metal-organic compounds

Tris(*tert*-butyl isocyanide)bis[tris(4-methoxyphenyl)phosphine]cobalt(I) perchlorate dichloromethane disolvate and tris(*tert*-butyl isocyanide)-bis[tris(4-methoxyphenyl)phosphine]-cobalt(II) bis(perchlorate) dichloro-methane disolvate: modification of a trigonal–bipyramidal structure with change of metal oxidation state

Clifford A. L. Becker,[a]* Robert S. Black[b] and Roy P. Forbes[b]

[a]Department of Chemistry, Faculty of Science, University of Botswana, P/Bag 0022, Gaborone, Botswana, and [b]Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, PO Wits 2050, South Africa
Correspondence e-mail: beckerca@mopipi.ub.bw

The title complexes, $[Co(C_5H_9N)_3(C_{21}H_{21}O_3P)_2]ClO_4 \cdot 2CH_2Cl_2$, (I), and $[Co(C_5H_9N)_3(C_{21}H_{21}O_3P)_2](ClO_4)_2 \cdot 2CH_2Cl_2$, (II), respectively, crystallize in the hexagonal space group $P6_3/m$ and the monoclinic space group $P2_1/n$, respectively. The cation of complex (I) has D_{3h} site symmetry around the Co atom and the overall symmetry is C_{3h}. Complex (II) is best described as having a distorted trigonal–bipyramidal coordination, with a Co site symmetry of C_s. Compounds (I) and (II) form an analogous pair of five-coordinate Co^I and Co^{II} complexes with the same ligands, making it possible to establish (i) if the Co site coordination for both complexes is indeed trigonal–bipyramidal, as initially assumed, and (ii) if significant structural differences occur when the oxidation state of the metal is changed.

Comment

Numerous tris(alkyl isocyanide)bis(triarylphosphine)cobalt(I) perchlorate complexes, $[Co(CNR)_3(PR'_3)_2]ClO_4$, have been reported in the literature (Becker *et al.*, 1986, 1991, 1995). Many, but not all, of these Co^I complexes can be converted to the analogous five-coordinate Co^{II} complexes, $[Co(CNR)_3(PR'_3)_2](ClO_4)_2$, through oxidation with $AgClO_4$ (Becker, 2000). Routine characterization has been reported for these complexes, but structural determinations are lacking. Coordination structures for both the Co^I and Co^{II} complexes are expected to be trigonal–bipyramidal. IR data for $\nu(-N\equiv C)$,

in solution and the solid state, suggest that the Co^{II} complexes could have D_{3h} symmetry for the CN*R* ligands (*i.e.* one band), while the Co^I complexes may be distorted from idealized trigonal–bipyramidal coordination (*i.e.* two or three bands), but IR patterns are by no means conclusive for structural determination. There is disagreement in the literature over this assignment, however, particularly with respect to the interpretation of the quasi-reversible cyclic voltammograms (Hanzlik *et al.*, 1980; Becker *et al.*, 1995), which have since been shown to be reversible (Ahmad *et al.*, 2003).
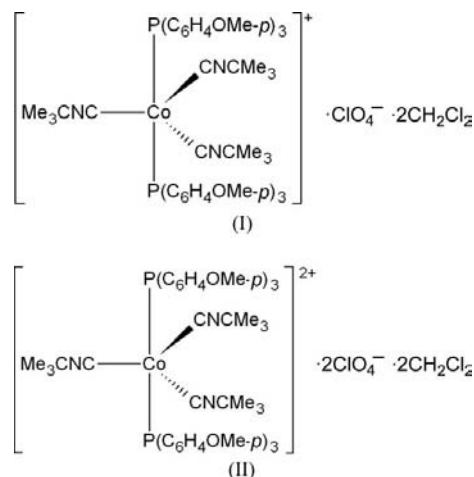
A crystallographic investigation of these complexes seems merited for several reasons. Very few crystal structures are known for phosphine-substituted pentakis(organo isocyanide)cobalt(I) complexes, those few being with aryl isocyanide, not alkyl isocyanide, ligands, and, to our knowledge, no analogous structure for Co^{II} has been reported. Five-coordination for both Co^I and Co^{II} complexes with identical ligands poses several questions: (i) are both coordination structures trigonal–bipyramidal, as usually assumed, and if so, (ii) are there any significant differences in coordination structure? Is one structure closer to idealized D_{3h} Co site symmetry than the other, and if so, is it the Co^I or the Co^{II} complex? These questions can only be answered by a crystallographic study. $[Co(CNCMe_3)_3\{P(C_6H_4OMe-p)_3\}_2]ClO_4$, (I), and $[Co(CNCMe_3)_3\{P(C_6H_4OMe-p)_3\}_2](ClO_4)_2$, (II), have been selected as an appropriate pair of complexes for this study.

