

Data collection

Siemens R3M diffractometer $R_{\text{int}} = 0.032$
 $\theta/2\theta$ scans $\theta_{\text{max}} = 25.15^\circ$
 Absorption correction: $h = -14 \rightarrow 13$
 ψ scan (SHELXTLPC; $k = 0 \rightarrow 11$
 Sheldrick, 1994) $l = 0 \rightarrow 22$
 $T_{\text{min}} = 0.127$, $T_{\text{max}} = 0.185$ 2 standard reflections
 3997 measured reflections every 98 reflections
 3785 independent reflections intensity decay: <2%
 2614 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\text{max}} = <0.01$
 $R[F^2 > 2\sigma(F^2)] = 0.027$ $\Delta\rho_{\text{max}} = 0.512 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.055$ $\Delta\rho_{\text{min}} = -0.489 \text{ e } \text{\AA}^{-3}$
 $S = 0.926$ Extinction correction: none
 3785 reflections Scattering factors from
 287 parameters *International Tables for*
 H atoms riding *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.024P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected bond lengths (Å)

Re—C1	1.927 (7)	Re—N1	2.217 (4)
Re—C2	1.900 (6)	Re—N2	2.217 (4)
Re—C3	1.912 (6)	Re—Br	2.630 (1)

Data collection: P3/P4-PC (Siemens, 1991). Cell refinement: P3/P4-PC. Data reduction: SHELXTLPC (Sheldrick, 1994). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: SHELXTLPC. Software used to prepare material for publication: CSD (Allen & Kennard, 1993), SHELXL97 and PARST (Nardelli, 1983).

Data collection was performed at the Universidad de Chile on a single-crystal diffractometer purchased by Fundación Andes.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1459). Services for accessing these data are described at the back of the journal.

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Bis(1-ethyl-3-methylimidazolium) Tetra-chloropalladate(II)

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Abstract

The title compound, (C₆H₁₁N₂)₂[PdCl₄], is a salt that consists of a square-planar tetrachloropalladate(II) anion having interactions, *via* the chlorides, to ring H atoms on two 1-ethyl-3-methylimidazolium (MEI⁺) cations. The Pd atom resides at a center of inversion. Cl[−]⋯H distances range from 2.75 to 3.24 Å, some of which suggest hydrogen bonding. As the title compound was obtained from an acidic room-temperature melt of the chloride salt of the MEI⁺ cation and AlCl₃, a possible use of this type of system as an alternate medium for crystallization is indicated.

Comment

The 1-ethyl-3-methylimidazolium cation (MEI⁺) is an important constituent of the room-temperature molten salt system produced by mixing 1-ethyl-3-methylimidazolium chloride (MEIC) and aluminium chloride. Previous studies (Scordilis-Kelly & Carlin, 1993; Carlin *et al.*, 1994; De Long *et al.*, 1994; Lee *et al.*, 1996) of this unique molten salt system have centered around electrochemical studies of its utility as a room-temperature electrolyte for rechargeable energy-storage batteries, as well as a medium for electrodeposition of metal species solvated in the melt.

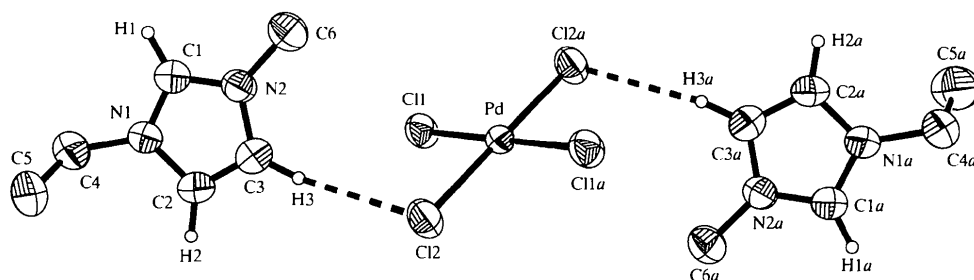
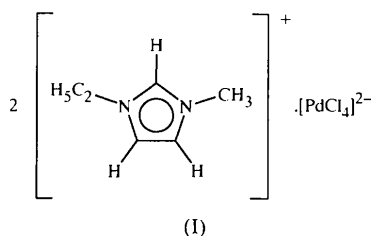


Fig. 1. View of the $(\text{MEI})_2\text{PdCl}_4$ molecule showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small spheres of arbitrary radii.

