Metallocenophanes, VII[◇]

Preparation and Characterisation of the Disilver(I) Complexes of Conjugated Polyenes with [2.2.2]Paracyclophanyl End Groups

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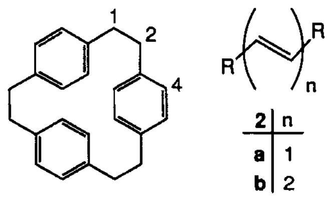
The preparation of the disilver(I) complexes **3** and **4**, polyene metal complexes that are terminally substituted with [2.2.2]paracyclophanyl units, is described. NMR spectroscopic studies on the disilver perchlorate complex **3b** showed that (a) the sites of complexation are the cyclophane groups and (b) the olefinic spacers do not overly perturb the overall complexation properties of the individual [2.2.2]paracyclophanyl groups. The crystal structures of the disilver hexafluoroantimonate complexes **4a**–**b** were determined. The use of the hexafluoroantimonate counterion and solvent mixtures containing toluene both proved crucial in obtaining single crystals; toluene is incorportated into the crystal lattices.

Hydrocarbons with π-electron-rich cavities can form stable endohedral complexes with soft metallic cations. The best known case is that of [2.2.2]paracyclophane **1**, whose complexation with silver(I)[2] and some main group metals[3] has already been described. One obvious goal of further studies is to improve the π complexation properties beyond those of **1**. Although this might be accomplished through optimisation of the hydrocarbon host structure[4], the lengthy multistep syntheses are a drawback. Furthermore, these substances have not yet provided direct evidence of endohedral guest binding. An alternative approach to increasing the π ligand binding efficiency is based on systems capable of the simultaneous complexation of several metal atoms[5] and the ready availability of **1** was especially convenient for their construction. We have already described the preparation and properties of conjugated polyenes **2**, which are terminally substituted with [2.2.2]-paracyclophanyl groups, as models for highly conjugated oligo [2.2.2]paracyclophanyl systems[6]. These compounds are suited for an investigation of the relationship between spacer conjugation length and the complexation properties of the bidentate π ligands. We now continue these studies by describing the preparation and characterisation of their disilver(I) complexes.



2	n
a	1
b	2

1

R = 4-[2.2.2]paracyclophanyl

Disilver Perchlorate Complexes

Compound **3b**, the disilver perchlorate complex of butadiene **2b**, is precipitated after combining solutions of the ligand and two equivalents of silver perchlorate in toluene or dichloromethane and toluene, respectively. Its constitution was confirmed by combustion analysis and its spectroscopic properties are in accord with those reported for the silver(I) complexes of other derivatives of [2.2.2]paracyclophane. The complicated absorption profiles of the ^{1}H NMR spectra of bidentate ligand **2b** and complex **3b** preclude the assessment of the rates of inter- and intramolecular exchange of the silver cation (see Figure 1). Figure 1b shows the aromatic region of ligand **2b** in the presence of one equivalent of silver perchlorate to be comprised of two distinct aromatic absorption bands, corresponding to complexed and uncomplexed [2.2.2]paracyclophanyl residues. We therefore conclude that the inter- and intramolecular exchange of silver atoms is a slow process on the ^{1}H NMR

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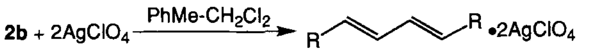
spectroscopic time scale[7]. Furthermore, the invariance of the olefinic shifts throughout Figure 1a, b and c confirms the preferential binding of silver to the [2.2.2]paracyclophanyl residues and not to the olefinic chain.



3b
(R = 4-[2.2.2]paracyclophanyl)

The ^{13}C NMR and DEPT spectra of complex **3b** show a total of twelve C, twenty-two CH and eleven CH_2 lines, in contrast to the seven, thirteen and six lines expected for a symmetrical disilver complex[8]. Boekelheide et al. report line broadening in the low-temperature ^{13}C NMR spectra of the simple silver(I) complexes of **1** and related substances[2c]. For our compounds, we infer the existence of either two diastereomeric complexes in solution or a dissymmetrical conformation of the **2b** · Ag_2^{2+} cation in solution. The first possibility is supported by the documented existence of distinct *anti-meso-R,S* (*R,R*) and *anti-R,R-* (*S,S*) conformations for bis-[2.2.2]paracyclophanyl derivatives in the solid state and the conformational rigidity of related silver(I) complexes[5,9]. The second possibility implies that the binding of one metal atom affects that of the second one.