Complex (I) is observed to crystallize in the hexagonal space group $P6_3/m$ with six effectively equivalent molecules but three crystallographically independent structures in the unit cell. Where significant differences in the bond lengths and angles are quoted, the three independent values and/or average have been given. The molecular structure is shown in Figs. 1 and 2, with selected bond lengths and angles listed in Table 1. The site symmetry around the Co atom is effectively D_{3h} (point group) symmetry. The entire $Co(C\equiv NC)_3$ moiety is planar with three equivalent Co—C bonds and C—Co—C bond angles of exactly $120°$ (by symmetry), three almost equivalent $C\equiv N$ bonds with Co—$C\equiv N$ bond angles close to the idealized value of $180.0°$ [averaging $179.16 (1)°$] and three almost equivalent N—C bonds, again with $C\equiv N$—C bond angles approaching $180°$ [averaging $177.97 (1)°$]. This gives an

Figure 1
A view of (I) (30% probability displacement ellipsoids). H atoms and disorder have been omitted for clarity.
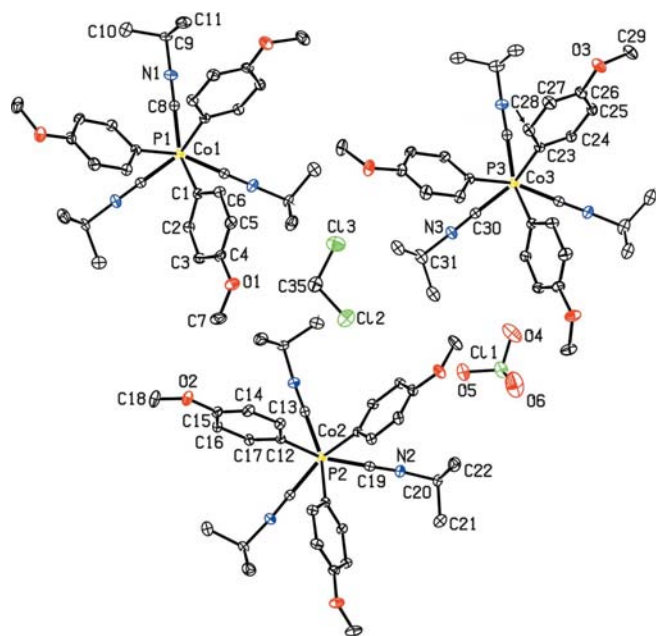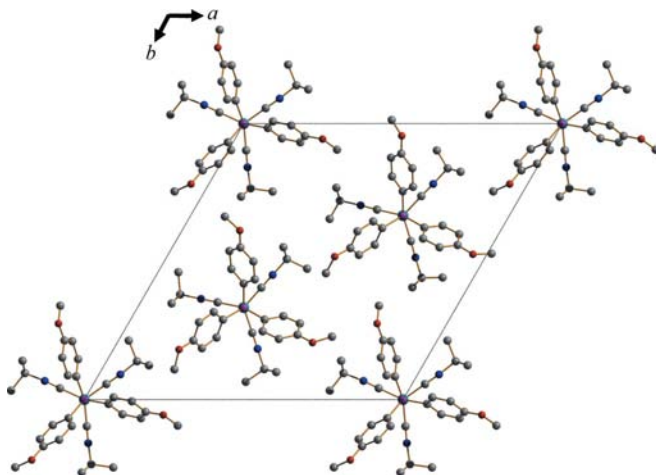

Figure 3
A view of (II) (30% probability displacement ellipsoids). H atoms and disorder have been omitted for clarity.

