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trans-Chlorido(phenyl)bis(triphenylphosphine)nickel(II) and its 1:1 cocrystal with chloridobis(triphenylphosphine)nickel(I)

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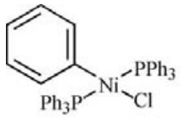
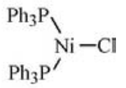
Two conformational polymorphs of *trans*-chlorido(phenyl)bis(triphenylphosphine)nickel(II), $[\mathrm{Ni(C_6H_5)Cl(C_{18}H_{15}P)_2}]$, (1), *viz.* orange needle-shaped crystals (form I) and brown prism-shaped crystals (form II), were obtained under different crystallization conditions from a mixture of toluene and *n*-hexane, and characterized by single-crystal X-ray diffraction at low temperature. These two forms were compared with that published previously [Zeller, Herdtweck & Strassner (2003). *Eur. J. Inorg. Chem.* pp. 1802–1806], characterized at room temperature. Additionally, blue–green prisms of a 1:1 cocrystal of complex (1) with chloridobis(triphenylphosphine)nickel(I), (2), *viz.* *trans*-chlorido(phenyl)bis(triphenylphosphine)nickel(II)–chloridobis(triphenylphosphine)nickel(I) (1/1), $[\mathrm{Ni(C_6H_5)Cl(C_{18}H_{15}P)_2}]\cdot[\mathrm{NiCl(C_{18}H_{15}P)_2}]$, (3), were obtained concomitantly with form I. In forms I and II, as well as in the cocrystal, the overall crystal packings are determined by an energetic interplay between intramolecular torsions and weak intermolecular C—H$\cdots\pi$ and C—H$\cdots$Cl interactions.

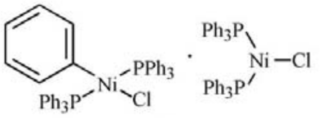
Comment

In the last decade, a new class of neutral nickel catalysts based on salicylaldimine or anilinotropone ligands, which are highly active in alkene polymerization and which do not need to be activated by the expensive methylaluminoxane (MAO) co-catalyst, has attracted increasing interest in academia and industry (Wang *et al.*, 1998; Younkin *et al.*, 2000; Hicks & Brookhart, 2001). Due to their reduced oxophilicity and better tolerance to functional groups, these catalysts are able to copolymerize alkenes with polar co-monomers showing good activities. Such polymerizations can be run in polar media, even in aqueous solutions or emulsions (Bauers & Mecking, 2001; Mecking *et al.*, 2002; Held *et al.*, 2000; Korthals *et al.*, 2006; Soula *et al.*, 2001; Tomov *et al.*, 2000). In addition, they are capable of forming polymers with controllable topologies by virtue of the ‘chain walking’ mechanism (Johnson *et al.*, 1995).

A key intermediate and organometallic precursor for the synthesis of this type of catalyst is the title compound, *trans*-$[\mathrm{Ni(Ph)Cl(PPh_3)_2}]$, (1). Compound (1) and its analogues *trans*-$[\mathrm{Ni}(R)X(\mathrm{P}R'_3)_2]$ (X = Cl or Br; R = $\mathrm{C_6H_5}$, 2-$\mathrm{ClC_6H_4}$, $\mathrm{C_6F_5}$, $\mathrm{CF{=}CF_2}$, *etc.*; R' = Ph, Me or Et) have been prepared mainly by two methods, namely the reaction of compounds of the type $[\mathrm{Ni}X_2(\mathrm{P}R_3)_2]$ with aryl Grignard reagents or alkali metal compounds (Chatt & Shaw, 1960; Rausch & Tibbetts, 1970; Miller *et al.*, 1968), and the oxidative addition of aryl halides to nickel(0) complexes (Dahey, 1970; Hidai *et al.*, 1971). Recently, Zeller *et al.* (2003) reported a one-pot synthesis of complex (1) from readily available and inexpensive reagents, with an apparently improved overall yield, and they reported its structure at 293 K [Cambridge Structural Database (Allen, 2002) refcode VALCIV].


