}$O$_3$SSi)$_2$-(C$_4$H$_6$N$_2$O)], is five-coordinated by two O and two S atoms from the *O,S*-chelating silanethiolate ligand and by one N atom from (1*H*-imidazol-4-yl)methanol; the hydroxy group forms an intramolecular hydrogen bond with sulfur. Molecules of this complex pack as zigzag chains linked by N—H···O hydrogen bonds. These structures provide reference details for cysteine- and histidine-ligated metal centers in proteins.

Comment

Structural and spectroscopic studies on heteroleptic transition-metal tri-*tert*-butoxysilanethiolates have been undertaken to provide a source of reference data for cysteine-ligated metal centers in proteins (Becker, Zalewska *et al.*, 2001; Becker *et al.*, 2002; Dołęga *et al.*, 2004, 2007, 2008; Kropidłowska *et al.*, 2007). Unfortunately, [113]Cd NMR and UV–vis solution studies revealed low stability of these complexes; in solution, N-containing ligands are discarded and homoleptic metal thiolates restored (Becker, Zalewska *et al.*, 2001; Dołęga *et al.*, 2007; Dołęga & Walewski, 2007). We have not noticed

any correlation between ligand–metal bond lengths in solids and the stability of the obtained complexes in solution. Even complexes with short metal–nitrogen bonds in the solid state, such as imidazole derivatives, tend to dissociate (Dołęga *et al.*, 2007). Since our aim is to obtain solution UV–vis and NMR spectroscopic parameters correlated with well defined metal coordination, we decided to use N-containing ligands with additional chelating OH and NH$_2$ groups in order to stabilize the resulting species in solution (Barszcz, 2005). Histamine, (I), and (1*H*-imidazol-4-yl)methanol, (II), have been applied as potentially chelating ligands. The crystal structures of one CoII and two ZnII complexes have been determined.


(I)   (II)
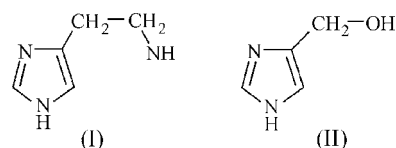
The molecular structure of [2-(1*H*-imidazol-4-yl-*κN³*)ethylamine-*κN*]bis(tri-*tert*-butoxysilanethiolato-*κS*)cobalt(II), (III), is shown in Fig. 1. The zinc analog, (IV), is isomorphous; geometric parameters are compared in Table 4. As in some previously described complexes (*eg.* Wojtczak *et al.*, 1990; Garnuszek *et al.*, 2002), histamine acts as a bidentate ligand, forming a six-membered ring including the metal ion, the latter displaying a distorted tetrahedral geometry in (III) and (IV). Complexation of the amine N atom with the metal ion is stabilized by hydrogen bonds with O atoms from the tri-*tert*-butoxysilanethiolate ligands. These additional intramolecular interactions influence the regularity of the crystal packing of molecular tri-*tert*-butoxysilanethiolates; bulky alkoxy substituents of tri-*tert*-butoxysilanethiol often exhibit static disorder in crystals (Kloskowska *et al.*, 2006). Sometimes it is not possible to find an appropriate model for the disordered groups – such results then remain unpublished. If intramolecular hydrogen bonds are formed between ligands and adjacent *tert*-butoxy groups, the possibility of rotation and disorder is significantly diminished (Becker, Dołęga *et al.*, 2001; Dołęga *et al.*, 2006, 2008). In (III) and (IV), the methyl groups at C21 exhibit disorder and so were refined over two positions. The refinement of (IV) was stable without additional constraints; in (III), atom pairs based on C23 and C24 were refined with isotropic displacement parameters.


(III) *M* = Co
(IV) *M* = Zn
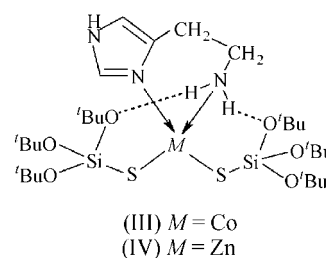
Compounds (III) and (IV) are the first structurally characterized complexes of histamine with ZnII and CoII. The