Figure 2
A packing diagram for (I). The solvent molecules and H atoms have been omitted for clarity.

Figure 4
A packing diagram for (II). The solvent molecules and H atoms have been omitted for clarity.

effective σ_h through the entire Co(CNC)$_3$ unit. The linear P—Co—P bonds are perpendicular to the CoC$_3$ plane, forming the threefold rotation axis. Through the proper alignment of both the nine –CMe$_3$ and six –C$_6$H$_4$OMe-p groups, the P1—Co1—P1 axis is also a crystallographic threefold rotation axis. The upper and lower P(C$_6$H$_4$OMe-p)$_3$ rings are exactly eclipsed but are not properly 60° staggered (rather 43.8 and 76.2° asymmetrically staggered) between the Co—C≡N bonds, preventing three σ_vs, and reducing the overall (point group) symmetry for the [Co(CNCMe$_3$)$_3${P(C$_6$H$_4$OMe-p)$_3$}$_2$]$^+$ cation to C_{3h}. This is still, nevertheless, a very symmetrical ion.

The Co—P bond averaging 2.1783 (6) Å is shorter than that which is normally expected for a Co—P single bond [Cambridge Structural Database (CSD), Conquest 1.11; Allen, 2002], giving support for some degree of $d\pi \rightarrow \pi^*$ back-
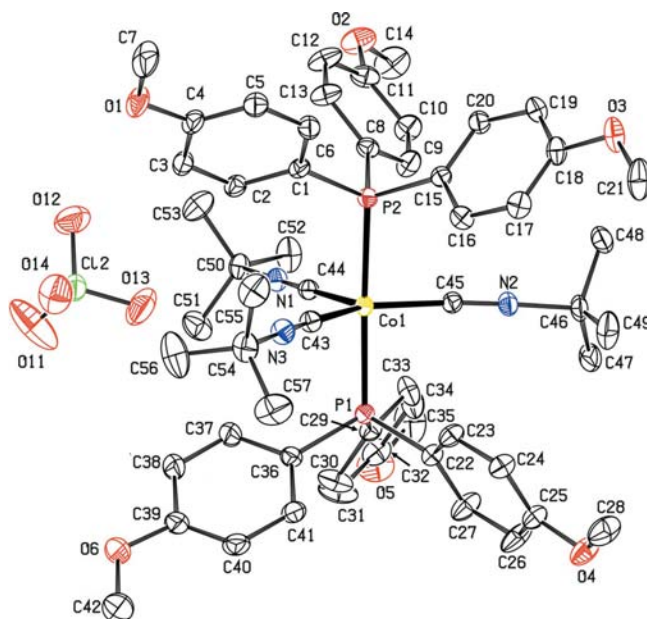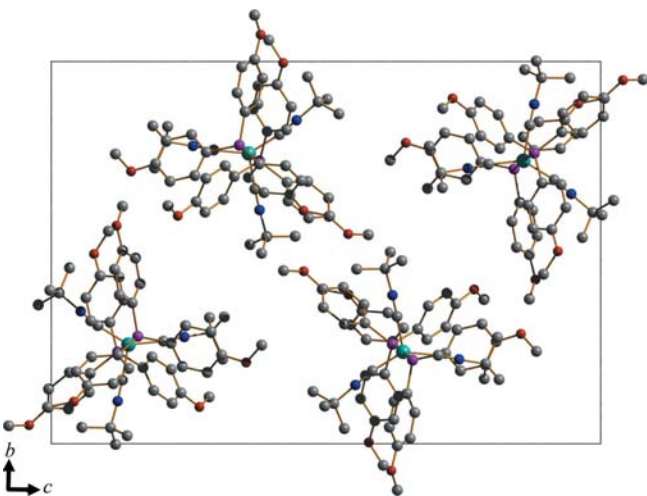
bonding, although less than the very short Co—P bond [*i.e.* 2.052 (5) Å] observed in HCo(PF$_3$)$_4$ (Frenz & Ibers, 1970). The averaged Co—C bond [1.826 (6) Å] is also quite short, supportive of the more extensive back-bonding expected for the organo isocyanide ligands. There is no evidence for hydrogen bonding with either the ClO$_4^-$ anion or the CH$_2$Cl$_2$ molecules.

