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THE CRYSTAL STRUCTURE OF THE OLEFIN COMPLEX DI-1,5-CYCLOOCTADIENESILVER TETRAFLUOROBORATE

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Summary

The structure of di-1,5-cyclooctadienesilver tetrafluoroborate was determined from single crystal X-ray diffraction data. The silver atom is four coordinated to the olefinic ends of the two cyclooctadiene molecules in a modified tetrahedral coordination described as "cubical". Bond lengths and other structural parameters are discussed and compared with the corresponding data found for other d^{10} and d^8 olefin-metal complexes.

Introduction

A large number of olefin-silver(I) complexes have been synthesized [1], but in general they are quite unstable, and even poorly coordinating species such as NO_3^- or ClO_4^- may be more effective in coordinating to the metal atom, so that in order to obtain pure olefinic complexes BF_4^-, SbF_6^- or triflate must be used as counterions [2—5]. Because of their instability, even their spectroscopic characterization may be uncertain [2,7].

The stability of these compounds should be increased by use of chelating dienes [8], but the presence of four simultaneously coordinated olefins has been not fully confirmed even in the case of di-1,5-cyclooctadienesilver tetrafluoroborate, although it has been demonstrated for related isoelectronic compounds of nickel(0) [9], palladium(0), platinum(0) and copper(I) [12]. We therefore synthesized the title compound and determined its structure to clarify the coordination geometry.

Experimental

Anhydrous $AgBF_4$ and 1.5-cyclooctadiene (99.8% pure) were commercially available. CH_2Cl_2 was dried by refluxing over CaH_2 and distilled before use. IR spectra were recorded with a Perkin—Elmer 457 spectrophotometer.

Preparation of the complex. To a suspension of $AgBF_4$ (1.95 g, 10 mmol) in 80 ml of CH_2Cl_2 under nitrogen at —10°C, 25 ml of 1,5-cyclooctadiene (20 mmol) were added through a side arm fitted with a serum cap. After 12 h a white crystalline precipitate was formed. This was filtered off and dried under vacuum. The mother liquor was concentrated under a gentle N_2 flow to give further crystals of the product after 24 h (total yield 83%).

Crystal data. $AgC_{16}H_{24}BF_4$; mol. wt. 411.07, Space group either *Pnma* or $Pna2_1$ (acentric, interchanging h and l) from systematic absences, $Z = 4$. The least squares refined parameters are a 17.973(3), b 10.190(3), c 9.201(2) Å; V 1685.1 Å^3; D_{calc} 1.624 g cm^{-3}. The crystals are stable in the air and crystallize as white elongated prisms. A total of 1597 reflections (983 with $I \geqslant 3\sigma(I)$ were considered as observed) has been collected on a Philips four circle diffractometer up to a $\sin \sigma/\lambda = 0.595$ Å^{-1}, with an $\omega/2\sigma$ scan mode. (Mo-K_α monochromatized radiation, $\lambda = 0.71069$ Å; scan range = 1.20°, scan speed = 0.04° s^{-1}).

The structure was solved by Patterson and Fourier method and refined by full matrix least squares, assuming the centrosymmetric space group, with anisotropic temperature factors for Ag and isotropic for the other ones. The values for the scattering factors and anomalous dispersion were from reference 13. Any attempt to refine the structure in the acentric space group failed to converge satisfactorily, confirming the choice of the centric group. The final conventional agreement factor is $R = 0.072$ (0.097 with the unobserved included). A perspective view of the molecule is shown in Fig. 1; the relevant bond lengths and angles are reported in Table 1; final positional and temperature factors are in Table 2.

TABLE 1

BOND LENGTHS (Å) AND ANGLES (deg) IN THE ASYMMETRIC UNIT (The e.s.d.'s given in parentheses refer to the least significant digit)

