Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843, and Departamento de Quimica Inorganica,
Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Heterobinuclear PtAg Compounds with Platinum–Silver Bonds Unsupported by Covalent Bridges. Molecular Structure of $(C_6F_5)_3(SC_4H_8)PtAgPPh_3$

F. A. Cotton,* L. R. Falvello, R. Uson,* J. Fornies, M. Tomas, J. M. Casas, and I. Ara

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Reaction of anionic platinum(II) derivatives $(NBu_4)[Pt(C_6F_5)_3L]$ with $O_3ClOAgL'$ affords the neutral heterobinuclear complexes $(C_6F_5)_3LPtAgL'$ ($L' = PPh_3$, PEt_3; $L = SC_4H_8$, PPh_3, PEt_3, $PEtPh_2$, NC_5H_5) containing a direct Pt–Ag bond unsupported by covalent bridges. The molecular structure of a representative compound ($L = SC_4H_8$; $L' = PPh_3$) has been determined by a single-crystal X-ray diffraction study. The compound $(C_6F_5)_3(SC_4H_8)PtAgPPh_3$ crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 14.006$ (2) Å, $b = 17.441$ (3) Å, $c = 17.407$ (2) Å, $\beta = 110.74$ (1)°, $V = 3977$ (1) Å^3, and $Z = 4$. The structure was refined to least-squares residuals of $R = 0.0414$, $R_w = 0.0518$, and quality of fit = 0.95. The platinum atom is in a square-pyramidal environment, with SC_4H_8 and the three C_6F_5 ligands in the square plane and the Ag–PPh_3 moiety in the apical position. The Pt–Ag distance of 2.637 (1) Å is the shortest observed to date, indicating a direct Pt–Ag bond of substantial strength. The silver atom makes short contacts with *o*-fluorine atoms of the C_6F_5 groups (Ag···F(6) = 2.757 (7) Å; Ag···F(11) = 2.791 (7) Å; Ag···F(1) = 2.763 (8) Å). Acetone solutions of these complexes behave as 1:1 electrolytes because of cleavage of the Pt–Ag bond by the donor solvent. Addition of excess ligand L′ causes cleavage of the metal–metal bonds to give ionic derivatives of the type $[AgL'_n]^+[Pt(C_6F_5)_3L]^-$ (n = 2, 3).

Introduction

Our laboratories are engaged in a study of the reactivity of anionic pentahalophenyl (C_6X_5; X = F, Cl) platinum(II) derivatives with silver salts ($AgClO_4$, $AgNO_3$). To date several novel heteronuclear compounds of the types $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$, $(NBu_4)[PtAgCl_2(C_6F_5)_2PPh_3]$,[1] $(NBu_4)[Pt_2Ag(C_6F_5)_6(Et_2O)]$,[2] $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$,[3a] $(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PPh_3)]$,[3b] $Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag_2(PPh_2Me)_2$,[3b] and $(NBu_4)[Pt_2Ag(\mu\text{-}Cl)_2(C_6F_5)_4\cdot O(C_2H_5)_2]$[4] have been obtained.

During our study of this novel chemistry the following facts have been established:

(a) The pentahalophenyl ligands C_6F_5 and C_6Cl_5 play a critical role in establishing the nature of the product obtained, since short contacts between *o*-halide and silver atoms seem to be instrumental for the stability of the resulting clusters.

(b) Starting complexes of similar types, i.e., *trans*-$[PtCl_2(C_6F_5)_2]^{2-}$ and *trans*-$[PtCl_2(C_6Cl_5)_2]^{2-}$, lead to structurally very different end products, $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$[1] and $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$,[3] respectively.

(c) The reactivities of the new complexes with neutral ligands L are varied. The polymeric anion $[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x^{x-}$, which has no direct Pt–Ag bond, reacts with some neutral ligands (L = PPh_3, PEt_3, $AsPh_3$, $SbPh_3$) to give the Pt–Ag-bonded binuclear compounds $[PtCl(C_6Cl_5)_2(\mu\text{-}Cl)AgL]^-$; but with others (L = $PMePh_2$, $PEtPh_2$, PMe_2Ph) it gives trinuclear compounds of the type $PtAg_2Cl_2(C_6Cl_5)_2L_2$, without any direct Pt–Ag bond,[3] in which chlorine atoms bridge the metal centers.

(d) An essential feature of all the Pt-containing precursors is their anionic character, which enables them to act as nucleophiles toward the silver cation in the salts used ($AgClO_4$, $AgNO_3$, $O_3ClOAgL'$).

As a logical extension of this work, we have undertaken a study of the reactions between other suitable precursors, such as $(NBu_4)[Pt(C_6F_5)_3L]$[5,6] and $O_3ClOAgL'$.

In this paper we report the results of these studies, which open a general route for the synthesis of neutral heteronuclear compounds of the type $L(C_6F_5)_3PtAgL'$, containing direct Pt–Ag bonds unsupported by any covalent bridges. The structure of a representative complex ($L = SC_4H_8$, $L' = PPh_3$) has been established by a single-crystal X-ray analysis.

Results and Discussion

(a) Synthesis and Stability of $L(C_6F_5)_3PtAgL'$ Complexes (I–X). Stirring at room temperature, in the absence of light, of a dichloromethane solution of the reagents (1:1 ratio) affords (eq 1)[16]

$$(NBu_4)[Pt(C_6F_5)_3L] + O_3ClOAgL' \rightarrow (NBu_4)ClO_4 + L(C_6F_5)_3PtAgL' \quad (1)$$

$L' = PPh_3$, $L = SC_4H_8$ (I), PPh_3 (II), PEt_3 (III), $PEtPh_2$ (IV), NC_5H_5 (V); $L' = PEt_3$, $L = SC_4H_8$ (VI), PPh_3 (VII), PEt_3 (VIII), $PEtPh_2$ (IX), NC_5H_5 (X)

solutions of the complexes I–X, which can subsequently be isolated by evaporation to dryness and extraction with diethyl ether (to remove the insoluble $(NBu_4)ClO_4$). Evaporation to dryness of the resulting ether solutions gives residues containing ether, which are then dissolved in dichloromethane. Addition of *n*-hexane, in each case (I–X), yields a solvent-free, white sample of the product.