Complex (II) is observed to crystallize in the monoclinic space group $P2_1/n$. The molecular structure is shown in Figs. 3 and 4, with selected bond lengths and angles listed in Table 2. The cation is best described as distorted trigonal–bipyramidal. The actual site symmetry around the Co atom is low, *i.e.* C_s. The CoC$_3$ moiety appears to be approximately planar, in which case the highest site symmetry is C_s, otherwise it is only

Becker *et al.* · [Co(C$_5$H$_9$N)$_3$(C$_{21}$H$_{21}$O$_3$P)$_2$]ClO$_4$·2CH$_2$Cl$_2$ and –(ClO$_4$)$_2$·2CH$_2$Cl$_2$

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C_1. Three non-equivalent Co—C bonds form equatorial bond angles of 107.96 (11), 109.76 (10) and 142.27 (11)°, instead of the idealized 120.0° angle. The Co—C≡N [averaging 174.3 (2)°] and C≡N—C [averaging 177.5 (9)°] angles, however, are reasonably close to being linear. The C≡N and N—C bond lengths appear normal for these bonds.

In structure (II), the averaged Co—P bond length of 2.2526 (7) Å is also rather short for a Co—P single bond, though not as shortened as seen for (I). Although the ionic radius for Co^{II} is smaller than Co^I, the Co^{2+} ion requires far less $d\pi \rightarrow \pi^*$ electronic stabilization so the Co—P bond in (II) could be expected to be longer than in (I). The Co—C bond length is also shorter in (I) compared to (II), i.e. 1.826 (6) versus 1.888 (2) Å (averaged), while the C≡N bond lengths show a slight increase [i.e. 1.159 (5) versus 1.145 (9) Å (averaged)], as would also be expected. A general insensitivity of the C≡N bond length to apparent bond order, however, has been observed (Cotton et al., 1965). The two perchlorate anions are non-equivalent and somewhat distorted. Again, there is no evidence in (II) for hydrogen bonding with either the perchlorate anions or the CH_2Cl_2 molecules. This may explain why the solvated CH_2Cl_2 is normally so readily lost shortly after preparation of these complexes.

In this pair of complexes, then, the IR data notwithstanding, the five-coordinate Co^I complex, (I), has been shown to have rigorous trigonal–bipyramidal Co coordination (D_{3h}) while the analogous five-coordinate Co^{II} complex, (II), has distorted trigonal–bipyramidal coordination (C_s). Two disubstituted aryl isocyanide Co^I complexes from the literature show similarity with (I): $[Co(CNC_6H_4NO_2-p)_3\{PhP(OEt)_2\}_2]ClO_4$, (III) (Graziani et al., 1976), and $[Co(CNC_6H_4F-p)_3\{P(OCH_3)_3\}_2]$-$BF_4$, (IV) (Loghry et al., 1978). Structural comparisons with these complexes are shown in Table 3. Although (III) and (IV) are clearly trigonal–bipyramidal structures, they do not exhibit the high level of coordination symmetry around the Co atom shown by (I). No analogous structures for disubstituted five-coordinate Co^{II} organo isocyanide complexes could be found in the literature.

Experimental

Complexes (I) and (II) have been synthesized, and routinely characterized, as previously reported, (I) by reaction of excess triarylphosphine with $[Co(CNCMe_3)_4(H_2O)](ClO_4)_2$ (Becker et al., 1986) and (II) by $AgClO_4$ oxidation of (I) (Becker, 2000). X-ray quality crystals of (I), as the dichloromethane disolvate, were obtained by slow evaporation of a CH_2Cl_2/C_6H_{12} solution at room temperature and crystals of (II), also as a dichloromethane disolvate, were obtained by diffusion of C_6H_{12} into CH_2Cl_2 at room temperature.