(1)


(2)


(3)

In this context, we have prepared compound (1) employing Zeller’s method but we have found that, besides the orange monoclinic crystals of (1) (form I) already described (Zeller *et al.*, 2003), blue–green crystals of its 1:1 cocrystal, (3), with the $\mathrm{Ni^I}$ complex $[\mathrm{NiCl(PPh_3)_2}]$, (2), were also formed. This by-product very likely originates from the elimination of a phenyl radical from complex (1). In fact, while repeating Zeller’s procedure several times, we have consistently observed the presence of significant amounts of the paramagnetic $\mathrm{Ni^I}$ complex (2). This observation agrees with the characterization data presented in the original paper, namely the microanalysis of (1), which reported an experimental value of the carbon content 0.66% lower than that expected [corresponding to a fraction of (2) > 10 mol%], and with the corresponding ^{1}H NMR spectrum, the resonances of which were described as broad, not presenting the expected multiplicities (Zeller *et al.*, 2003). We have reacted complex (1), which was synthesized by the latter method, with iminopyrrolyl sodium salts (Bellabarba *et al.*, 2003; Carabineiro *et al.*, 2007, 2008) in order to obtain nickel iminopyrrolyl complexes of the type $[\mathrm{Ni}\{\kappa^2N,N'\text{-}\mathrm{NC_4H_3C}(R)\mathrm{{=}N\text{-}2,6\text{-}{}^{\mathit{i}}Pr_2C_6H_3}\}_2\mathrm{(Ph)(PPh_3)}]$ (R = H, Me) (Bellabarba *et al.*, 2003). After isolating the desired compound, we recovered from the mother liquor a new orthorhombic polymorph of unreacted (1) (form II). We report here the structures of complex (1) in the two polymorphic forms I

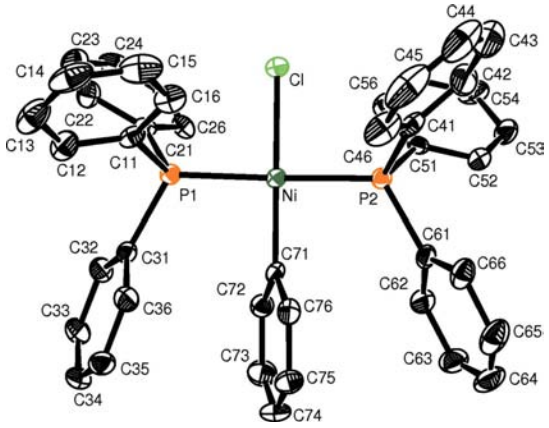


Figure 1
The molecular structure of complex (1) (form II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

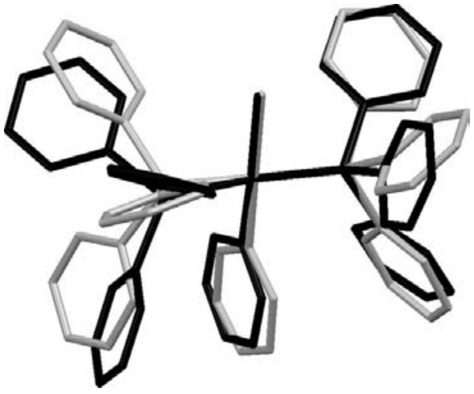


Figure 2
An overlay of complex (1) in the different polymorphs. Form I is shown in black and form II in grey.

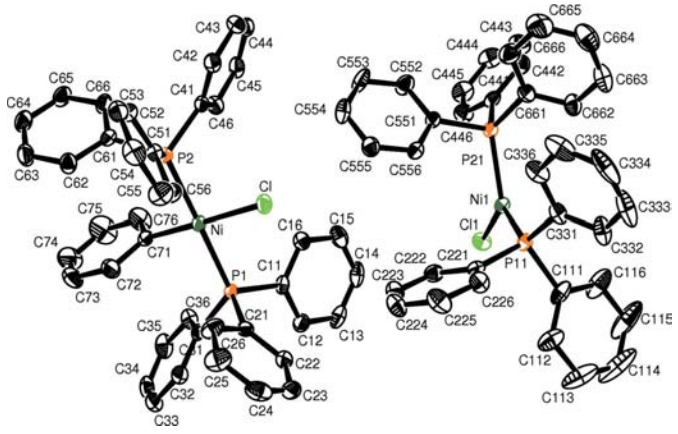


Figure 3
The molecular structures of complexes (1) and (2) in 1:1 cocrystal (3), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

and II, and in a 1:1 cocrystal of complex (1) with complex (2), *viz*. (3).