geometrical parameters of Zn^{II}-bonded histamine are comparable to those of other N^1,N^3-chelating histidine ligands in complexes with zinc(II) (Harding & Cole, 1963; Dalosto *et al.*, 2001). The bond lengths found in (III) are in the range typical for neutral tetrahedral Co^{II} complexes with imidazole-based and tri-*tert*-butoxysilanethiolate ligands (Becker, Zalewska *et al.*, 2001; Dołęga *et al.*, 2008). The Co—N bond lengths in a known complex of Co^{III} with histamine are certainly shorter than those in (III), but the chelating angles are close to those in (III) (Wojtczak *et al.*, 1990). Our results confirm the structural similarity of tetrahedral Zn^{II} and Co^{II} complexes with the same ligands (Horrocks *et al.*, 1982; Dołęga *et al.*, 2008).
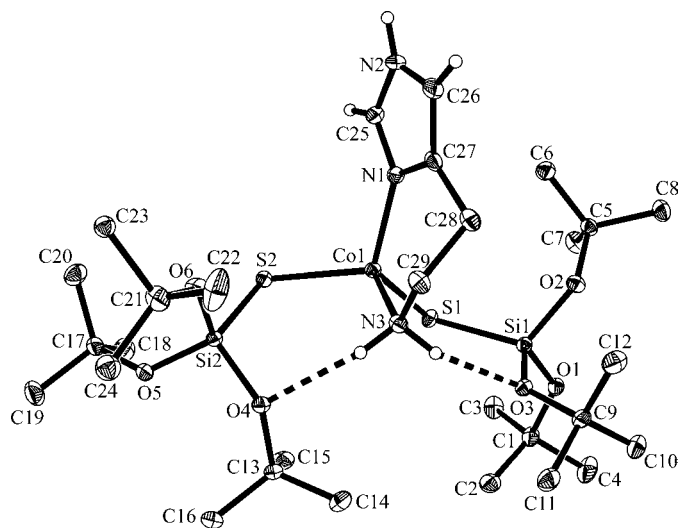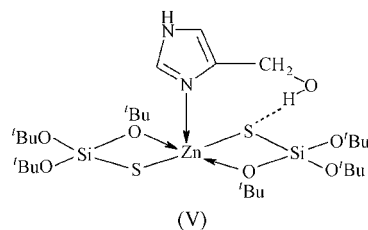

Figure 1
A view of the molecule of (III), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. All *tert*-butyl H atoms have been omitted for clarity. Only the major conformation of the disordered methyl groups on C21 is shown. Hydrogen bonds are indicated with dashed lines.
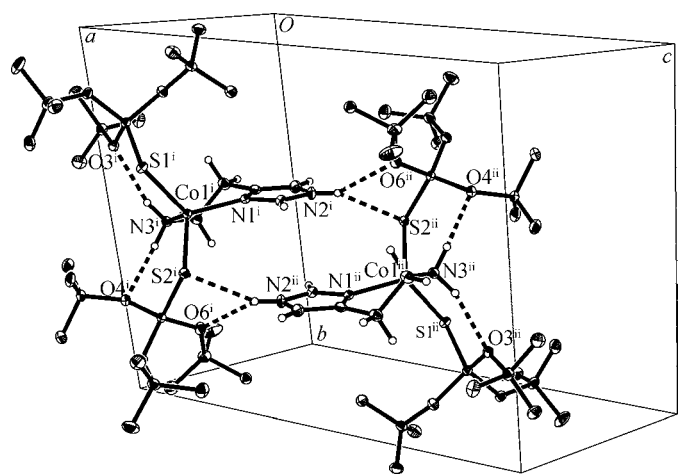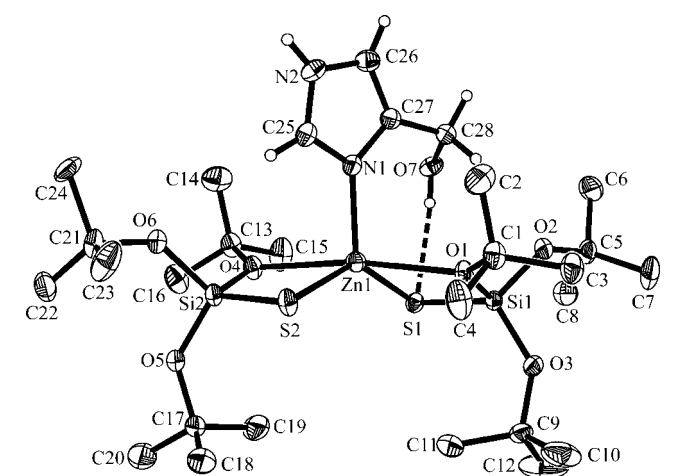
Centrosymmetrically related molecules of (III) and (IV) form hydrogen-bonded dimers (Table 1), which are shown in Fig. 2. The planes of the imidazole rings are parallel, but there are no stacking interactions because of the inter-ring distance.