Compound (I)

Crystal data

$[Co(C_5H_9N)_3(C_{21}H_{21}O_3P)_2]$-$ClO_4 \cdot 2CH_2Cl_2$
$M_r = 1282.32$
Hexagonal, $P6_3/m$
$a = 21.7568$ (3) Å
$c = 23.3983$ (6) Å

$V = 9591.9$ (3) Å^3
$Z = 6$
Mo $K\alpha$ radiation
$\mu = 0.58$ mm^{-1}
$T = 173$ K
$0.38 \times 0.38 \times 0.1$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.809$, $T_{max} = 0.944$

46534 measured reflections
6456 independent reflections
4167 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.152$
$S = 0.97$
6456 reflections

390 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.07$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}

Compound (II)

Crystal data

$[Co(C_5H_9N)_3(C_{21}H_{21}O_3P)_2]$-$(ClO_4)_2 \cdot 2CH_2Cl_2$
$M_r = 1381.77$
Monoclinic, $P2_1/n$
$a = 12.3461$ (3) Å
$b = 19.7566$ (5) Å
$c = 28.4452$ (7) Å

$\beta = 92.818$ (2)°
$V = 6929.9$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.59$ mm^{-1}
$T = 173$ K
$0.43 \times 0.31 \times 0.22$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.787$, $T_{max} = 0.882$

93953 measured reflections
16738 independent reflections
11549 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.146$
$S = 1.06$
16738 reflections
848 parameters

40 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

For both compounds, all H atoms were refined using a riding model, with a C—H distance of 0.98 Å and with $U_{iso}(H) = 1.5U_{eq}(C)$. The highest residual peak for (I) was 1.614 Å from atom Cl1 and for (II) was 0.900 Å from atom C36. The methyl disorder of compound (I) seen on C31 was apparent in the structure, hence atoms C32A/C34A and atoms C32B/C33A where refined with complementary

Table 1
Selected geometric parameters (Å, °) for (I).

Co1—C8^i	1.820 (4)	C30—N3	1.162 (6)
Co2—C19^{ii}	1.834 (4)	N1—C9	1.455 (6)
Co3—C30^{iii}	1.824 (5)	N2—C20	1.453 (6)
P1—Co1	2.1814 (13)	N3—C31	1.449 (7)
P2—Co2	2.1762 (12)	Cl1—O4	1.434 (5)
P3—Co3	2.1774 (13)	Cl1—O5	1.426 (4)
C8—N1	1.157 (6)	Cl1—O6	1.389 (4)
C19—N2	1.158 (6)		
N1—C8—Co1	179.7 (4)	P1^v—Co1—P1	180
N2—C19—Co2	179.2 (4)	P2—Co2—P2^v	180
N3—C30—Co3	178.6 (4)	P3^v—Co3—P3	180
C8—N1—C9	179.7 (5)	C8—Co1—P1^v	90
C19—N2—C20	175.8 (4)	C19—Co2—P2	90
C30—N3—C31	178.4 (5)	C30—Co3—P3	90
C8—Co1—C8^{iv}	120	O5—Cl1—O4	109.8 (3)
C19^{ii}—Co2—C19	120	O6—Cl1—O4	106.5 (2)
C30—Co3—C30^{iii}	120	O6—Cl1—O5	109.4 (2)

Symmetry codes: (i) $-x + y + 1, -x + 1, z$; (ii) $-x + y, -x, z$; (iii) $-y + 1, x - y + 1, z$; (iv) $-y + 1, x - y, z$; (v) $x, y, -z + \frac{3}{2}$.

Table 2
Selected geometric parameters (Å, °) for (II).

