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$[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}I)_4]^+[FeI_4]^-.\text{-}$ $[(\eta^5\text{-}C_5Me_5)_2Mo_2I_2(\mu\text{-}I)_2(\mu\text{-}O)]$

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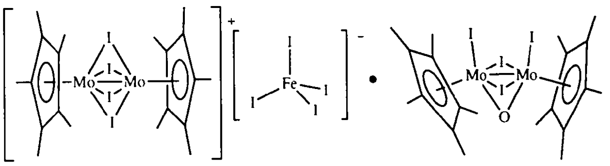
Abstract

The title compound, tetra-μ-iodo-bis[(η^5-pentamethylcyclopentadienyl)molybdenum](*Mo—Mo*) tetraiodoferrate(III) di-μ-iodo-μ-oxo-bis[iodo(η^5-pentamethylcyclopentadienyl)molybdenum](*Mo—Mo*), forms as a by-product of the thermal decarbonylation of $[(\eta^5\text{-}C_5Me_5)MoI_3(CO)_2]$ in tetrahydrofuran. The source of the iron is an impurity in the $[(\eta^5\text{-}C_5Me_5)_2Mo_2(CO)_3]_2$ starting material used to make the triiodide compound. The structure consists of three independent species, namely a $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}I)_4]^+$ cation with two pentamethylcyclopentadienylmolybdenum moieties bridged by four iodide ligands, a tetrahedral $[FeI_4]^-$ anion and a neutral dinuclear species comprising two pentamethylcyclopentadienyliodomolybdenum units bridged by two iodide and an oxo ligand. All three fragments sit on crystallographic mirror planes in the monoclinic space group $P2_1/m$.

Comment

The title compound, (I), crystallizes in the monoclinic space group $P2_1/m$ with one half of each moiety in the asymmetric unit. The cation $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}I)_4]^+$ (Fig. 1) sits on a mirror plane which passes through atoms Mo(21), Mo(22), I(21), I(22), C(211), C(2111), C(221) and C(2211). The pentamethylcyclopentadienyl groups are η^5-bonded to the Mo atoms with Mo—C distances in the range 2.28–2.36 Å. The two metal atoms are at a bonding distance of 2.704 (2) Å from each other and are bridged by four iodide ligands with Mo—I distances in the range 2.735–2.774 Å. The metal–metal distance compares rather well with that observed for the same cation in the triiodide salt [2.718 (3) Å] (Desai, Gordon, Kraatz, Lee, Owens-Waltermire, Poli, Rheingold & White, 1994) as well as with the distance in the reduced neutral complexes $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}I)_4]$ [2.708 (3) Å] (Shin & Parkin, 1994) and $[(\eta^5\text{-}C_9H_7)_2Mo_2(\mu\text{-}I)_4]$ [2.720 (4) Å] (Falvello, Mattamana & Poli, 1995). The Mo—Mo distance for this structural type is not sensitive to the oxidation state because electrons are being pulled from non-bonding orbitals (Green, Green, Mountford & Parkington, 1990). The Mo—I distances are also comparable to, although at the short end of the range of, those reported for the above-mentioned neutral and oxidized dimolybdenum complexes {2.77–2.80 Å for $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}I)_4]^+[I_3]^-$, 2.78–2.80 Å for $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}I)_4]$, and 2.80–2.82 Å for $[(\eta^5\text{-}C_9H_7)_2Mo_2(\mu\text{-}I)_4]$)}, in accord with our assignment of this fragment as a positively charged, $Mo_2^{III,IV}$ species.