Analytical and other data for complexes I–X are summarized in Table I. All the complexes are stable in the solid state for several hours in the absence of light. At −20 °C complexes I–V ($L' = PPh_3$) are stable for several months, while complexes VI–X ($L' = PEt_3$) turn brownish, because of partial decomposition, after ca. 1 month at −20 °C. The complexes are less stable in solution than in the solid state: After 7 h of refluxing, a dichloromethane solution of complex II yielded only 60% of the initial solvate (40% if the solvent was acetone). Complex VIII decomposes after several hours of stirring at room temperature and after 2 h in the presence of light.

(b) Crystal Structure of $(SC_4H_8)(C_6F_5)_3PtAgPPh_3$ (I). The properties of complexes I–X, as well as our previous studies on similar systems,[1,2] point to the formation of a donor–acceptor bond between the moieties $[R_3LPt]^-$ and $[AgL']^+$. In complex I, however, the S ligand attached to the platinum atom has another electron pair that should be able to interact with the silver center to give an S-bridged Pt–S–Ag binuclear complex—either with or without an additional platinum–silver bond. Therefore, the

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*To whom correspondence should be addressed: F.A.C., Texas A&M University; R.U., Universidad de Zaragoza-CSIC.

(1) (a) Uson, R.; Fornies, J.; Tomas, M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 2482. (b) Uson, R.; Fornies, J.; Menjon, B.; Cotton, F. A.; Falvello, L. R.; Tomas, M. *Inorg. Chem.* **1985**, *24*, 4651.

(2) Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 2556.

(3) (a) Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *Polyhedron* **1986**, *5*, 901. (b) Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R., submitted for publication in *Inorg. Chem.*

(4) Uson, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R., to be submitted for publication.

(5) Uson, R.; Fornies, J.; Martinez, F.; Tomas, M.; *J. Chem. Soc., Dalton Trans.* **1980**, 884.

(6) Uson, R.; Fornies, J.; Tomas, M.; Fandos, R. *J. Organomet. Chem.* **1984**, *263*, 253.

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Table I. Analytical Data for New Complexes

complex	anal.,[a] % C	H	N	mol wt[a]	Λ_M, Ω^{-1} cm^2 mol^{-1} acetone	CH_2Cl_2	mp, °C	yield, %
$(C_4H_8S)(C_6F_5)_3PtAgPPh_3$ (I)	41.79 (41.57)	2.27 (1.99)		1123.56 (1154.52)	85.28	0.49	148 dec	82
$PPh_3(C_6F_5)_3PtAgPPh_3$ (II)	48.08 (48.77)	2.41 (2.58)		1448.37 (1328.65)	74.62	4.10	154 dec	92
$PEt_3(C_6F_5)_3PtAgPPh_3$ (III)	42.49 (42.55)	2.57 (2.53)		1169.70 (1184.51)	85.75	3.98	106 dec	80
$PEtPh_2(C_6F_5)_3PtAgPPh_3$ (IV)	46.65 (46.85)	2.47 (2.34)		1180.54 (1280.60)	80.76	2.72	145 dec	83
$py(C_6F_5)_3PtAgPPh_3$ (V)	43.63 (42.95)	1.62 (1.74)	1.62 (1.22)	1099.53 (1145.45)	106.2	2.8	110 dec	81
$(C_4H_8S)(C_6F_5)_3PtAgPEt_3$ (VI)	33.47 (33.25)	2.74 (2.27)		995.79 (1010.39)	106.24	7.38	90 dec	52
$PPh_3(C_6F_5)_3PtAgPEt_3$ (VII)	42.47 (42.56)	2.76 (2.53)		1140.95 (1184.51)	104.31	9.28	120 dec	77
$PEt_3(C_6F_5)_3PtAgPEt_3$ (VIII)	35.19 (34.60)	3.60 (3.46)		1088.54 (1040.37)	93.24	7.81	103 dec	40
$PEtPh_2(C_6F_5)_3PtAgPEt_3$ (IX)	40.63 (40.12)	3.12 (2.64)		1060.97 (1136.47)	109.89	12.39	130 dec	58
$py(C_6F_5)_3PtAgPEt_3$ (X)	35.23 (34.75)	2.46 (1.99)	1.39 (1.40)	936.93 (1001.32)	115.63	6.18	88 dec	56
$[Ag(PPh_3)_2][Pt(C_6F_5)_3PPh_3]$ (XI)	54.79 (54.32)	3.08 (2.83)			75.14	31.47	198 dec	62
$[Ag(PPh_3)_3][Pt(C_6F_5)_3PPh_3]$ (XII)	58.68 (58.31)	3.56 (3.23)			59.21	29.77	208 dec	65

[a] Calculated values are given in parentheses; methods are given in the Experimental Section.