Very little work has centered around the chemical reactivity of this molten salt system with transition metal coordination compounds and organometallic complexes. Our studies have focused on the solvation and reaction of square-planar transition metal acetylacetonate (acac) complexes in order to understand their interactions with the $\text{MEIC}/\text{AlCl}_3$ system and characterize potential reaction products.

Previously, the title compound, (I), was synthesized by the solid-state reaction of MEIC and PdCl_2 at 423 K (De Long *et al.*, 1994), but no room-temperature synthesis or X-ray crystal structure of this compound has been published; in addition, it was suggested that Pd^{II} might exist in the melt as $\text{Pd}(\text{AlCl}_4)_n^{(2-n)-}$ (*sic*) [should be $(n-2)$]. Sun & Hussey (1989) report that Pd^{II} exists in the basic molten salt as PdCl_4^{2-} . Our work shows that PdCl_4^{2-} may be the likely species in the acidic melt as well.



Bond lengths of the imidazolium cation (Fig. 1) match well with studies performed by Levasseur & Beauchamp (1991). Though the C2—C3 distance is consistent with a localized double bond, delocalization appears to be present around C1 as C1—N1 and C1—N2 distances are within $\sim 2\sigma$ of each other. As the difference between the C2—N1 and C3—N2 lengths is just barely $>3\sigma$, inferences about localization are probably not justifiable. Bond distances and angles for the PdCl_4^{2-} anion are in agreement with those of Valle & Ettorre (1994). The N1—C4—C5 plane is at an angle of $66.8(3)^\circ$ to the ring plane.

All ring H atoms are involved in close interactions with Cl atoms at distances ranging from 2.74 to 3.24 Å. Each chlorine is involved in at least one short contact

with a ring hydrogen (asymmetric or symmetry-related unit) that is consistent with possible hydrogen bonding (see Table 2). Though each ring H atom is covalently bonded to a carbon, the $\delta(+)$ charge of each hydrogen appears to be high enough to facilitate attractions. Verification of this would be useful to understand the nature of the inter-ionic bonding better.

A Hartree-Fock/6-31G* basis set geometry-optimized calculation (*PC SPARTAN-Plus*; Wavefunction Inc., 1997) of MEI^+ gave the following $\delta(+)$ Mulliken charges for H1–H3, respectively: 0.307, 0.297 and 0.298. This favorably parallels an identical calculation of the corresponding H-atom charges in the unsubstituted imidazolium cation (0.333, 0.316 and 0.316). By way of comparison, a similar calculation for benzene shows that the H-atom $\delta(+)$ charge is 0.119, for ethylene is 0.176 and for ethylenic H atoms in *trans*-diaminoethylene is 0.164. All of these $\delta(+)$ charges are roughly half that found in MEI^+ , though not as large as that of the amide H atoms of the unsubstituted imidazolium ion (well known to form hydrogen bonds) at 0.471. So, although the $(\text{MEI})_2\text{PdCl}_4$ crystal is likely held together primarily by weak hydrogen bonds, the extent to which this type of interaction exists in the molten salt is yet to be proved.

Experimental

The title compound was synthesized by the reaction of planar $\text{Pd}(\text{acac})_2$ with an acidic room-temperature molten salt ($\text{MEIC}/\text{AlCl}_3$; $X = 0.33/0.67$). Upon initial addition of the $\text{Pd}(\text{acac})_2$ to the molten salt, an orange powder quickly precipitated. This was washed with cold benzene to remove excess melt and was then recrystallized at 258 K from MeOH to yield the crystal used in the analysis. Concurrently, crystals appeared in *ca* one week in an NMR tube of a saturated solution of the title compound in the melt. This discovery implies that this molten salt might also be useful as a new and unconventional means of product formation and/or crystallization.