Ag—C(1)	3.24(1)	F—B—F [a]	109(1)
Ag—C(2)	2.48(1)	C(1')—C(1)—C(2)	120.7(9)
Ag—C(3)	2.50(1)	C(1)—C(2)—C(3)	127.4(9)
Ag—C(4)	3.27(1)	C(2)—C(3)—C(4)	129.4(8)
Ag—C(5)	2.48(1)	C(3)—C(4)—C(4')	120.8(9)
Ag—C(6)	2.21(1)	C(5')—C(5)—C(6)	126.6(8)
Ag—C(7)	3.27(1)	C(5)—C(6)—C(7)	121.9(9)
Ag—C(8)	2.52(1)	C(6)—C(7)—C(8)	120.6(8)
B—F [a]	1.32(4)	C(7)—C(8)—C(8')	125.6(9)
C—C [a]	1.46(2)	C(1)—Ag—C(5)	110.6(4)
C(1)—C(1') [b]	1.54(2)	C(2)—Ag—C(2')	75.3(4)
C(1)—C(2)	1.46(2)	C(2')—Ag—C(3)	83.7(4)
C(2)—C(3)	1.33(2)	C(2)—Ag—C(6)	108.9(5)
C(3)—C(4)	1.50(2)	C(3)—Ag—C(7)	104.4(4)
C(4)—C(4')	1.52(2)	C(4)—Ag—C(8)	99.8(5)
C(5)—C(5')	1.32(2)	C(5)—Ag—C(8)	83.9(5)
C(5)—C(6)	1.46(2)		
C(6)—C(7)	1.44(2)		
C(7)—C(8)	1.51(2)		
C(8)—C(8')	1.38(2)		

[a] Average values. [b] The primed atoms are related to the unprimed atoms by the symmetry operation x; $1/2 - y$; z.

TABLE 2

POSITIONAL PARAMETERS AND TEMPERATURES FACTORS FOR ATOMS OF THE ASYMMETRIC UNIT

Atom	x	y	z	B (Å^2)	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ag	0.1036(1)	0.2500	0.1859(2)		4.01(5)	5.08(8)	5.18(12)	0	2.26(10)	0
C(1)	−0.056(3)	0.322(4)	0.321(3)	7.8(4)						
C(2)	0.012(3)	0.399(4)	0.305(4)	4.3(2)						
C(3)	0.072(2)	0.400(4)	0.392(3)	4.8(2)						
C(4)	0.084(4)	0.323(3)	0.528(3)	6.4(4)						
C(5)	0.111(3)	0.316(3)	−0.071(3)	5.8(3)						
C(6)	0.175(4)	0.402(4)	−0.087(3)	7.0(5)						
C(7)	0.336(3)	0.401(4)	0.011(4)	6.7(4)						
C(8)	0.237(4)	0.319(3)	0.147(4)	5.9(2)						
B	−0.127(3)	0.250	−0.134(2)	7.3(9)						
F(1)	−0.190(5)	0.250	−0.054(4)	9.5(11)						
F(2)	−0.129(6)	0.250	−0.262(5)	10.3(11)						
F(3)	−0.081(6)	0.352(5)	−0.082(5)	10.9(9)						

[a] The form of the anisotropic temperature factor is: $T = \exp[-1/4(B_{11}a^{*}h^2 + B_{22}b^{*}k^2 + B_{33}c^{*}l^2 + B_{12}a^{*}b^{*}hk \pounds B_{13}a^{*}c^{*}hl + B_{23}b^{*}c^{*}kl)]$.

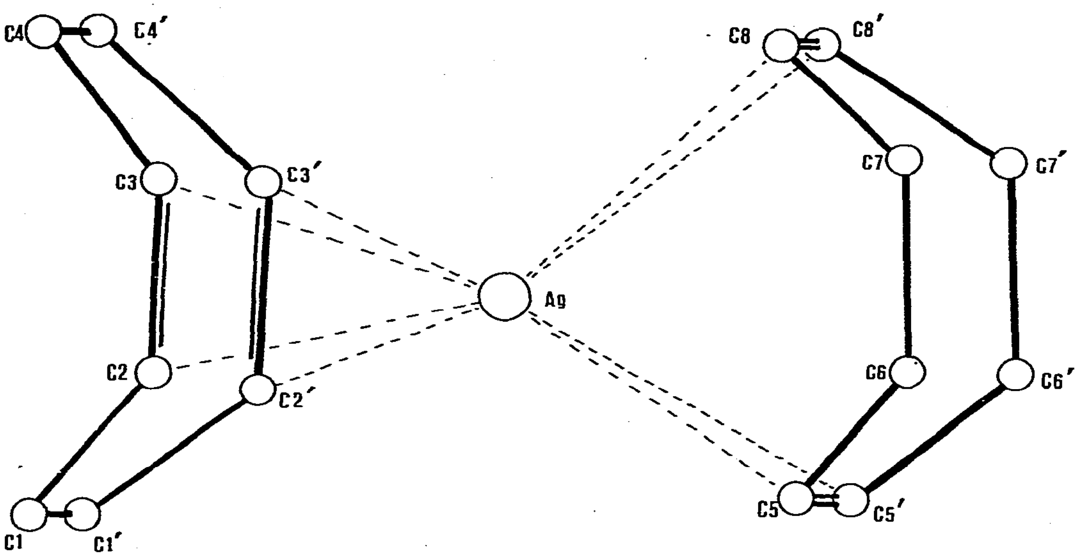

Fig. 1. Perspective view of the $[Ag(1,5\text{-}C_8H_{12})_2]^+$ ion. The primed atoms are related to the unprimed by the symmetry operator *x*, 1/2 — *y*, *z*.