(I)

The anion (Fig. 2) sits on a mirror plane which passes through the Fe, I(31) and I(32) atoms. The geometry is close to ideal tetrahedral, the I—Fe—I angles being in the narrow range 107.4 (1)–111.4 (1)°. The Fe—I distances are in the range 2.510 (3)–2.546 (3) Å [average 2.531 (15) Å]. These compare very well with those found for the previously reported structures of $[FeI_4]^-$ salts, namely (all values are averages over chemically equivalent distances) 2.531 (3) and 2.539 (2) Å for tetragonal and orthorhombic crystals, respectively, of the tetraethylammonium salt (Pohl & Saak, 1985), 2.539 (21) Å for $[Fe(CH_2O)_6][FeI_4]_2.I_2$ (Saak & Pohl, 1987), 2.541 (15) Å for $[(Me_2N)_2CSSC(NMe_2)_2]^{2+}[FeI_4^-]_2$ (Bierbach, Saak, Haase & Pohl, 1990), 2.533 (15) Å for $[\{(\eta^5\text{-}C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2\}_2Fe]^+[FeI_4]^-$ (Pasynskii, Eremenko, Stomakhina, Nefedov, Ellert, Yanovsky & Struchkov, 1991) and 2.541 (12) Å for $[SbPh_4]$-

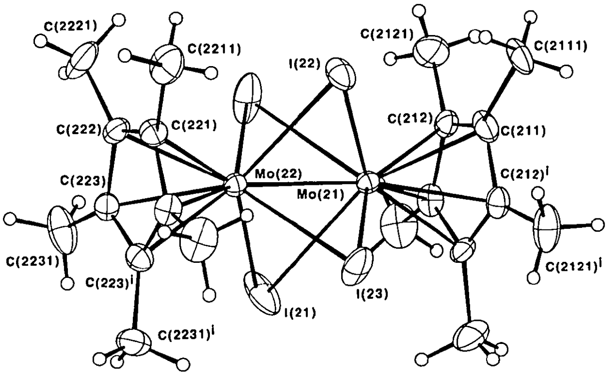


Fig. 1. An *ORTEP*II (Johnson, 1976) view of the $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}I)_4]^+$ cation. Ellipsoids are plotted at the 50% probability level.

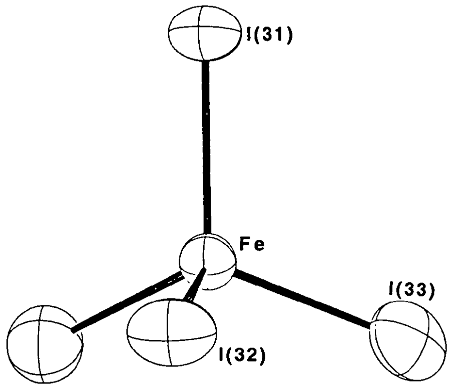


Fig. 2. An *ORTEP*II (Johnson, 1976) view of the $[FeI_4]^-$ anion. Ellipsoids are plotted at the 50% probability level.

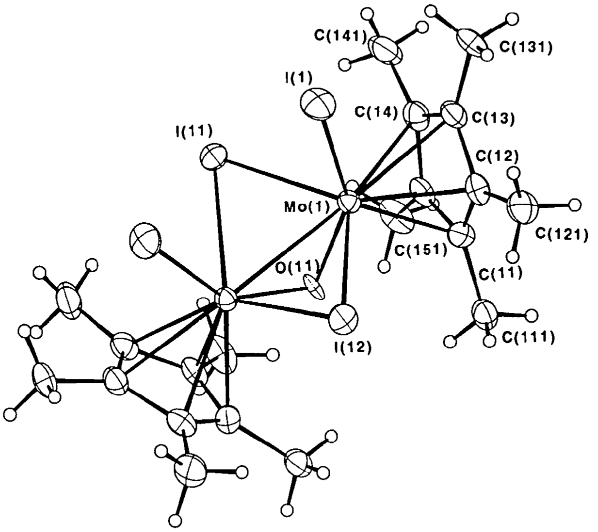


Fig. 3. An *ORTEP*II (Johnson, 1976) view of the $[(\eta^5\text{-}C_5Me_5)_2Mo_2I_2(\mu\text{-}I)_2(\mu\text{-}O)]$ neutral fragment. Ellipsoids are plotted at the 50% probability level.