Crystal data

$(\text{C}_6\text{H}_{11}\text{N}_2)_2[\text{PdCl}_4]$
 $M_r = 470.54$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Monoclinic

 $P2_1/c$ $a = 9.049 (3) \text{ \AA}$ $b = 12.898 (4) \text{ \AA}$ $c = 9.391 (2) \text{ \AA}$ $\beta = 115.65 (2)^\circ$ $V = 988.0 (5) \text{ \AA}^3$ $Z = 2$ $D_x = 1.582 \text{ Mg m}^{-3}$ D_m not measured

Cell parameters from 50 reflections

 $\theta = 7.0\text{--}20.9^\circ$ $\mu = 1.478 \text{ mm}^{-1}$ $T = 288 (2) \text{ K}$

Spearpoint

 $0.63 \times 0.38 \times 0.19 \text{ mm}$

Orange

Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXTL/PC* and *SHELXL93*.

We are grateful to Jonathan E. Stevens for help with the quantum calculations.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1431). Services for accessing these data are described at the back of the journal.

Data collection

Siemens P3 diffractometer

 $\theta/2\theta$ scans

Absorption correction:

empirical via 8 ψ scansin 10° steps (Siemens,

1991a)

 $T_{\min} = 0.724$, $T_{\max} = 0.755$

2425 measured reflections

1742 independent reflections

1432 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.013$ $\theta_{\max} = 25.04^\circ$ $h = -1 \rightarrow 10$ $k = -3 \rightarrow 15$ $l = -11 \rightarrow 10$

3 standard reflections

every 50 reflections

intensity decay: average

of 0.88% in $\sigma(I)$ **Refinement**Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.030$ $wR(F^2) = 0.078$ $S = 1.081$

1738 reflections

98 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2$ $+ 0.2846P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.896 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.296 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)Table 1. Selected geometric parameters (\AA , $^\circ$)

Pd—C11	2.3001 (10)	N2—C1	1.317 (5)
Pd—C12	2.3094 (11)	N2—C3	1.365 (5)
N1—C1	1.325 (5)	N2—C6	1.460 (5)
N1—C2	1.382 (5)	C2—C3	1.325 (6)
N1—C4	1.469 (5)	C4—C5	1.477 (7)
C11—Pd—C12	90.49 (4)	C3—N2—C6	125.5 (4)
C1—N1—C2	107.4 (3)	N2—C1—N1	109.0 (3)
C1—N1—C4	126.5 (4)	C3—C2—N1	107.4 (4)
C2—N1—C4	125.8 (3)	C2—C3—N2	107.6 (4)
C1—N2—C3	108.5 (3)	N1—C4—C5	111.2 (5)
C1—N2—C6	125.9 (3)		

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

$D\text{---}H\text{---}A$	$D\text{---}H$	$H\text{---}A$	$D\text{---}A$	$D\text{---}H\text{---}A$
C1—H1...C11 ⁱ	0.96	2.79	3.527 (5)	134
C2—H2...C11 ⁱⁱ	0.96	2.75	3.666 (5)	160
C3—H3...C12	0.96	2.74	3.664 (5)	162
C6—H6B...C11 ⁱ	0.96	2.77	3.657 (5)	153

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.H-atom refinement was constrained with C—H distances of 0.96 \AA . Methyl H atoms were located in a difference map and then idealized.Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991a). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).**References**

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Acta Cryst. (1998). **C54**, 1596–1600**fac-Tricarbonylchlorobis(pyridine-N)-rhenium and fac-Tricarbonylchlorobis(4,4'-bipyridine-N)rhenium**

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AbstractStructural analyses for the title compounds, (OC-6-32)-tricarbonylchlorobis(pyridine-N)rhenium(I), $[ReCl(C_5H_5N)_2(CO)_3]$, and (OC-6-32)-tricarbonylchlorobis-