(1*H*-Imidazol-4-yl)methanol does not act as a bidentate chelating ligand in [(1*H*-imidazol-4-yl-κN^3)methanol]bis(tri-*tert*-butoxysilanethiolato-$\kappa^2 O,S$)zinc(II), (V), but instead is bonded to zinc only *via* an N atom of the imidazole ring (Fig. 3). Ignoring the asymmetric conformation of the imidazole ring, (V) would exhibit an approximate twofold symmetry. The positions of the ligating atoms in (V) may be approximated to a distorted trigonal bipyramid, which is a coordination geometry often observed in mixed-ligand zinc tri-*tert*-butoxysilanethiolates (Becker *et al.*, 1996; Dołęga *et al.*, 2004). Atoms O1 and O4 occupy the apical positions of the bipyramid and the O1—Zn1—O4 angle is close to 180°. The deviations from the least-squares equatorial plane are −0.0152 (3) Å for Zn1, 0.0055 (5) Å for S1, 0.0052 (5) Å for S2 and 0.0045 (18) Å for N1, with O1 and O4 displaced by −2.3833 (16) and 2.3894 (16) Å, respectively. The methyl groups bound to C21 exhibit disorder, and it was necessary to refine them over two positions.

(V)

Complex (V) possesses a typically large (> 120°) S—Zn—S angle, as is always found in five-coordinated zinc tri-*tert*-butoxysilanethiolates with $ZnNO_2S_2$ kernels (Becker *et al.*, 1996; Dołęga *et al.*, 2004, 2005). This angle becomes much smaller when the Zn coordination geometry approaches

Figure 2
The packing of (III). Displacement ellipsoids are drawn at the 30% probability level. All *tert*-butyl H atoms have been omitted for clarity. Only the major conformations of the disordered methyl groups on C21 are shown. Hydrogen bonds are indicated with dashed lines. [Symmetry codes: (i) $x + 1, y, z$; (ii) $−x + 1, −y + 1, −z + 1$.]

Figure 3
A view of the molecule of (V), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. All *tert*-butyl H atoms have been omitted for clarity. Only the major conformations of the disordered methyl groups on C21 are shown. Hydrogen bonds are indicated with dashed lines.
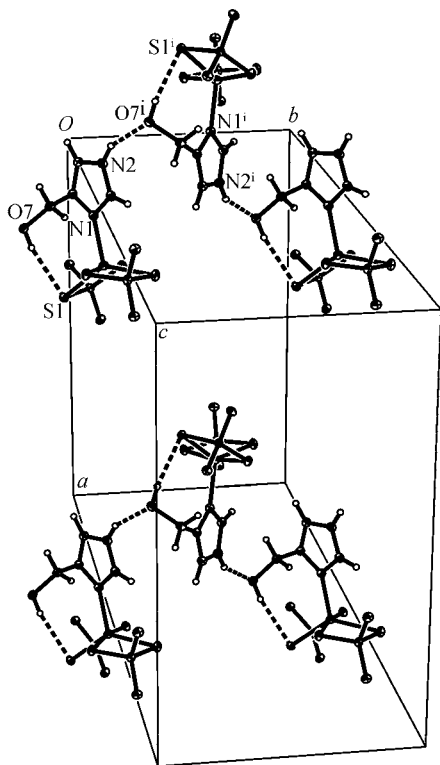
Figure 4
A view of the one-dimensional chains of molecules of (V) linked by hydrogen bonds. Displacement ellipsoids are drawn at the 30% probability level. All *tert*-butyl groups have been omitted for clarity. Only the major conformation of the disordered methyl groups on C21 is shown. Hydrogen bonds are indicated with dashed lines. [Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.]

tetrahedral in complexes with ZnN_2S_2 or $ZnNOS_2$ coordination cores and it is the most pronounced change here (Becker, Dołęga *et al.*, 2001; Dołęga *et al.*, 2004, 2008; Table 4).

We do not think that an additional weak intramolecular O—H···S interaction between (1*H*-imidazol-4-yl)methanol and tri-*tert*-butoxysilanethiolate observed here (Table 3) would enhance the stability of (V) in solution. It is evident that the side chain must be extended to achieve chelation in the studied systems. The molecules in (V) pack in one-dimensional zigzag chains linked by N—H···O hydrogen bonds that are approximately parallel to the *b* axis (Fig. 4).