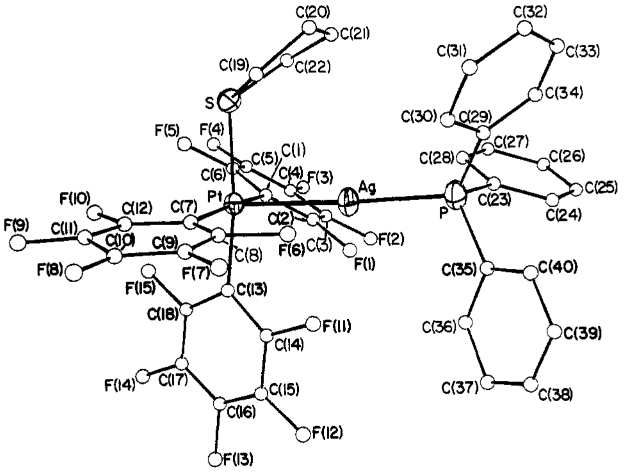

Figure 1. ORTEP drawing of $(C_6F_5)_3(SC_4H_8)PtAgPPh_3$. The Pt, Ag, S, and P atoms are represented by their 40% probability ellipsoids; for clarity, all other atoms are represented by small circles.

structure of complex I was determined by single-crystal X-ray diffraction. General crystallographic information is collected in Table II. Positional parameters and selected bond distances and angles are given in Tables III and IV, respectively.

The molecule consists of a Pt atom in a basal position in a square pyramid, the apical position of which is occupied by the Ag atom with its PPh_3 ligand. Figure 1 is an ORTEP drawing of the molecule.

The C_6F_5 groups and the SC_4H_8 ligand are coordinated to the Pt atom in a nearly regular square-planar configuration. The angles between cis ligands around the platinum center range from 86.7 (4) to 94.4 (3)°. The angles between trans ligands are identical within experimental error (173.4 (3) and 173.2 (5)°). The dihedral angle between the planes Pt–S–C(1) and Pt–C(7)–C(13) is 172°. The Pt–C bond lengths, which range from 2.00 (1) to 2.10 (1) Å, are similar to other Pt–C distances for terminal C_6F_5 groups.[1,2] The shortest distance, 2.00 (1) Å, belongs to the carbon trans to the SC_4H_8 group. The Pt–C distances for the two C_6F_5 groups trans to each other are similar: 2.07 (1) and 2.10 (1) Å. The Pt–S bond length is 2.328 (3) Å.

There is no interaction between the S atom of the SC_4H_8 ligand and the silver center; thus, the moieties $[(SC_4H_8)R_3Pt]^-$ and $[AgPPh_3]^+$ are directly bonded by a strong donor–acceptor Pt–Ag bond, with a distance of 2.637 (1) Å. This bond is roughly perpendicular to the platinum plane, with angles ranging from 88 to 99°.

The silver atom is also bonded to PPh_3, and the bond angle Pt–Ag–P is 174.3 (1)°; the Ag–P bond distance of 2.358 (3) Å is within the range found for other Pt–Ag complexes (2.350 (6) Å in $[PtAgCl_2(C_6F_5)_2(PPh_3)]^-$,[1] 2.370 (2) Å in $[PtAgCl_2(C_6Cl_5)_2(PPh_3)]^{-}$[3b]) and is shorter than the values found for $ClAg(PPh_3)_n$ (n = 1–4), which range from 2.376 to 2.668 Å, increasing with n.[7]

Table II. Crystal Data for $(C_6F_5)_3(SC_4H_8)PtAgPPh_3$

formula	$PtAgSPF_{15}C_{40}H_{23}$
fw	1154.6
space group	$P2_1/n$
systematic absences	$(0k0)$, $k \neq 2n + 1$; $(h0l)$, $h + l \neq 2n + 1$
a, Å	14.006 (2)
b, Å	17.441 (3)
c, Å	17.407 (2)
β, deg	110.74 (1)
V, Å^3	3977 (1)
Z	4
d_{calcd}, g/cm^3	1.928
cryst size, mm	0.25 × 0.19 × 0.18
μ(Mo Kα), cm^{-1}	43.8
data collecn instrument	Nicolet P3/F
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)
orientation reflecns: no.; range (2θ), deg	25; 21 < 2θ < 33
temp, °C	22 ± 1
scan method	ω–2θ
data collecn range, 2θ, deg	4.0–50.0
no. of unique data, total	6130
no. of data with $F_o^2 > 3\sigma(F_o^2)$	4101
no. of params refined	532
transmission factors: max, min	0.45, 0.20 (calcd); 1.00, 0.90 (obsd)
R^a	0.0414
$R_w{}^b$	0.0518
quality-of-fit indicator[c]	0.951
largest shift/esd, final cycle	0.06
largest, peak, e/Å^3	0.78

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table III. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $(C_4H_8S)(C_6F_5)_3PtAgPPh_3$[a]