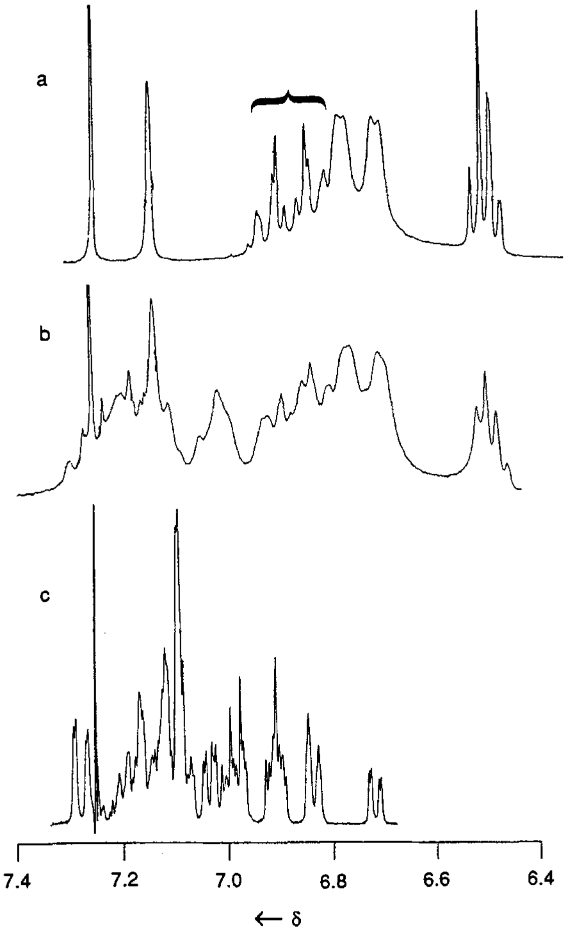
Disilver Hexafluoroantimonate Complexes

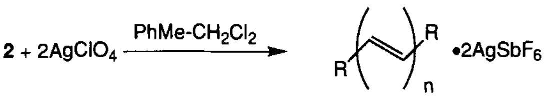
It was clearly desirable to characterise the disilver(I) complexes of ligands **2** through X-ray crystallography. In no case however, could well-formed single crystals be obtained from the $AgClO_4$ complex **3b**; non-crystalline materials or imperfect crystals were always isolated. However, single crystals of the disilver hexafluoroantimonate complexes **4a** and **4b**, from the ethene and butadiene derivatives **2a** and **2b**, were obtained by addition of two equivalents of the corresponding silver salt in toluene to one of the ligands in dichloromethane. The necessity of using this particular solvent mixture is indicated by the results of the elemental analyses for complex **4b**, prepared in both dichloromethane-toluene and dichloromethane-benzene. The analyses are closest to compositions having one toluene molecule per molecule of complex and two benzenes per molecule of complex. In the dichloromethane-benzene solvent mixture, however, only poorly ordered crystals of **4b** could be isolated. The analysis of complex **4a** supports a formulation with two molecules of toluene per complex.

Crystal Structures

The disilver hexafluoroantimonate complex **4a**, of ethene **2a**, crystallises in the space group $P2_1/n$ (see Figure 2 and Table 1). The cation displays crystallographic inversion symmetry. The two [2.2.2]paracyclophanyl groups thereby adopt an *anti-meso-R,S* (*S,R*) conformation. The length of the olefinic double bond is 1.327(7) Å and it is twisted by 27° out of the plane of the adjoining benzenoid ring. The resulting stilbenoid geometry agrees well with that found for (*E*)-2,2′,5,5′-tetramethylstilbene[10].

Figure 1. A section of the ^{1}H-NMR spectra in $CDCl_3$: (a) Ligand **2b** (b) a 1:1 solution of **2b** and disilver perchlorate complex **3b** and (c) **3b**. Olefinic absorptions indicated with bracket





4	n
a	1
b	2

(R = 4-[2.2.2]paracyclophanyl)

Complexation occurs from the side of the [2.2.2]paracyclophanyl groups more distant from the olefinic spacer. The silver atoms are thereby η^2-bonded 2.484–2.617 Å from a single pair of aromatic C atoms in each of the three component rings (average distance 2.539 Å) but are at least 5.46 Å from the toluene molecule (neglecting H atoms). Contact of the hexafluoroantimonate anions to silver is observed; Ag···F4 2.712(3) Å. The silver atoms lie 0.08 Å outside of the edge of the cyclophane cavity, or 0.15–0.16 Å less than in the silver(I) complexes of **1**[2a,c]. The intramolecular Ag···Ag distance is 10.56 Å and the shortest intermolecular

Ag···Ag contact is 8.15 Å. One toluene molecule per asymmetric unit is observed and occupies the channels parallel to the y axis at x, $z \approx 1/4, 3/4$ (see Figure 3).