The molecular and crystal structure of (1) in form I is the same as in VALCIV, the only difference being the data collection temperature (VALCIV at 293 K and form I at 150 K), whereas the molecular and crystal structures of (1) in form II are noticeably different from those in form I. Complex (1) crystallizes in the monoclinic space group $P2_1/c$ (form I) and in the orthorhombic space group *Pbca* (form II). Table 1 summarizes the most relevant bond distances, angles and torsion angles of the two polymorphic forms. The molecules of (1) in both forms I and II are structurally similar. The Ni^{II} atom is coordinated by two PPh_3 groups in a *trans* fashion, by a Cl atom and by a phenyl group, in total showing a square-planar geometry, as displayed in Fig. 1. A more pronounced distortion around the metal centre, as given by the dihedral angle between the planes formed by atoms P1/Ni/Cl and P2/Ni/C71, can be observed in form I [12.09 (4)°], whereas in form II the molecules show a virtually undistorted square-planar geometry [1.67 (3)°] which deviates very slightly from an optimum value of 0°. The corresponding dihedral angle observed for complex (1) in the cocrystal is 2.96 (6)°. Fig. 2 compares schematically the differences in the molecules of (1) in forms I and II. It can be seen that forms I and II lead to different conformers. In molecule (1), the phenyl groups are subjected to rotations about the single bonds P*n*—C*m*1 (n = 1 or 2, m = 1–6) and Ni—C71, ultimately leading to diverse molecular conformations (see Table 1).

Molecular conformations can differ by rotations about single bonds (intramolecular torsions), which commonly involve energies of around 1–3 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) (Nangia, 2008). The packing of molecules in crystals depends upon diverse intermolecular interactions, including hydrogen-bonding and van der Waals interactions. Generally, the energies of the intramolecular torsions and intermolecular interactions lie in the same range of magnitude, meaning that they can compensate each other. In the molecular packing of complex (1), due to the absence of strong intermolecular interactions (*e.g.* hydrogen bonds), the torsional geometries produced in forms I and II are mainly compensated by diverse weak intermolecular interactions. Form I only has weak C—H$\cdots\pi$ interactions, while polymorph II presents stronger C—H$\cdots$Cl interactions, which are responsible for the different conformation. Table 2 summarizes these weak intermolecular interactions as well as those present in the cocrystal.

Complexes of nickel(I) are far less known than those of nickel(0) and nickel(II). Compounds of the type [NiX(PR_3)$_2$] have been reported to be either dimeric or oligomeric, since these 15-electron species could possibly associate due to their unsaturated nature (Cundy & Nöth, 1971; Lappert & Speier, 1974; Aresta *et al.*, 1975). Recently, the monomeric complex (2) and its tetrahydrofuran (THF) solvate have been prepared as side-products from the decomposition of (1) or [NiCl(PPh$_3$)$_3$] and crystallographically characterized (Ellis & Spek, 2000; Norman *et al.*, 2002). Consistent with the findings of those workers, complex (2) is monomeric in the present 1:1 cocrystal with complex (1) (Fig. 3). The Ni centre is coordi-

Acta Cryst. (2009). C**65**, m110–m114 Li *et al.* • $[\text{Ni}(\text{C}_6\text{H}_5)\text{Cl}(\text{C}_{18}\text{H}_{15}\text{P})_2]$ and $[\text{Ni}(\text{C}_6\text{H}_5)\text{Cl}(\text{C}_{18}\text{H}_{15}\text{P})_2]\cdot[\text{NiCl}(\text{C}_{18}\text{H}_{15}\text{P})_2]$ **m111**

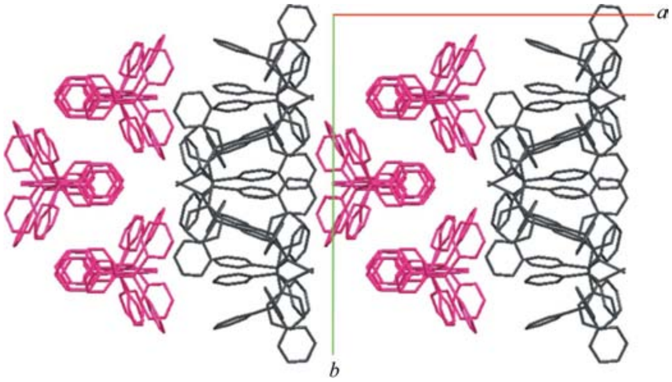


Figure 4
A view of the crystal packing of cocrystal (3) along *c*, showing the alternating layers along *a*.