$[FeI_4].Ph_3SbI_2$ (Lane, Godfrey, McAuliffe & Pritchard, 1994). The tetraiodoferrate(II) ion, on the other hand, exhibits substantially longer Fe—I distances, for instance 2.63 (1) Å for Rb_2FeI_4 (Zanbergen, Verschoor & Ijdo, 1979) and 2.63 (3) Å for $[Fe(MeCN)_2(Ph_2PCH_2PPh_2)_2]^{2+}[FeI_4]^{2-}.2H_2O$ (Barclay, Evans, Hughes & Leigh, 1993). The related $[Fe_2I_4(\mu\text{-}I)_2]^{2-}$ ion also exhibits longer terminal Fe^{II}—I distances, namely 2.594 (17) Å (Saak, Haase & Pohl, 1988), thereby supporting our assignment of the oxidation state III to the Fe centre in the title compound.

The neutral fragment $[(\eta^5\text{-}C_5Me_5)_2Mo_2I_2(\mu\text{-}I)_2(\mu\text{-}O)]$ (Fig. 3) sits on a mirror plane passing through the three bridging atoms I(11), I(12) and O(11). This species is novel and consists of two Mo centers, each bonded to an η^5-pentamethylcyclopentadienyl ring and an iodide ligand, and being bridged by an oxo and two iodide ligands. The geometry around each metal atom can be described as a four-legged piano stool, the ring being the stool and the terminal I and bridging I and O atoms being the legs. The bridging O atom is *trans* relative to the terminal I ligand. The two metals have the formal oxidation state IV and are at a bonding distance of 2.816 (2) Å from each other. The geometry of this species is identical to that of the isoelectronic compound $[(\eta^5\text{-}C_5Me_5)_2Mo_2Cl_2(\mu\text{-}Cl)_3]^+$ (Abugideiri, Fettinger & Poli), which also exhibits a similar metal–metal distance [2.866 (2) Å].

Experimental

The title compound is the unexpected by-product of the thermal decarbonylation of $[(\eta^5\text{-}C_5Me_5)MoI_3(CO)_2]$ in tetrahydrofuran. This thermal decarbonylation has been investigated in other solvents, giving rise to purple $[(\eta^5\text{-}C_5Me_5)_2Mo_2I_2(\mu\text{-}I)_2]$ in boiling dichloromethane and green $\{[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}I)_4]^+\}_2[I^-][I_3^-]$ in boiling toluene (Desai, Gordon, Kraatz, Lee, Owens-Waltermire, Poli, Rheingold & White, 1994), both these compounds having the same minimum formula, $(\eta^5\text{-}C_5Me_5)MoI_3$. It has been demonstrated that the purple product transforms into the green one upon further thermal treatment and, indeed, the main product of the thermal treatment in tetrahydrofuran is the same green material obtained from toluene. After filtering off the green precipitate, the mother liquor was evaporated to dryness and crystals of the title compound were obtained by dissolution into dichloromethane followed by slow diffusion of a heptane layer. The $\{[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}I)_4]^+\}_2[I^-][I_3^-]$ compound which is the main product of the reaction, is probably the source of both the cation and the anion (*via* reaction of the I^- and I_3^- ions with an Fe^{3+} impurity) in the title compound. The neutral molecule is probably produced by an oxygen/iodine exchange between an $[(\eta^5\text{-}C_5Me_5)MoI_3]$ intermediate and the tetrahydrofuran solvent. The source of the Fe atom in the tetrahedral $[FeI_4]^-$ fragment has been traced to the molybdenum compound used as a starting material. This is obtained by diiodine oxidation of the pentamethylcyclopentadienyltricarbonylmolybdenum dimer, which is in turn obtained by oxidation of pentamethylcyclopentadienyltricarbonylmolybdate, $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3]^-$, with iron sulfate in water. Evidently, the $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3]_2$ product remained contaminated with small but significant amounts of iron products.