Results and discussion

The $[Ag(1,5\text{-}C_8H_{12})_2]^+BF_4^-$ complex shows in the IR spectrum (Nujol mull) the ν(C=C) as single peak at 1603 xm^{-1}. This is consistent with four coordinated double bonds in the solid state, in contrast with the situation in solution [5].

The crystal structure consists of $[Ag(1,5\text{-}C_8H_{12})_2]^+$ cations and BF_4^- counter-ions. The asymmetric unit is half of the molecule (umprimed atoms), the Ag atom lies on a crystallographic mirror-plane bisecting the C(1)—C(1)′, C(4)– C(4)′, C(5)—C(5)′ and C(3)—C(3)′ cyclooctadiene bonds. The BF_4^- molecule is also in a special position, having the B and two F atoms on the same mirror plane. The B—F bond lengths (average (±0.04) Å) are in the expected range. Residual peaks in the Fourier difference maps show that the BF_4^- molecules are disordered between many possible orientations, preventing any interpretation of this disorder. The geometry of the olefinic ligands is that expected for d^{10} tetrakis-olefin complexes, i.e., a modified tetrahedral coordination called "cubical" [14], analogous to that found in the isoelectronic compounds $Ni(1,5\text{-}C_8H_{12})_2$ [9] and $Pt(1,5\text{-}C_8H_{12})_2$ [15]. The two molecules of the diene are asymmetrically bonded to the central metal atom (mean Ag—C bond lengths are 2.50 ± 0.02 Å; and 3.25 ± 0.03 Å for Ag—C non bonded intermolecular distances).

Tetrahedral coordination has been predicted to be the most stable arrangement for four coordinated d^{10} complexes [14], and this geometry may be particularly favourable for maximizing the overlap between the available metal and olefin orbitals. The geometry of the $1,5\text{-}C_8H_{12}$ groups is consistent with previously reported data [10], showing some deformations with respect to the free $1,5\text{-}C_8H_{12}$ (mean C—C bond length 1.46 ± 0.03 Å, and C=C 1.34 ± 0.02 Å).

It is noteworthy that the silver(I)—double bond distances of 2.50(1) Å are significantly shorter than in those the tribullvalene silver cation [17] (viz. 2.63 and 2,66 Å) and in the case of arene-silver(I) derivatives [18], but somewhat longer than those in mono-coordinated olefin complexes [19]. Thus, the coordination around silver(I) may in our case be considered as a compromise between the relatively large chelating ability of 1,5-C_8H_{12} and the well known decrease in the stability of d^{10} olefin-metal complexes as the number of coordinated olefin increases [1,10,12]. Moreover the metal—olefin bond length in $[Ag(1,5\text{-}C_8H_{12})_2]^+$ (2.48 Å) is longer (even allowing for the difference in the covalent radii) than in Ni(1,5-C_8H_{12})$_2$ (2.16 Å) [9], $[Cu(1,5\text{-}C_8H_{12})Cl]_2$ (2.05–2.22 Å) [20], $[Cu(C_7H_8)Cl]_4$ (2.05 Å) [21], trinorborneneplatinum (2.18 Å) [10] and in $Pt(C_8H_{12})_2$ [15] (2.221(6) Å); this may be reflected in the greater lability of the olefin-silver(I) complexes compared with other d^{10} analogues.

The C=C bond distances found in the present case may be compared with the C=C bond lengths of other purely olefinic d^{10} complexes for which values of 1.38 Å for Ni(1,5-C_8H_{12})$_2$ [9], 1.39 Å for trinorborneneplatinum [10], and 1.39, 1.37, 1.31, 1.28 Å for tribullvalensilver [17] have been reported. Other relevant values of the double bond lengths for olefins coordinated to similar compounds are 1.432(6) and 1.410(9) Å in $Pt(C_8H_{12})_2$ [15] and 1.400(8) for the ethylene group in $Pt(C_2H_4)_2(C_2F_4)$ [22]. In the case of d^8 olefin-metal complexes a tendency toward longer values was found; it may suggest the presence of stronger π back-bonding in d^8 compounds compared with their d^{10} counterparts.

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