Figure 2. A projection of the crystal structure of disilver hexafluoroantimonate complex **4a**

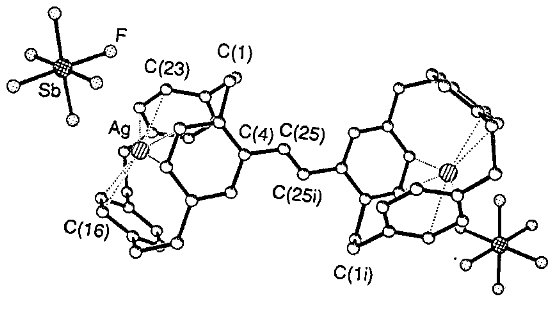
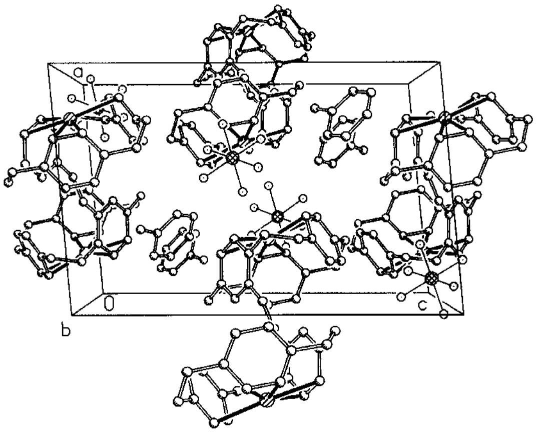


Figure 3. Packing diagram of complex **4a**



The crystal structure of the bis-[2.2.2]paracyclophanyl butadiene disilver hexafluoroantimonate complex **4b** exhibits a solid state ligand conformation similar to that of compound **4a**, although here the butadienyl spacer subtends a smaller angle (16°) to the adjoining aromatic rings (see Table 1). Exact centrosymmetry is observed again (see Figure 4).

The binding geometry of silver in **4b** parallels that of **4a**, with distances between the metal and closest cyclophane sp^2 ring atoms lying between 2.477(6) and 2.649(7) Å (average separation 2.563 Å). The extended coordination sphere of silver here is however different from that of **4a**: two molecules of toluene are present in the asymmetric unit, of which one is disordered across the inversion centre present around the butadienyl spacer. Thus, the overall ratio of complex to toluene is 1:3[11]. The ordered toluene forms weak contacts to silver; the shortest is C 95···Ag 2.999(7) Å. There are no short Ag···F contacts; the shortest is 4.9 Å. The intramolecular Ag···Ag distance is 8.15 Å; while the shortest intermolecular Ag···Ag separation is 8.32 Å.

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Figure 4. A projection of the crystal structure of disilver hexafluoroantimonate complex **4b**

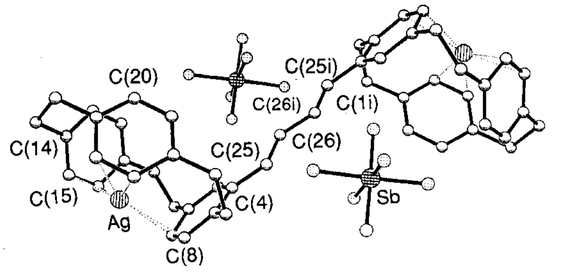
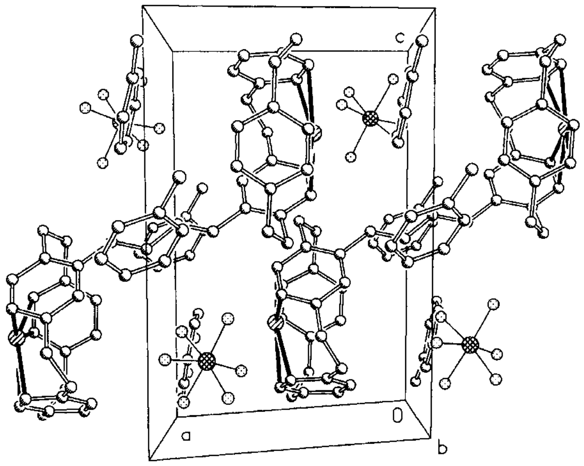


Figure 5. Packing diagram of complex **4b**. The disordered toluene molecule (only one orientation of which is shown) is located around the butadienyl spacer



P. G. J. thanks the *Fonds der Chemischen Industrie* for financial support.

Experimental

Toluene was freshly distilled from sodium/benzophenone. Silver hexafluoroantimonate was used as received from Aldrich. Spectrometers and other equipment used are described elsewhere[6].