Crystal data

$[Mo_2(C_{10}H_{15})_2I_4][FeI_4]$.-
  $[Mo_2(C_{10}H_{15})_2I_4O]$
$M_r = 2519.38$
Monoclinic
$P2_1/m$
$a = 12.0939\,(7)$ Å
$b = 15.464\,(4)$ Å
$c = 16.854\,(2)$ Å
$\beta = 105.295\,(6)^\circ$
$V = 3040.5\,(14)$ Å^3
$Z = 2$
$D_x = 2.75$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.5\text{–}11.5^\circ$
$\mu = 7.077$ mm^{-1}
$T = 20$ K
Plate
$0.32 \times 0.30 \times 0.10$ mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
  $T_{\min} = 0.14$, $T_{\max} = 0.28$
4140 measured reflections
4140 independent reflections

3198 observed reflections
  $[I > 3\sigma(I)]$
$\theta_{\max} = 22.5^\circ$
$h = -13 \rightarrow 12$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 18$
3 standard reflections
  frequency: 83 min
  intensity decay: < 5%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.063$
$S = 1.619$
3198 reflections
283 parameters
H atoms not refined, $U = 1.3U_{\rm eq}$ of bonding atom

$w = 1/[\sigma^2(F_o) + (0.020F_o)^2 + 1.0]$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 2.19$ e Å^{-3}
$\Delta\rho_{\min} = -1.32$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
I(1)	−0.17329 (10)	0.12283 (8)	0.38087 (6)	0.0558 (3)
I(11)	−0.00759 (10)	1/4	0.25322 (9)	0.0431 (4)
I(12)	−0.40782 (10)	1/4	0.22749 (9)	0.0438 (4)
I(21)	0.58640 (13)	1/4	0.46977 (9)	0.0908 (8)
I(22)	0.38782 (11)	1/4	0.68095 (8)	0.0526 (4)
I(23)	0.48674 (10)	0.09349 (7)	0.57687 (8)	0.0726 (4)
I(31)	0.00373 (13)	1/4	0.88158 (11)	0.0644 (5)
I(32)	0.34553 (13)	1/4	0.89677 (10)	0.0696 (5)
I(33)	0.23559 (11)	0.11593 (9)	1.07091 (9)	0.0786 (4)
Mo(1)	−0.21411 (8)	0.15894 (7)	0.21330 (7)	0.0287 (3)
Mo(21)	0.58933 (12)	1/4	0.63337 (9)	0.0258 (4)
Mo(22)	0.38679 (12)	1/4	0.51708 (9)	0.0267 (4)
Fe	0.2028 (2)	1/4	0.98116 (18)	0.0408 (8)
O(11)	−0.2340 (10)	1/4	0.1344 (7)	0.029 (3)
C(11)	−0.3063 (12)	0.0777 (10)	0.1015 (9)	0.042 (4)
C(12)	−0.3168 (11)	0.0315 (10)	0.1699 (9)	0.041 (4)
C(13)	−0.2060 (12)	0.0009 (9)	0.2124 (9)	0.040 (4)
C(14)	−0.1262 (11)	0.0349 (9)	0.1734 (9)	0.041 (4)
C(15)	−0.1894 (11)	0.0819 (9)	0.1022 (8)	0.039 (4)
C(111)	−0.4023 (13)	0.1118 (10)	0.0337 (9)	0.048 (4)
C(121)	−0.4234 (13)	0.0045 (11)	0.1922 (11)	0.060 (5)
C(131)	−0.1771 (15)	−0.0655 (10)	0.2799 (11)	0.060 (5)
C(141)	−0.0017 (13)	0.0164 (11)	0.1944 (12)	0.064 (5)
C(151)	−0.1382 (13)	0.1204 (11)	0.0393 (9)	0.053 (4)
C(211)	0.6901 (17)	1/4	0.7720 (12)	0.047 (6)
C(212)	0.7234 (11)	0.1765 (9)	0.7360 (8)	0.037 (4)
C(213)	0.7747 (10)	0.2039 (9)	0.6734 (8)	0.036 (3)
C(221)	0.1842 (14)	1/4	0.4821 (12)	0.039 (5)
C(222)	0.2217 (11)	0.1762 (9)	0.4476 (9)	0.038 (4)
C(223)	0.2833 (11)	0.2029 (10)	0.3906 (8)	0.038 (3)
C(2111)	0.6410 (16)	1/4	0.8470 (12)	0.056 (7)
C(2121)	0.7154 (16)	0.0857 (12)	0.7656 (11)	0.069 (5)
C(2131)	0.8366 (13)	0.1484 (13)	0.6268 (11)	0.068 (5)
C(2211)	0.1052 (19)	1/4	0.5377 (17)	0.067 (8)
C(2221)	0.1891 (14)	0.0837 (11)	0.4591 (13)	0.067 (6)
C(2231)	0.3232 (14)	0.1471 (14)	0.3342 (10)	0.069 (5)