atom	*x*	*y*	*z*	*B*
Pt	0.07258 (3)	0.12722 (2)	0.18365 (2)	2.382 (6)
Ag	−0.08419 (6)	0.15819 (6)	0.22885 (5)	3.61 (2)
S	−0.0198 (2)	0.0235 (2)	0.1098 (2)	2.96 (6)
P	−0.2328 (2)	0.1904 (2)	0.2559 (2)	3.43 (6)
F(1)	−0.0531 (5)	0.2939 (4)	0.1592 (4)	4.9 (2)
F(2)	−0.1114 (7)	0.3920 (5)	0.0349 (5)	7.2 (2)
F(3)	−0.0706 (8)	0.3632 (5)	−0.1045 (5)	8.0 (3)
F(4)	0.0284 (6)	0.2336 (5)	−0.1156 (4)	6.0 (2)
F(5)	0.0789 (6)	0.1302 (4)	0.0062 (4)	4.9 (2)
F(6)	0.0371 (5)	0.0687 (5)	0.3568 (4)	5.0 (2)
F(7)	0.1535 (7)	−0.0203 (5)	0.4786 (4)	6.9 (2)
F(8)	0.3281 (7)	−0.0849 (6)	0.4742 (6)	8.5 (3)
F(9)	0.3851 (6)	−0.0577 (6)	0.3421 (6)	8.5 (3)
F(10)	0.2706 (5)	0.0316 (5)	0.2180 (5)	6.1 (2)
F(11)	0.0814 (5)	0.2374 (5)	0.3383 (4)	5.6 (2)
F(12)	0.2019 (7)	0.3537 (5)	0.4076 (5)	7.5 (2)
F(13)	0.3569 (6)	0.3947 (5)	0.3547 (5)	6.4 (2)
F(14)	0.3829 (6)	0.3182 (5)	0.2271 (5)	6.6 (2)
F(15)	0.2624 (5)	0.2001 (5)	0.1573 (4)	5.1 (2)
C(1)	0.0130 (8)	0.2045 (6)	0.0885 (6)	2.8 (2)
C(2)	−0.0338 (9)	0.2742 (7)	0.0904 (6)	3.7 (3)
C(3)	−0.064 (1)	0.3271 (7)	0.0269 (9)	5.1 (4)
C(4)	−0.041 (1)	0.3130 (7)	−0.0430 (7)	4.6 (3)
C(5)	0.0044 (9)	0.2461 (7)	−0.0488 (6)	3.9 (3)
C(6)	0.0311 (8)	0.1943 (7)	0.0152 (6)	3.6 (3)
C(7)	0.1500 (8)	0.0545 (7)	0.2818 (6)	3.2 (2)
C(8)	0.1265 (8)	0.0369 (7)	0.3499 (7)	3.6 (3)
C(9)	0.182 (1)	−0.0079 (8)	0.4135 (7)	4.9 (3)
C(10)	0.271 (1)	−0.0389 (8)	0.4125 (8)	5.4 (4)
C(11)	0.2966 (9)	−0.0278 (8)	0.3419 (9)	4.9 (3)
C(12)	0.2381 (8)	0.0193 (7)	0.2823 (7)	4.1 (3)
C(13)	0.1656 (7)	0.2118 (6)	0.2440 (6)	2.6 (2)
C(14)	0.1562 (8)	0.2551 (7)	0.3083 (6)	3.6 (3)
C(15)	0.221 (1)	0.3157 (8)	0.3460 (8)	5.1 (3)
C(16)	0.293 (1)	0.3365 (7)	0.3153 (8)	5.0 (3)
C(17)	0.3081 (9)	0.2974 (7)	0.2538 (6)	3.7 (3)
C(18)	0.2451 (8)	0.2361 (7)	0.2208 (6)	3.5 (3)
C(19)	−0.0713 (9)	−0.0385 (7)	0.1716 (7)	4.3 (3)
C(20)	−0.186 (1)	−0.042 (1)	0.1246 (9)	7.6 (5)
C(21)	−0.223 (1)	0.016 (1)	0.067 (1)	7.7 (5)
C(22)	−0.145 (1)	0.0495 (7)	0.0334 (8)	4.5 (3)
C(23)	−0.3141 (8)	0.2568 (7)	0.1819 (6)	3.7 (3)
C(24)	−0.3821 (9)	0.3060 (8)	0.1994 (7)	4.5 (3)
C(25)	−0.444 (1)	0.3541 (7)	0.1410 (8)	5.0 (3)
C(26)	−0.439 (1)	0.3572 (9)	0.0611 (9)	6.1 (4)
C(27)	−0.370 (1)	0.3082 (9)	0.0433 (8)	5.8 (4)
C(28)	−0.308 (1)	0.2590 (9)	0.1033 (8)	5.2 (3)
C(29)	−0.3126 (9)	0.1094 (7)	0.2601 (7)	4.3 (3)
C(30)	−0.264 (1)	0.0423 (9)	0.2978 (9)	5.7 (4)
C(31)	−0.324 (1)	−0.0215 (9)	0.3041 (9)	7.5 (4)
C(32)	−0.429 (1)	−0.019 (1)	0.268 (1)	8.6 (5)
C(33)	−0.474 (1)	0.049 (1)	0.232 (1)	9.6 (6)
C(34)	−0.419 (1)	0.112 (1)	0.225 (1)	7.7 (5)
C(35)	−0.1988 (9)	0.2378 (7)	0.3547 (7)	4.0 (3)
C(36)	−0.125 (1)	0.297 (1)	0.3723 (9)	6.2 (4)
C(37)	−0.093 (1)	0.331 (1)	0.453 (1)	8.5 (6)
C(38)	−0.138 (1)	0.303 (1)	0.5078 (9)	7.0 (4)
C(39)	−0.210 (1)	0.248 (1)	0.4905 (9)	7.9 (5)
C(40)	−0.238 (1)	0.2146 (9)	0.4155 (7)	6.1 (4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The platinum atom is coordinated by a square array of three C_6F_5 groups and a tetrahydrothiophene molecule, with the C_6F_5 groups oriented in such a way that one *o*-fluorine atom of each C_6F_5 group makes a close contact with the silver atom: Ag···F(6) = 2.757 (7) Å; Ag···F(11) = 2.791 (7) Å; Ag···F(1) = 2.763 (8) Å. These contacts are likely to facilitate attractive forces which contribute to the stability of the molecule. In order to obtain an Ag···F(1) distance similar to the other two Ag···F distances, the ring containing F(1) is tilted (39°) from the Pt–Ag–C(1) plane and the C(1)–Pt–Ag angle (87.9 (3)°) is smaller than the other two C–Pt–Ag angles (97, 98.5°). Elimination of the twist of the ring would yield a series of unacceptable contacts, making the following changes in nonbonded distances (in Å): Ag···F(1), from 2.76 to 2.31; C(6)···F(15), from 3.31 to 2.76; F(5)···C(18), from 4.08 to 2.82; F(5)···F(15), from 3.20 to 1.86; F(1)···P, from 3.93 to 3.29; F(1)···C(23), from 3.87 to 3.12; F(1)···C(28), from 3.41 to 2.36; F(2)···C(27), from 3.96 to 2.89. The orientation of the C_6F_5 rings is also conducive to enhancing two stabilizing factors: (i) the silver–*o*-fluorine interactions and (ii) minimization of the repulsive interactions between the six arene rings (three C_6F_5 and three C_6H_5) present in the molecule.