Co1—C45	1.876 (3)	N3—C54	1.466 (3)
Co1—C43	1.879 (3)	O7—Cl1	1.392 (3)
Co1—C44	1.910 (3)	O8—Cl1	1.385 (3)
Co1—P1	2.2515 (7)	O9—Cl1	1.416 (3)
Co1—P2	2.2536 (7)	O10—Cl1	1.387 (3)
C44—N1	1.148 (3)	O11—Cl2	1.380 (3)
C45—N2	1.147 (3)	O12—Cl2	1.415 (3)
C43—N3	1.142 (3)	O13—Cl2	1.412 (3)
N1—C50	1.463 (3)	O14—Cl2	1.422 (3)
N2—C46	1.467 (3)		
N1—C44—Co1	177.8 (2)	C45—Co1—P2	89.49 (8)
N2—C45—Co1	170.8 (2)	P1—Co1—P2	177.84 (3)
N3—C43—Co1	174.5 (2)	O7—Cl1—O9	111.4 (2)
C43—N3—C54	177.7 (3)	O8—Cl1—O7	110.4 (2)
C44—N1—C50	177.0 (3)	O8—Cl1—O9	110.3 (2)
C45—N2—C46	178.0 (3)	O8—Cl1—O10	111.0 (3)
C45—Co1—C43	142.25 (12)	O10—Cl1—O7	108.3 (3)
C45—Co1—C44	109.77 (11)	O10—Cl1—O9	105.4 (2)
C43—Co1—C44	107.97 (11)	O11—Cl2—O12	111.9 (3)
C43—Co1—P1	90.57 (8)	O11—Cl2—O13	112.1 (3)
C44—Co1—P1	90.19 (8)	O11—Cl2—O14	109.2 (2)
C45—Co1—P1	88.37 (8)	O12—Cl2—O14	108.0 (2)
C43—Co1—P2	91.31 (8)	O13—Cl2—O12	106.2 (2)
C44—Co1—P2	90.25 (8)	O13—Cl2—O14	109.4 (2)

Table 3
Comparison of selected geometric parameters (Å, °) for (I), with two analogous Co^I–aryl isocyanide complexes.

Parameter	(I)	(III)	(IV)
Co—C	1.825 (6)	1.78 (1)	1.85 (1)
		1.81 (2)	1.83 (1)
C≡N	1.159 (5)	1.16 (2)	1.17 (2)
		1.17 (2)	1.14 (2)
Co—P	2.1784 (12)	2.18 (1)	2.137 (3)
C—Co—C	120	105.0 (5)	115.7 (5)
		125.5 (7)	122.2 (4)
Co—C≡N	179.2 (1)	176 (1)	176 (1)
		177(1.5)	180
		178 (1)	
C≡N—C	178.0 (1)	171 (2)	178 (1)
		172 (2)	180
P—Co—P	180	178.4 (2)	179.7 (4)

Notes: identification of compounds: [Co(CNC$_6$H$_4$NO$_2$-*p*)$_3$[PhP(OEt)$_2$}$_2$]ClO$_4$, (III), and [Co(CNC$_6$H$_4$F-*p*)$_3${P(OMe)$_3$}$_2$]BF$_4$, (IV).

occupancies. The orientational disorder was refined over two positions using an EADP restraint (*SHELXTL*; Sheldrick, 2008); the final occupancy was 0.545 (5) for C32*A*/C34*A* and 0.454 (5) for C32*B*/C33*A*. The apparent solvent disorder in structure (II) was seen on dichloromethane atoms C58/C58*A*, and hence atoms Cl3*A*/Cl4*A* and Cl3*B*/Cl4*B* were refined with complementary occupancies. The orientational disorder was refined over two positions using bond length (DFIX) restraints [1.73 (2) Å] for the C—Cl bond lengths as

well as EADP restraints for C58/C58*A* (*SHELXTL*; Sheldrick, 2008); the final occupancy was 0.489 (8) for Cl3*A*/Cl4*A* and 0.511 (8) for Cl3*B*/Cl4*B*. For satisfactory convergence it was also necessary to fix the coordinates of atoms C58, C58*A*, Cl4*A* and Cl4*B* during refinement. The further solvent disorder seen on C59 and C60*A–D* with its respective Cl atoms were refined with occupancies having been refined as a restrained linear sum of the free variables. These partial molecules have a sum of occupancies of 1.08 (CH$_2$Cl$_2$) (using a SUMP restraint), hence giving rise to discrepancies in the reported molecular weight and densities of the crystal.

For both compounds, data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-NT* (Bruker, 2005); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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