Table 2. *Selected geometric parameters (Å, °)*

I(1)—Mo(1)	2.7923 (15)	I(22)—Mo(22)	2.759 (2)
I(11)—Mo(1)	2.7906 (15)	I(23)—Mo(21)	2.7715 (14)
I(12)—Mo(1)	2.7971 (15)	I(23)—Mo(22)	2.7735 (13)
Mo(1)—Mo(1$^{\rm i}$)	2.816 (2)	Mo(21)—Mo(22)	2.704 (2)
Mo(1)—O(11)	1.908 (9)	Mo(21)—C(211)	2.33 (2)
Mo(1)—C(11)	2.294 (15)	Mo(21)—C(212)	2.331 (14)
Mo(1)—C(12)	2.341 (15)	Mo(21)—C(213)	2.278 (12)
Mo(1)—C(13)	2.446 (15)	Mo(22)—C(221)	2.364 (18)
Mo(1)—C(14)	2.375 (14)	Mo(22)—C(222)	2.330 (14)
Mo(1)—C(15)	2.305 (14)	Mo(22)—C(223)	2.287 (14)
I(21)—Mo(21)	2.748 (2)	I(31)—Fe	2.546 (3)
I(21)—Mo(22)	2.735 (2)	I(32)—Fe	2.510 (3)
I(22)—Mo(21)	2.7592 (19)	I(33)—Fe	2.535 (2)
Mo(1)—I(11)—Mo(1$^{\rm i}$)	60.61 (5)	I(21)—Mo(21)—I(23)	76.65 (5)
Mo(1)—I(12)—Mo(1$^{\rm i}$)	60.46 (5)	I(22)—Mo(21)—I(23)	75.54 (5)
I(1)—Mo(1)—I(11)	87.07 (5)	I(23)—Mo(21)—I(23$^{\rm i}$)	121.69 (7)
I(1)—Mo(1)—I(12)	86.72 (5)	I(21)—Mo(22)—I(22)	121.38 (7)
I(1)—Mo(1)—O(11)	144.0 (3)	I(21)—Mo(22)—I(23)	76.84 (5)
I(11)—Mo(1)—I(12)	116.22 (5)	I(22)—Mo(22)—I(23)	75.51 (5)
I(11)—Mo(1)—O(11)	74.7 (4)	I(23)—Mo(22)—I(23$^{\rm i}$)	121.54 (7)
I(12)—Mo(1)—O(11)	74.6 (3)	I(31)—Fe—I(32)	107.37 (13)
Mo(1)—O(11)—Mo(1$^{\rm i}$)	95.1 (6)	I(31)—Fe—I(33)	111.42 (8)
Mo(21)—I(21)—Mo(22)	59.09 (5)	I(31)—Fe—I(33$^{\rm i}$)	111.42 (8)
Mo(21)—I(22)—Mo(22)	58.68 (5)	I(32)—Fe—I(33)	108.39 (8)
Mo(21)—I(23)—Mo(22)	58.36 (5)	I(32)—Fe—I(33$^{\rm i}$)	108.39 (8)
I(21)—Mo(21)—I(22)	120.86 (7)	I(33)—Fe—I(33$^{\rm i}$)	109.73 (14)

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

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN*.