Complex **3b** *from Dichloromethane/Toluene:* A solution of 0.10 g (0.15 mmol) of butadiene **2b** in 120 ml of toluene was layered with a solution of 63 mg (0.30 mmol) silver perchlorate in 2 ml of toluene. The mixture was left standing overnight under N_2 and 10 ml of petroleum ether was added. After 6 d the resulting precipitate was removed by filtration and dried under vacuum (10^{-2} mbar) at 60 °C to give 0.12 g (73%) of the disilver perchlorate complex **3**. – m.p. 233 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 1595 cm^{-1} (w), 1508 (m), 1110 (s), 1047 (s), 623 (s). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 138.82, 138.43, 138.36, 138.26, 138.21, 138.12, 138.09, 137.51, 137.16, 136.25, 136.20, 129.04 (C), 132.74, 132.30, 130.38, 130.00, 128.91, 128.23, 127.95, 127.38, 127.13, 126.87, 126.50, 126.17, 126.07, 125.83, 125.57, 125.30, 124.94, 124.60, 124.21, 122.66, 122.35, 121.22 (CH), 33.20, 33.11, 33.01, 32.94, 32.87, 32.81, 32.74, 32.69, 32.29, 32.17, 32.06. – FAB-MS [*p*-nitrobenzyl alcohol (NBA), most intense signal from isotopic spread of given ion stated]: *m/z* (%): 989.3 $[C_{52}H_{50}Ag_2ClO_4^+]$ (74), 781.3 $[C_{52}H_{50}Ag^+]$ (100). – $C_{52}H_{50}Ag_2Cl_2O_8$ (1089.6): calcd. C 57.32, H 4.36, Cl 6.51; found C 57.77, H 4.67, Cl 3.97.

Complex **4a** *from Dichloromethane/Toluene:* A solution o 32 mg (0.049 mmol) of the bidentate ligand **2a** in 14 ml of absolute dichloromethane was layered with 33 mg (0.096 mmol) of silver hexafluoroantimonate in 3 ml of toluene. After standing 17 d under N_2 in the absence of daylight, crystals suitable for X-ray crystallography had formed. – m.p. 260–265 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3022 cm^{-1} (m), 2925 (s), 1442 (s), 814 (s), 662 (vs). – FAB-MS (NBA, most intense signal from isotropic spread of given ion stated): *m/z* (%) = 1099.1 [$C_{50}H_{48}Ag_2F_6Sb^+$] (52.2), 755.3 [$C_{50}H_{48}Ag^+$] (100). – $C_{50}H_{48} \cdot 2\ C_7H_8 \cdot 2\ H_2O$ ($C_{64}H_{68}Ag_2F_{12}O_2Sb_2$, 1336.2): calcd. C 49.39, H 4.40; found C 49.00, H 4.06.

Complex **4b** *from Dichloromethane/Benzene:* Complex **4b** was initially prepared from 34 mg (0.050 mmol) of **2b** and 41 mg (0.12 mmol) silver hexafluoroantimonate in a manner similar to that used for **3**. The solid complex was dissolved in 9 ml of absolute dichloromethane, layered with 5 ml of absolute benzene and concentrated at atmospheric pressure and N_2 over a week. Colourless cubes had formed at the end of this time. – m.p. 270–280 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2929 cm^{-1} (s), 1508 (s), 1442 (s), 814 (s), 661 (vs). – FAB-MS (NBA, most intense signal from isotopic spread of given ion stated): *m/z* (%) = 1124.9 [$C_{52}H_{50}Ag_2F_6Sb^+$] (70), 781 [$C_{52}H_{50}Ag^+$] (100). – $C_{52}H_{50} \cdot 2\ AgSbF_6 \cdot 2\ C_6H_6 \cdot 2\ H_2O$ ($C_{64}H_{68}Ag_2F_{12}O_3Sb_2$, 1518.4): calcd. C 49.4, H 4.3; found C 49.3, H 4.2.