Turning again to the Pt–Ag bond, we observe that it is entirely unsupported by any covalent bridge and that the bond distance (2.637 (1) Å) is shorter than any previously reported (2.759 (1),[1] 2.772 (3),[4] 2.787 (1) Å[8]). It seems sensible to correlate the short Pt–Ag distance in these complexes (I–X) with the presence of only two ligands on the silver center, which thus withdraws electron density from only two covalently bound sources; in all the other complexes with Pt–Ag bonds, the silver atom displays higher coordination numbers. The Pt–Ag bond is almost perpendicular to the platinum coordination plane, thus facilitating overlap between the silver and platinum orbitals.

Table V lists IR absorptions of structural interest for these complexes. Neither the absorptions due to the perchlorato ligand in the starting silver complex (1130 vs, br, 1100 vs, 878 s, 625 s, 615 s cm^{-1})[9] nor those due to the NBu_4^+ cation (880, 737 cm^{-1}) in the platinum precursor appear in the IR spectra of complexes I–X.

Dichloromethane solutions of the complexes I–X are nonconducting, but the complexes behave as 1:1 electrolytes in ~5 × 10^{-4} M acetone solutions, because of the cleavage of the Pt–Ag bond by the solvent to give $[Pt(C_6F_5)_3L]^-$ and $[AgL'(OCMe_2)_x]^+$ ions. Evaporation to dryness of the acetone solution of complex II regenerates the binuclear Pt–Ag-bonded complex.

Complex II reacts with PPh_3 in CH_2Cl_2 solution (molar ratio 1:1 and 1:2 or higher, up to 1:12, respectively) to give $[Ag(PPh_3)_2][Pt(C_6F_5)_3PPh_3]$ (XI) and $[Ag(PPh_3)_3][Pt(C_6F_5)_3PPh_3]$ (XII), respectively) according to eq 2. Thus, after addition of

$$(PPh_3)(C_6F_5)_3PtAgPPh_3 \xrightarrow{+PPh_3} [Ag(PPh_3)_2][Pt(C_6F_5)_3PPh_3] \xrightarrow{+PPh_3} [Ag(PPh_3)_3][Pt(C_6F_5)_3PPh_3] \quad (2)$$

excess L′, the competition between the nucleophilic platinum center and the neutral ligand favors the latter, and the metal–metal bond is cleaved to give the ionic derivatives XI and XII.

Complexes XI and XII behave in acetone solution as 1:1 electrolytes. Even in dichloromethane solution their conductivities point to the presence of ions (Table I). A Pt–Ag interaction in the solid state cannot, however, be ruled out.

The process represented in eq 1 is a fairly general, but not universal, one. The platinum precursor $[Pt(C_6F_5)_3L]^-$ can be unreactive if L = CO; the use of ClAgL′ instead of $O_3ClOAgL'$ is also unproductive: in both cases the unreacted starting materials are recovered after 24 h of stirring at room temperature.

Experimental Section

Infrared spectra, C, H, and N analyses, and conductance and melting point determinations were performed as described elsewhere.[1] Molecular weight determinations were made with a Knauer vapor pressure osmometer. All the reactions were carried out with exclusion of light.

Preparation of the $(NBu_4)[Pt(C_6F_5)_3L]$ Precursors. These compounds were synthesized according to a previously reported procedure.[6] To a solution of $(NBu_4)_2[PtCl(C_6F_5)_3]$ (0.5 g, 0.4 mmol) in dichloromethane was added the stoichiometric amount of L (36.23 μL (L = C_4H_8S), 0.108 g (L = PPh_3), 60.65 μL (L = PEt_3), 88 μL (L = $PEtPh_2$), 33 μL (L =

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(7) Engelhardt, L. M.; Pakawatchai, C.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1985**, 125 and references therein.

(8) Lippert, B.; Neugebauer, D. *Inorg. Chem.* **1982**, *21*, 541.

(9) Uson, R.; Royo, P.; Fornies, J. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 157.

Table IV. Important Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $(C_6F_5)_3(SC_4H_8)PtAgPPh_3$