We are grateful to the NSF (PYI award, CHE-9058375) for support of this work.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1202). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Forms of Bromo(cycloheptatrienylidene)bis(triphenylphosphine)platinum(II)

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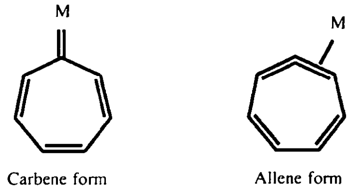
Abstract

The title complex crystallizes in two different crystal systems: one form in the monoclinic system, as $[PtBr(C_7H_6)(C_{18}H_{15}P)_2]BF_4.CD_2Cl_2.C_4D_8O$, and the other in the orthorhombic crystal system, as $[PtBr(C_7H_6)(C_{18}H_{15}P)_2]BF_4.C_4H_8O$. The crystal structure determination of the complex bromo(cycloheptatrienylidene)bis(triphenylphosphine)platinum(II), $[PtBr(C_7H_6)(C_{18}H_{15}P)_2]$, revealed that the Pt^{II} cation is coordinated to a Br atom, two triphenylphosphine donors and cycloheptatrienylidene. The complex has square-planar geometry around Pt with the triphenylphosphine ligands being *trans* to each other. The plane of the cycloheptatrienylidene ligand is almost perpendicular to the coordination plane.

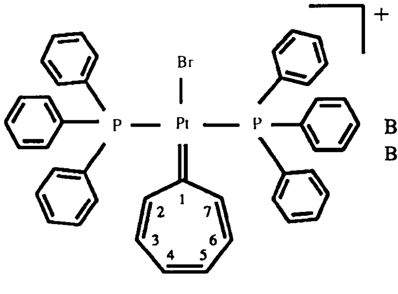
Comment

It has been shown that when monocyclic C_7H_6 is attached to a transition metal it can exist in two different forms, an allene or a carbene. The preference for one form over the other depends on the transition metal and its oxidation state (Winchester, 1985).



Carbene form Allene form

Several carbene complexes containing monocyclic C_7H_6 have been synthesized and two of them have been structurally characterized (Riley, Davis, Allison & Jones, 1980). The only transition metal for which both forms have been observed is platinum. The Pt^0 complex was found to be exclusively in the allene form both in solution (Winchester & Jones, 1985) and in the crystal (Abboud, Lu & Jones, 1992). Recently, a Pt^{II} complex containing monocyclic C_7H_6 was synthesized and was shown spectroscopically to exist in carbene form in solution (Lu, Jones & Winchester, 1993). This study confirms that the carbene form is also preferred in the crystalline state. Suitable light-yellow crystals of (I) were obtained from a solution mixture of deuterized methylene chloride and thf-d^8. Initial attempts at crystallizing the Pt^{II} complex yielded light-yellow crystals from a mixture of methylene chloride and thf. After several recrystallizations to obtain better crystals, data were collected on a small crystal and the structure, (II), was found to be in the orthorhombic system. The change in the solvent mixture from methylene chloride and thf to deuterized methylene chloride and thf-d^8 caused a change in the crystal system from orthorhombic ($P2_12_12_1$) to monoclinic ($P2_1/n$).



$BF_4^-.CD_2Cl_2.C_4D_8O$ (I)
$BF_4^-.C_4H_8O$ (II)

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