Complex **4b** *from Dichloromethane/Toluene:* A solution of 17 mg (0.025 mmol) of the bidentate ligand **2b** in 7 ml of abs. dichloromethane was layered with 18 mg (0.050 mmol) of silver hexafluoroantimonate in 2.5 ml of toluene. After standing 18 d under N_2 in the absence of daylight, the volume of the solution was reduced in vacuo to ca. 4 ml. Crystallisation commenced after another 4 d and was continued over a period of ca. 2 months by further concentrating the solution under vacuum. Crystals suitable for X-ray crystallography finally resulted. – m.p. 140–150 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3023 cm^{-1} (w), 2923 (m), 1442 (m), 660 (vs). – FAB-MS (NBA, most intense signal from isotopic spread of given ion stated): *m/z* (%) = 1125.2 [$C_{52}H_{50}Ag_2F_6Sb^+$] (86), 781 [$C_{52}H_{50}Ag^+$] (100). – $C_{52}H_{50} \cdot 2\ AgSbF_6 \cdot C_7H_8$ ($C_{59}H_{58}Ag_2F_{12}Sb_2$; 1454.3): calcd. C 48.7, H 4.02; found C 48.9, H 3.93.

Crystal Structure Analyses: Crystal data are presented in Table 1. Data collection: data were collected with Mo-K_α radiation on a Siemens R3 diffractometer equipped with an LT-2 low temperature device. Cell constants were refined from setting angles of ca. 50 reflections in the 2Θ range 20–23°. Absorption corrections were based on ψ scans. Structure solution: heavy-atom method. Structure refinement: anisotropic refinement on F^2 (program SHELXL-93, G. M. Sheldrick, Univ. Göttingen), H atoms with riding model, weighting scheme $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants optimised by the program. Special features of refinement for **4b**: Toluene methyl H atoms were not located. One toluene molecule is disordered over an inversion centre and was refined isotropically with idealised geometry. The SbF_6 ion is also disordered over (at least) two positions about the axis F1–Sb–F2.

Complete details of the X-ray structure analyses have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. This material can be obtained on citing the complete literature reference and the deposition number CSD-401781 (**4a**), 401782 (**4b**).

Table 1. Crystal structure parameters

Compound	**4a**•2C_7H_8	**4b**•3C_7H_8
Formula	$C_{64}H_{64}Ag_2F_{12}Sb_2$	$C_{73}H_{74}Ag_2F_{12}Sb_2$
M_r	1520.39	1638.56
Crystal habit	Colourless prism	Colourless prism
Crystal size (mm)	0.5 x 0.2 x 0.2	0.4 x 0.3 x 0.25
Space group	$P2_1/n$	$P\bar{1}$
Temperature (°C)	-95	-95
Cell constants:		
a (Å)	11.297(3)	9.913(4)
b (Å)	14.824(4)	12.144(4)
c (Å)	17.551(5)	14.636(5)
α(°)	90	82.39(3)
β(°)	95.50(3)	89.63(3)
γ(°)	90	72.29(3)
V (Å^3)	2925.7(14)	1662.6(10)
Z	2	1
D_x (Mg m^{-3})	1.726	1.637
F(000)	1504	816
μ (mm^{-1})	1.65	1.46
Transmission factors	0.75-0.81	0.60-0.71
$2\Theta_{max}$ (°)	55	50
No. of reflections:		
measured	8547	6248
independent	6730	5881
R_{int}	0.018	0.018
$wR(F^2$, all refl.)	0.083	0.107
$R(F, F>4\sigma(F))$	0.032	0.039
No. of parameters	362	423
No. of restraints	0	666
S	1.00	1.06
Max. Δ/σ	<0.001	0.007
Max. Δρ (e Å^{-3})	0.94	0.99

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[8] [^{13}C NMR spectrum of **2b** ($CDCl_3$, 100 MHz): δ = 136.51, 136.24, 136.08, 135.77, 134.70, 133.85 (C), 129.98, 129.56, 127.88, 127.82, 127.68, 127.10, 124.92 (CH), 33.21, 33.16, 32.94, 32.80, 32.53, 31.47 (CH_2).

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[11] The preliminary drying of the sample for combustion analysis at 10^{-2} mbar and 60 °C over ca. 24 h may account for the analysis of **4b** indicating one and not three equivalent of toluene.

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