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Pt	Ag	2.637 (1)	S	C(22)	1.846 (13)	C(7)	C(12)	1.38 (2)
Pt	S	2.328 (3)	P	C(23)	1.805 (14)	C(13)	C(14)	1.394 (15)
Pt	C(1)	2.068 (11)	P	C(29)	1.819 (14)	C(13)	C(18)	1.38 (2)
Pt	C(7)	2.096 (12)	P	C(35)	1.814 (13)	Ag	F(1)	2.763 (8)[a]
Pt	C(13)	2.002 (11)	C(1)	C(2)	1.39 (2)	Ag	F(6)	2.757 (7)[a]
Ag	P	2.358 (3)	C(1)	C(6)	1.40 (2)	Ag	F(11)	2.791 (7)[a]
S	C(19)	1.843 (12)	C(7)	C(8)	1.37 (2)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ag	Pt	S	88.00 (8)	Pt	Ag	P	174.31 (9)	Pt	C(1)	C(2)	127.8 (9)
Ag	Pt	C(1)	87.9 (3)	Pt	S	C(19)	112.9 (5)	Pt	C(1)	C(6)	119.7 (9)
Ag	Pt	C(7)	97.2 (3)	Pt	S	C(22)	114.1 (4)	C(2)	C(1)	C(6)	112. (1)
Ag	Pt	C(13)	98.5 (3)	C(19)	S	C(22)	95.4 (6)	Pt	C(7)	C(8)	128.8 (9)
S	Pt	C(1)	94.4 (3)	Ag	P	C(23)	112.9 (4)	Pt	C(7)	C(12)	119 (1)
S	Pt	C(7)	90.4 (3)	Ag	P	C(29)	114.9 (4)	C(8)	C(7)	C(12)	113 (1)
S	Pt	C(13)	173.4 (3)	Ag	P	C(35)	110.1 (5)	Pt	C(13)	C(14)	126.3 (9)
C(1)	Pt	C(7)	173.2 (5)	C(23)	P	C(29)	106.6 (6)	Pt	C(13)	C(18)	121.0 (9)
C(1)	Pt	C(13)	86.7 (4)	C(23)	P	C(35)	105.7 (6)	C(14)	C(13)	C(18)	113 (1)
C(7)	Pt	C(13)	88.0 (5)	C(29)	P	C(35)	105.9 (7)				

[a] Nonbonded distance.

Table V. Characteristic Group IR Absorptions (cm^{-1}) for Complexes $L(C_6F_5)_3PtAgL'$[a]

complex	L	L′	$\nu(C_6F_5)$[b]	ν(L)	ν(L′)
I	tht	PPh_3	805 (s), 776 (s)	1270 (w)	520 (s), 501 (s), 491 (s)
II	PPh_3	PPh_3	791 (s), 780 (s), 770 (s)	531 (s), 523 (s), 512 (s), 497 (s)	
III	PEt_3	PPh_3	794 (w), 775 (s), 760 (s)	620 (w)	520 (s), 503 (s), 490 (s)
IV	$PEtPh_2$	PPh_3	791 (w), 771 (s)	530 (m), 520 (s), 503 (s), 490 (s)	
V	py	PPh_3	805 (s), 788 (m), 776 (s)	1604 (m), 760 (m)	520 (s), 498 (s)
VI	tht	PEt_3	798 (s)	1270 (m)	640 (sh), 620 (m)
VII	PPh_3	PEt_3	798 (s), 780 (sh), 772 (s)	528 (s), 510 (s), 494 (s)	635 (sh), 620 (m)
VIII	PEt_3	PEt_3	795 (m), 775 (s)	638 (m), 620 (m)	
IX	$PEtPh_2$	PEt_3	796 (m), 775 (s)	532 (s), 488 (m)	620 (m)
X	py	PEt_3	802 (s), 798 (m), 774 (s)	1605 (s), 760 (s), 693 (s)	640 (w), 620 (s)
XI	$[Ag(PPh_3)_2][Pt(C_6F_5)_3PPh_3]$		793 (s), 769 (s)	537 (s), 513 (s), 501 (s), 488 (s)	
XII	$[Ag(PPh_3)_3][Pt(C_6F_5)_3PPh_3]$		792 (s), 770 (m)	692 (s), 532 (m), 511 (s), 496 (s)	

[a] Abbreviations: tht, tetrahydrothiophene; py, pyridine. [b] Only the absorptions corresponding to the X-sensitive mode—that is, aromatic group modes sensitive to the nature of the substituent on the group.

pyridine (py))) and then $AgClO_4$[16] (0.0851 g, 0.411 mmol). After 1 h of stirring, the AgCl precipitate was removed by filtration and the dichloromethane solution was evaporated to dryness. Subsequent addition of isopropyl alcohol (ca. 10 mL) afforded the corresponding $(NBu_4)[Pt(C_6F_5)_3L]$ compounds. L = PEt_3: 70% yield. Anal. Found (calcd): C, 44.88 (45.41); H, 4.59 (4.82); N, 1.14 (1.32). L = $PEtPh_2$: 70% yield. Anal. Found (calcd): C, 49.39 (49.95); H, 4.21 (4.42); N, 1.19 (1.21). L = py: 88% yield. Anal. Found (calcd): C, 46.10 (45.99); H, 3.95 (4.02); N, 2.92 (2.75).

$(NBu_4)[Pt(C_6F_5)_3L]$, L = C_4H_8S and PPh_3, had previously been prepared by other procedures. However, higher yields can be obtained by the method described above (L = C_4H_8S, 64% vs. 56% yield; L = PPh_3, 85% vs. 67% yield).

Preparation of $O_3ClOAgL$ (L = PPh_3, PEt_3).[16] A solution of ClAgL (L = PPh_3,[10] 1.64 g (0.05 mmol); L = PEt_3, 1.2 g (4.6 mmol)) in dichloromethane was stirred for 1 h with $AgClO_4$ (1.68 g (8.09 mmol) and 1.908 g (9.181 mmol), respectively). The AgCl precipitate and the unreacted $AgClO_4$ were removed by filtration. Evaporation to dryness of the resulting dichloromethane solution gave $O_3ClOAgPPh_3$ as a white solid (93% yield). This compound had previously been obtained by another method.[11]

When L = PEt_3,[12] analogous treatment did not afford any solid; the dichloromethane solution was therefore used directly, and the concentration of the $O_3ClOAgPEt_3$ compound was evaluated according to the amount of AgCl formed in the reaction.