Experimental

Commercial histamine dihydrochloride (98%+, Alfa Aesar) and (1*H*-imidazol-4-yl)methanol (97%, Aldrich) were used. The synthesis of tri-*tert*-butoxysilanethiol was as described by Pięko & Wojnowski (1962) and the synthesis of zinc acetylacetonate was as described by Hassanein & Hewaidy (1970).

For the preparation of (III), triethylamine (2 mmol, 0.28 ml) was added to a cobalt(II) chloride hexahydrate (0.5 mmol, 0.12 g) solution in water (50 ml). Histamine dihydrochloride (2 mmol, 0.37 g) and neat tri-*tert*-butoxysilanethiol (1 mmol, 1.37 ml) were added to the resulting suspension. The reaction flask was closed with a rubber septum and the suspension was shaken vigorously for 20 min. A blue hydrophobic precipitate was collected, washed with water and dried

in air. The dry solid was dissolved in methanol, the solution was filtered and the filtrate was left at 273–278 K. After a weekend, dark-blue crystals were collected [m.p. 403–423 K (slow decomposition), black product melts at 456–458 K; yield 78% (crude product)].

Compound (IV) was synthesized in the same manner as (III). Zinc(II) chloride hexahydrate (0.5 mmol, 0.12 g) was used instead of cobalt(II) chloride hexahydrate, and the resulting white hydrophobic precipitate was recrystallized from a methanol–acetonitrile mixture (4:1 *v/v*) [m.p. 471–475 K (with decomposition); yield 99% (crude product)].

For the preparation of (V), zinc acetylacetonate (1 mmol, 0.27 g) and tri-*tert*-butoxysilanethiol (6 mmol, 0.9 ml) were suspended in methanol (5 ml) and warmed until dissolved. (1*H*-Imidazol-4-yl)methanol (1 mmol, 0.098 g) in methanol (1 ml) was added to the reaction mixture. Crystallization occurred immediately. Crystals were collected and recrystallized from a toluene/methanol mixture (1:1 *v/v*) (yield 87% of crude product).

Compound (III)

Crystal data

$[Co(C_{12}H_{27}O_3SSi)_2(C_5H_9N_3)]$	$\gamma = 107.336\ (4)°$
$M_r = 729.05$	$V = 1990.3\ (2)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.2498\ (4)$ Å	Mo $K\alpha$ radiation
$b = 14.3000\ (9)$ Å	$\mu = 0.64$ mm^{-1}
$c = 16.0164\ (11)$ Å	$T = 120\ (2)$ K
$\alpha = 95.190\ (5)°$	$0.16 \times 0.10 \times 0.06$ mm
$\beta = 96.805\ (4)°$	

Data collection

Oxford Diffraction KM-4-CCD diffractometer	13851 measured reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)	7381 independent reflections
	6248 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.026$
$T_{min} = 0.842$, $T_{max} = 0.93$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	407 parameters
$wR(F^2) = 0.093$	H-atom parameters constrained
$S = 1.10$	$\Delta\rho_{max} = 0.64$ e Å^{-3}
7381 reflections	$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···S2[iii]	0.88	2.49	3.2365 (16)	143
N2—H2···O6[iii]	0.88	2.60	3.367 (2)	146
N3—H3D···O4	0.92	2.23	3.0626 (19)	150
N3—H3E···O3	0.92	2.20	3.0654 (19)	157

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

Compound (IV)

Crystal data

$[Zn(C_{12}H_{27}O_3SSi)_2(C_5H_9N_3)]$	$\gamma = 107.337\ (3)°$
$M_r = 735.49$	$V = 1990.55\ (12)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.2535\ (3)$ Å	Mo $K\alpha$ radiation
$b = 14.3163\ (5)$ Å	$\mu = 0.82$ mm^{-1}
$c = 15.9899\ (6)$ Å	$T = 120\ (2)$ K
$\alpha = 95.086\ (3)°$	$0.20 \times 0.15 \times 0.09$ mm
$\beta = 96.805\ (3)°$	

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Table 2
Hydrogen-bond geometry (Å, °) for (IV).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2\cdots S2^{i}$	0.88	2.52	3.2481 (14)	140
$N2-H2\cdots O6^{i}$	0.88	2.57	3.355 (2)	148
$N3-H3D\cdots O4$	0.92	2.24	3.0550 (17)	147
$N3-H3E\cdots O2$	0.92	2.20	3.0592 (17)	156