nated by two PPh_3 groups, with Ni1—P distances of 2.2152 (7) and 2.2128 (7) Å, and by a Cl atom, with an Ni1—Cl1 distance of 2.1566 (8) Å, and it lies 0.1302 (4) Å out of the P11$\cdots$P21$\cdots$Cl1 plane, thus showing a distorted trigonal–planar geometry. The P11—Ni1—P21 angle of 113.60 (3)° is significantly smaller than the corresponding Cl1—Ni1—P angles of 121.87 (3) and 123.48 (3)°, their sum [358.95 (5)°] being slightly lower than the expected value of 360°. These angular differences are thought to be caused by a first-order Jahn–Teller effect (Norman *et al.*, 2002). These Ni—P and Ni—Cl bonds in the present cocrystal are slightly shorter than those reported for the crystal of the pure complex [Ni—P = 2.2536 (5) and 2.2393 (5) Å; Ni—Cl = 2.1666 (6) Å; Ellis & Spek (2000)], while the reported P—Ni—P [114.94 (2)°] and Cl—Ni—P angles [121.12 (2) and 123.56 (2)°] are very similar to those in cocrystal (3). Comparisons of compound (2) in the cocrystal with that in the THF solvate (Norman *et al.*, 2002) also show some differences. All the Ni—P and Ni—Cl bond distances of (2) in the cocrystal are slightly longer than those in the THF solvate [Ni—P = 2.2091 (6) and 2.2012 (6) Å; Ni—Cl = 2.1481 (6) Å]. Of the Cl—Ni—P angles in the THF solvate [121.33 (2) and 126.98 (2)°], the latter shows the largest difference to those of (2) in the cocrystal. Additionally, the P—Ni—P angle in the solvate [111.52 (2)°] is slightly smaller than the corresponding angle in the cocrystal.

In the cocrystal concomitantly crystallized with form I, the main intermolecular interactions are of the C—H$\cdots\pi$ type and are present between molecules of complex (1) (C35—H35$\cdots$*Cg*4^{iii} and C63—H63$\cdots$*Cg*1^{iv}; see Table 2 for symmetry codes and geometry), between molecules of complex (2) (C114—H114$\cdots$*Cg*5^{v}) and between molecules of (1) and (2) (C223—H223$\cdots$*Cg*1 and C554—H554$\cdots$*Cg*3). Fig. 4 shows the overall crystal packing viewed along the *c* axis, where alternating layers of complex (1) can be seen packed in an almost completely eclipsed fashion, and complex (2) packed in a staggered manner. As described above, both the molecular and crystal structures of forms I and II of complex (1) and of cocrystal (3) are determined by an energetic interplay between intramolecular torsions and weak intermolecular interactions (*e.g.* C—H$\cdots\pi$ and C—H$\cdots$Cl).

Experimental

The synthetic procedure used by Zeller *et al.* (2003) for the preparation of (1) was followed. Orange monoclinic crystals of (1) (form I), contaminated by blue–green 1:1 cocrystals (3), were grown from toluene double-layered with *n*-hexane at 253 K.

Brown prism-shaped crystals of (1) (form II) were isolated in the work-up procedure of an equimolar reaction of the iminopyrrolyl salt $Na[NC_4H_3C(H){=}N\text{-}2,6\text{-}{}^iPr_2C_6H_3]$ with complex (1), prepared according to the procedure of Zeller *et al.* (2003), under similar conditions to those reported by Bellabarba *et al.* (2003). The toluene reaction mixture was concentrated by partial evaporation of the solvent, and *n*-hexane was added, with stirring, to precipitate the desired compound, *viz.* $[Ni\{\kappa^2N,N'\text{-}NC_4H_3C(H){=}N\text{-}2,6\text{-}{}^iPr_2C_6H_3\}_2(Ph)(PPh_3)]$, at room temperature, which was isolated by filtration. The remaining mother liquor was cooled to 253 K, from which crystals of unreacted complex (1) (form II) were grown.

Form I of compound (1)

Crystal data

$[Ni(C_6H_5)Cl(C_{18}H_{15}P)_2]$
M_r = 695.80
Monoclinic, $P2_1/c$
a = 15.6010 (10) Å
b = 11.8690 (9) Å
c = 19.857 (2) Å
β = 112.139 (4)°
V = 3405.8 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.77 mm^{-1}
T = 150 (2) K
0.17 × 0.10 × 0.06 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.880, T_{max} = 0.955
77866 measured reflections
6506 independent reflections
5091 reflections with $I > 2\sigma(I)$
R_{int} = 0.069

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.073
S = 1.04
6506 reflections
415 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Form II of compound (1)