Preparation of $[L(C_6F_5)_3PtAgL']$ (L′ = PPh_3, L = C_4H_8S (I), PPh_3 (II), PEt_3 (III), $PEtPh_2$ (IV), py (V); L′ = PEt_3, L = C_4H_8S (VI), PPh_3 (VII), PEt_3 (VIII), $PEtPh_2$ (IX), py (X)). L′ = PPh_3. To dichloromethane solutions of $(NBu_4)[Pt(C_6F_5)_3L]$ (L = C_4H_8S, 0.15 g (0.15 mmol); L = PPh_3, 0.4 g (0.3 mmol); L = PEt_3, 0.5 g (0.4 mmol); L = $PEtPh_2$, 0.25 g (0.20 mmol); L = py, 0.3 g (0.3 mmol)) were added stoichiometric amounts of $O_3ClOAgPPh_3$ (0.068 g (0.15 mmol), 0.156 g (0.330 mmol), 0.192 g (0.411 mmol), 0.1018 g (0.1952 mmol), 0.1383 g (0.2947 mmol), and 0.0709 g (0.151 mmol), respectively). The resulting solutions were stirred for 2 h at room temperature and then evaporated to dryness. Addition of diethyl ether afforded solid $(NBu_4)ClO_4$, which was removed by filtration. The diethyl ether filtrates were evaporated to dryness, and the residues were dissolved in ca. 5 mL of dichloromethane. Addition of hexane gave the corresponding white $[L(C_6F_5)_3PtAgPPh_3]$ compounds (yields are listed in Table I).

Suitable crystals for the X-ray structure determination of complex I, $(C_4H_8S)(C_6F_5)_3PtAgPPh_3$, were obtained by slow diffusion (ca. 3 weeks) of hexane into a dichloromethane solution of the complex, at −25 °C.

L′ = PEt_3. A procedure analogous to that used for $O_3ClOAgPPh_3$ was followed for the reaction with $O_3ClOAgPEt_3$. Because of the failure to obtain the latter reagent in the solid state, solutions of this compound in dichloromethane were used. The amounts of the starting materials were as follows for $(NBu_4)[Pt(C_6F_5)_3L]$: L = C_4H_8S, 0.4 g (0.4 mmol); L = PPh_3, 0.353 g (0.294 mmol); L = PEt_3, 0.25 g (0.24 mmol); L = $PEtPh_2$, 0.25 g (0.21 mmol); L = py, 0.2 g (0.2 mmol). The following respective volumes of different $O_3ClOAgPEt_3$ solutions, corresponding to a 1:1 molar ratio, were used: 8.60 mL (0.0454 M); 8.25 mL (0.0357 M); 6.60 mL (0.0357 M); 4.80 mL (0.0454 M); 5.50 mL (0.035 M). The mixtures were stirred for 1 h each. Yields are given in Table I.

Preparation of $[Ag(PPh_3)_2][Pt(C_6F_5)_3PPh_3]$ (XI). To a solution of 0.2 g (0.2 mmol) of complex II in dichloromethane was added 0.0395 g (0.15 mmol) of PPh_3. The solution was stirred at room temperature for 2 h and then evaporated to dryness. Treatment of the residue with diethyl ether and hexane rendered complex XI.

Preparation of $[Ag(PPh_3)_3][Pt(C_6F_5)_3PPh_3]$ (XII). Addition of 0.078 g (0.30 mmol; 2:1), 0.235 g (0.903 mmol; 6:1), or 0.472 g (1.80 mmol; 12:1) of PPh_3 to a diethyl ether solution of 0.2 g (0.2 mmol) of complex II gave rise to the precipitation of complex XII, which after 30 min of stirring was separated by filtration.

X-ray Structure Analysis of $(C_4H_8S)(C_6F_5)_3PtAgPPh_3$ (I). X-ray diffraction data were taken by an automated four-circle diffractometer (Nicolet P3/F), from a colorless crystal of dimensions 0.25 × 0.19 × 0.18

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(10) Teo, B.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2467.
(11) Dikhoff, T. G. M. H.; Goel, R. G. *Inorg. Chim. Acta* **1980**, *44*, L72.
(12) Churchill, M. R.; Donahue, J.; Rotella, F. R. *Inorg. Chem.* **1976**, *15*, 2752.
(13) Maslowsky, E., Jr. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977; p. 437, and references given therein.

Inorg. Chem. **1987**, *26*, 1370–1375

mm mounted at the end of a glass fiber. The procedures used have been described previously.[14] Crystal data, including lattice dimensions and data-collection parameters, are summarized in Table II. The lattice dimensions and Laue group were verified by axial photography.

Three check reflections, which were rescanned at regular intervals during intensity data collection, did not show any appreciable change in intensity over the 140 h of X-ray exposure time.

The data were reduced by standard procedures. Calculations were done by a PDP-11/60 computer with programs from the package SDP-PLUS. An empirical absorption correction[15] was based on azimuthal scans of nine reflections with diffractometer angle χ near 90°.

Systematic absences uniquely identified the space group as $P2_1/n$. The position of the unique Pt atom was derived from a Patterson map. The full structure was developed in a series of alternating least-squares refinements and difference Fourier maps. For the final refinement all 59 unique atoms were treated with anisotropic displacement parameters. In all, 532 variable parameters were fitted to 4101 data, giving a data-to-parameter ratio of 7.7. The final residuals are defined and summarized in Table II.

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Supplementary Material Available: For the crystal structure of $(C_4H_8S)(C_6F_5)_3PtAgPPh_3$, full lists of bond distances, bond angles, and anisotropic displacement parameters (6 pages); a list of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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[14] Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

[15] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

[16] Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive.