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

Table 3
Hydrogen-bond geometry (Å, °) for (V).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2\cdots O7^{i}$	0.88	1.94	2.751 (3)	152
$O7-H7\cdots S1$	0.84	2.37	3.1959 (17)	168

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

Data collection

Oxford Diffraction KM-4-CCD diffractometer	13696 measured reflections
	7386 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)	6730 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.021$
$T_{min} = 0.79$, $T_{max} = 0.857$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	427 parameters
$wR(F^2) = 0.082$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{max} = 0.74$ e Å^{-3}
7386 reflections	$\Delta\rho_{min} = -0.32$ e Å^{-3}

Compound (V)

Crystal data

[Zn(C$_{12}$H$_{27}$O$_3$SSi)$_2$(C$_4$H$_6$N$_2$O)]	$V = 3917.39$ (18) Å^3
$M_r = 722.45$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 16.2546$ (5) Å	$\mu = 0.83$ mm^{-1}
$b = 9.2094$ (2) Å	$T = 120$ (2) K
$c = 26.1831$ (7) Å	$0.39 \times 0.2 \times 0.04$ mm
$\beta = 91.874$ (2)°	

Data collection

Oxford Diffraction KM-4-CCD diffractometer	25278 measured reflections
	7283 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)	6253 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.043$
$T_{min} = 0.685$, $T_{max} = 0.855$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	429 parameters
$wR(F^2) = 0.112$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{max} = 0.99$ e Å^{-3}
7283 reflections	$\Delta\rho_{min} = -0.41$ e Å^{-3}

The *tert*-butyl groups attached to atom O6 are disordered over two orientations. In (III), the disordered atoms were set as isotropic. The site occupancies of the disordered groups are 0.641 (9) and 0.359 (9) in (III), 0.612 (17) and 0.388 (17) in (IV), and 0.65 (3) and 0.35 (3) in (V). H atoms were positioned geometrically and refined using a riding model {C—H = 0.95–0.99 Å, N—H = 0.88–0.92 Å and O—H = 0.84 Å, and U_{iso}(H) = 1.2U_{eq}(C,O,N), 1.3U_{eq}(C,N) [all methylene C and NH$_2$ in (IV)] or 1.5U_{eq}(C) (all methyl C)}.

Table 4
Comparative geometrical parameters (Å, °) for (III), (IV) and (V).

	(III)[a]	(IV)[b]	(V)[b]
$M1-S1$	2.2724 (5)	2.2813 (4)	2.2835 (6)
$M1-S2$	2.3028 (5)	2.3005 (4)	2.2841 (6)
$M1-N1$	2.0116 (15)	2.0350 (13)	2.0357 (19)
$M1-N3$	2.0754 (15)	2.0804 (13)	–
$M1-O1$	–	–	2.4477 (15)
$M1-O4$	–	–	2.4789 (16)
$N1-M1-N3$	96.46 (6)	95.74 (5)	–
$N1-M1-S1$	122.45 (4)	119.20 (4)	116.34 (6)
$N1-M1-S2$	112.32 (4)	110.88 (4)	107.66 (6)
$N3-M1-S1$	106.17 (5)	107.25 (4)	–
$N3-M1-S2$	115.05 (4)	116.88 (4)	–
$S1-M1-S2$	104.567 (18)	107.053 (15)	135.97 (2)
$N1-M1-O1$	–	–	96.30 (7)
$N1-M1-O4$	–	–	91.81 (7)
$O1-M1-S1$	–	–	75.89 (4)
$O1-M1-S2$	–	–	101.51 (4)
$O4-M1-S1$	–	–	100.81 (4)
$O4-M1-S2$	–	–	75.56 (4)
$O1-M1-O4$	–	–	171.88 (5)

Notes: (*a*) $M1 = $ Co1; (*b*) $M1 = $ Zn1.

There were missing reflections reported by *PLATON* in (III) and (IV). An inspection of the structure factors has revealed that the missing reflections are located either below θ_{min} or above $\theta = 19°$. The calculated values of intensity for the missing reflections above $\theta = 19°$ [13 for (III) and 19 for (IV)] indicate that their intensity is low or very low. Since the overall completeness of both measurements is above 99%, we assume that the missing reflections do not have a significant influence on the refinement results.

The most discrepant low-angle reflections (outliers) removed from the refinements were 100 for (III); 1$\bar{1}$1 for (IV); and 111, 200, 110 and 112 for (V).

For all three compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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