Crystal data

$[Ni(C_6H_5)Cl(C_{18}H_{15}P)_2]$
M_r = 695.80
Orthorhombic, $Pbca$
a = 11.7990 (5) Å
b = 23.368 (2) Å
c = 25.1300 (11) Å
V = 6928.8 (7) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.76 mm^{-1}
T = 150 (2) K
0.22 × 0.14 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.851, T_{max} = 0.942
35219 measured reflections
6075 independent reflections
3874 reflections with $I > 2\sigma(I)$
R_{int} = 0.094

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.088
S = 0.97
6075 reflections
415 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Cocrystal (3)

Crystal data

$[Ni(C_6H_5)Cl(C_{18}H_{15}P)_2]\cdot[NiCl(C_{18}H_{15}P)_2]$
$M_r = 1314.50$
Monoclinic, $P2_1/c$
$a = 24.183\ (6)$ Å
$b = 12.257\ (3)$ Å
$c = 23.712\ (5)$ Å
$\beta = 113.781\ (8)^\circ$
$V = 6432\ (3)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.81$ mm^{-1}
$T = 150\ (2)$ K
$0.23 \times 0.17 \times 0.07$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.835$, $T_{max} = 0.945$
109681 measured reflections
13903 independent reflections
10162 reflections with $I > 2\sigma(I)$
$R_{int} = 0.078$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.093$
$S = 1.04$
13903 reflections
775 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

All H atoms were placed in idealized positions and allowed to refine riding on their parent C atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

For all compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *WinGX* (Farrugia, 1999).

Table 1
Selected geometric parameters for forms I and II of (1) (Å, °).

	Form I	Form II
Ni—Cl	2.2195 (6)	2.2369 (9)
Ni—C71	1.8824 (19)	1.893 (3)
Ni—P1	2.2197 (6)	2.2149 (8)
Ni—P2	2.2106 (6)	2.2099 (8)
Cl—Ni—P1	92.39 (2)	88.71 (3)
Cl—Ni—P2	88.25 (2)	89.55 (3)
C71—Ni—P1	88.59 (6)	91.41 (9)
C71—Ni—P2	91.98 (6)	90.33 (9)
Cl—Ni—P1—C11	−47.09 (8)	−65.73 (11)
Cl—Ni—P1—C21	72.23 (8)	55.42 (10)
Cl—Ni—P1—C31	−165.63 (9)	173.50 (9)
Cl—Ni—P2—C41	63.46 (7)	53.51 (12)
Cl—Ni—P2—C51	−55.18 (9)	−64.20 (11)
Cl—Ni—P2—C61	−176.84 (10)	171.78 (10)
C71—Ni—P1—C11	139.55 (10)	114.24 (13)
C71—Ni—P1—C21	−101.13 (10)	−124.62 (12)
C71—Ni—P1—C31	21.01 (11)	−6.53 (12)
C71—Ni—P2—C41	−123.24 (10)	−126.46 (14)
C71—Ni—P2—C51	118.12 (11)	115.83 (13)
C71—Ni—P2—C61	−3.55 (12)	−8.19 (12)
P2—Ni—P1—C11	46.26 (17)	−21.89 (80)
P2—Ni—P1—C21	165.58 (14)	99.25 (78)
P2—Ni—P1—C31	−72.28 (16)	−142.67 (72)
P1—Ni—P2—C41	−30.26 (17)	9.69 (80)
P1—Ni—P2—C51	−148.90 (15)	−108.01 (78)
P1—Ni—P2—C61	89.44 (16)	127.97 (77)

Table 2
Intermolecular interactions (Å, °) in forms I and II of (1), and in cocrystal (3).

*Cg*1, *Cg*2, *Cg*3, *Cg*4 and *Cg*5 are the centroids of the rings C11–C16, C21–C26, C41–C46, C51–C56 and C441–C446, respectively.

	D—H$\cdots A$	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
Form I of (1)	C63—H63$\cdots Cg2^{i}$	2.94	3.788 (3)	151
Form II of (1)	C54—H54$\cdots Cl^{ii}$	2.83	3.499 (3)	130
Cocrystal (3)	C35—H35$\cdots Cg4^{iii}$	2.89	3.763 (3)	158
	C63—H63$\cdots Cg1^{iv}$	2.76	3.607 (3)	152
	C114—H114$\cdots Cg5^{v}$	2.96	3.794 (4)	150
	C223—H223$\cdots Cg1$	2.80	3.629 (3)	149
	C554—H554$\cdots Cg3$	2.80	3.673 (3)	156

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3267). Services for accessing these data are described at the back of the journal.

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