Contribution from the Chemistry Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Structural and Molecular Mechanics Studies of Bis(dibutyl phosphato)aquastrontium–18-Crown-6 and Analogous Alkaline-Earth-Metal Complexes

John H. Burns* and Richard M. Kessler

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The stability of bis(dibutyl phosphato)aquastrontium–18-crown-6 (**1**) has been compared with analogous real and hypothetical alkaline-earth-metal complexes by use of molecular mechanics calculations. Trial molecular structures from which energy minimization proceeded were obtained by crystal structure analysis of **1** and from its previously analyzed Ba analogue. Existence of these molecules in solution was also verified by IR and NMR spectra. Crystals of **1** are monoclinic, $P2_1/c$, with $a = 9.23$ (1) Å, $b = 27.24$ (3) Å, $c = 31.55$ (3) Å, $\beta = 94.95$ (6)°, and $Z = 8$. In the two independent molecules of the crystal each Sr^{2+} ion is coordinated by six O atoms of a crown ether, by two monodentate dibutyl phosphato ions, and by one H_2O molecule. The differences in calculated total energies among these complexes are due primarily to the Coulombic contributions, the strain in the crown molecules being relatively unimportant within wide geometrical limits. An estimate of the selectivity of the crown/dibutyl phosphate combination among the hydrated alkaline-earth-metal ions suggests that they are selected in the order Ba > Sr > Ca > Ra > Mg.

Introduction

The stabilities of crown ether complexes with various cations have been the subject of study by many methods.[1] Early estimates of the relative stabilities were made by using solvent extraction of alkali-metal complexes with picrate as the counterion.[2] Subsequently extraction equilibria for crown ether picrates of all the alkali-metal and alkaline-earth-metal ions have been determined.[3] Enhanced extractability has been achieved by using mixtures of crown ethers and organophilic acids as cation exchangers, and several systems of this type have been investigated.[4] The distribution of the various complexes to the organic phase has been found generally to parallel the thermodynamic stabilities found in the aqueous phase. Because the latter have been correlated with the match between macrocycle size and cation radius, it has been suggested that these synergistic mixtures can provide a means of separation of ions on the basis of size.

The work to be described here was undertaken to examine the stabilities of model systems containing a crown ether, 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), an organophilic acid, HDBP (di-*n*-butyl phosphoric acid), and the Sr^{2+} and Ba^{2+} ions. The first step was to obtain the crystal structures of the complexes which these components produce, the second step was to correlate these with their NMR and IR spectra in solution, and the final step was to calculate the molecular energies and minimize them by the methods of molecular mechanics. To examine further the effect on the energy of the size of the extracted ion, hypothetical complexes containing Mg^{2+}, Ca^{2+}, and Ra^{2+} ions were treated by the same calculational methods. Previously, molecular mechanics was used by Wipff, Wiener, and Kollman (WWK)[5] to evaluate the energies of crown ether and cryptand complexes of the alkali metals, and the energies of the 18-crown-6 molecule, in various configurations, were minimized by Bovill, Chadwick, Sutherland, and Watkin (BCSW).[6] We have used procedures similar to WWK to facilitate comparison. The crystal structure of $Ba(DBP)_2(H_2O)\cdot 18$-crown-6 was already available.[7]

Experimental Section

Preparation of $Sr(DBP)_2(H_2O)\cdot 18$-crown-6. Di-*n*-butyl phosphoric acid was separated from a mixture of mono- and dibutyl phosphoric acids (Mobil Chem. Co., Richmond, VA) by dissolving the mixture in benzene and extracting out the mono acid with water. A 1:1:2 mixture of $Sr(OH)_2\cdot 8H_2O$, 18-crown-6 (Aldrich Chem. Co.), and HDBP were mixed neat and allowed to react. The resulting colorless thin platelets of $Sr(DBP)_2(H_2O)\cdot 18$-crown-6 were removed from the wet mixture. These crystals lost water under conditions of low humidity and recrystallized when the humidity rose.

NMR and IR Measurements. Samples were prepared by dissolving crystals of $Sr(DBP)_2(H_2O)\cdot 18$-crown-6 and $Ba(DBP)_2(H_2O)\cdot 18$-crown-6, made earlier,[7] in $CHCl_3$ for IR and in $CDCl_3$ (1% Me_4Si) for NMR measurements. ^1H NMR spectroscopy was performed by use of a Varian EM360L instrument and Fourier-transform IR spectroscopy by use of

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[1] Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271.

[2] Pederson, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 391.

[3] Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 4684. Danesi, P. R.; Meider-Gorican, H.; Chiarizia, R.; Scibona, G. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1479. Takeda, Y.; Kato, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1027; Takeda, Y.; Goto, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1920.

[4] Kinard, W. F.; McDowell, W. J.; Shoun, R. R. *Sep. Sci. Technol.* **1980**, *15*, 1013. Kinard, W. F.; McDowell, W. J. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2947. Clark, G. A.; Izatt, R. M.; Christensen, J. J. *Sep. Sci. Technol.* **1983**, *18*, 1473. Moyer, B. A.; McDowell, W. J.; Ontko, R. J.; Bryan, S. A.; Case, G. N. *Solvent Extr. Ion Exch.* **1986**, *4*, 83.

[5] Wipff, G.; Weiner, P.; Kollman, P. *J. Am. Chem. Soc.* **1982**, *104*, 3249. Wipff, G.; Kollman, P. *Nouv. J. Chim.* **1985**, *9*, 457.

[6] Bovill, M. J.; Chadwick, D. J.; Sutherland, I. O.; Watkin, D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1529.

[7] Burns, J. H. *Inorg. Chim. Acta* **1985**, *102*, 15.

0020-1669/87/1326-1370$01.50/0